was withdrawn from the reaction vessel and injected through a syringe cap into a dry nmr tube. The latter was cooled with liquid nitrogen and sealed with a hot flame. Another sample was titrated with 0.1 N hydrochloric acid (methyl orange as indicator), indicating a 1.5 M solution (95%). The nmr spectrum of the hydrolysate showed absorption only for 1,1-dimethylcyclobutane (τ 8.90).

Registry No.—3,3-Dimethylcyclobutyl bromide, 4237-75-6; 2,2-dimethylcyclopentyl bromide, 22228-38-2; isopropylidenecyclobutane, 1528-22-9; 2,2-dimethylcyclohexyl bromide, 28268-91-9; 1-isopropylcyclopentene, 1462-07-3; isopropylidinecyclopentane, 765-83-3; 3,3-dimethylcyclohexyl bromide, 25090-98-6; 4,4-dimethylcyclohexyl bromide, 25090-97-5; 3,3-dimethylcyclobutylmagnesium bromide, 4237-72-3; 3,3-dimethylcyclohexylmagnesium bromide, 28268-97-5; 4,4-dimethylcyclohexylmagnesium bromide, 28268-98-6; 2,2-dimethylcyclohexylmagnesium bromide, 28268-99-7; 2,2-dimethylcyclopentylmagnesium bromide, 28269-00-3.

Acknowledgment.—This research was supported in part by the Air Force Office of Scientific Research, Grant No. 251-65, and by the National Institutes of Health, Grant No. GM-08686.

Organophosphorus Compounds. XII.[1a] ^1H and ^{31}P Nuclear Magnetic Resonance Spectroscopic Studies of the Protonation and Cleavage of Trialkyl (Aryl) Phosphates and Phosphites, Dialkyl Phosphonates, and Phosphorus Oxy Acids in FSO_3H and FSO_3H–SbF_5 Solution

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Received July 8, 1970

Protonation and cleavage of phosphoric acid, phosphonic acid, phosphinic acid, trialkyl (aryl) phosphates, trialkyl (aryl) phosphites, and dialkyl phosphonates were studied in fluorosulfuric acid and fluorosulfuric acid–antimony pentafluoride solution. ^1H and ^{31}P nmr spectra of the phosphonium ions [including the hydroxyphosphonium ions $H_nP(OH)_{4-n}^+$, n = 0–2], as well as those of the precursors, were obtained generally at −60°. Tetravalent phosphoryl compounds were protonated on the phosphoryl oxygen atom; tervalent compounds were protonated at the phosphorus atom. The nmr data showed that in the protonated intermediates there was a substantial amount of back-donation of the oxygen nonbonded electron pairs to the empty phosphorus d orbital. By raising the temperature, several of the protonated compounds were subject to decomposition reactions, including carbon–oxygen bond cleavage and fluorination.

The chemical behavior of phosphates and phosphites under acidic conditions has long been a subject of interest to many investigators.[2] The acidic solvolyses[3] and the dealkylation by hydrogen halides[4] of phosphate triesters have been examined in detail. Arbuzov's classic paper[5] is the foundation of our understanding of the reactions of phosphite triesters with hydrogen halides.[4] Not only have interactions of phosphite triesters with other strong acids been studied,[6] but protonation by a variety of donors has also been invoked.[2] Dialkyl phosphonates are similarly dealkylated by hydrogen halides;[4] they also participate in other acid-catalyzed reactions.[7]

The chemistry of the parent monophosphorus oxy acids with regard to other acids is of interest as a model for the reactions of the organophosphorus compounds. The electrochemistry[8] and self-condensation[9] of orthophosphoric acid have been explained by autoprotolysis: $2H_3PO_4 \rightleftharpoons P(OH)_4^+ + H_2PO_4^-$. Oxygen isotope exchange between phosphoric acid and water is acid catalyzed.[10] The acid-catalyzed equilibration of the tautomeric forms of phosphonic acid[11] and phosphinic acid has been considered to be important in the many acid-catalyzed oxidation and isotope exchange experiments which have been conducted with these acids.[2]

However, fewer efforts have been made to obtain protonated phosphates and phosphites (the intermediates assumed to arise from the interactions with acids) sufficiently stable for direct observation. There are varying views on the stability of the complexes that phosphoric acid forms with hydrochloric acid and perchloric acid,[12] where phosphoric acid is thought to be a proton acceptor. Sulfuric acid is viewed as a proton donor to phosphoric acid,[12e,13] and ^{31}P nuclear magnetic resonance chemical shifts of phosphates in sulfuric acid

(1) (a) Part XI: G. A. Olah and C. W. McFarland, *J. Org. Chem.*, **34**, 1832 (1969). (b) National Institutes of Health Predoctoral Research Fellow, 1968–1970. (c) Taken in part from the Ph.D. Dissertation of C. W. McFarland, Case Western Reserve University, 1971.

(2) The reactions with acids of the types of phosphorus compounds with which this paper is concerned, with emphasis on the involvement of protonated intermediates, have been thoroughly reviewed: C. W. McFarland, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1971.

(3) Recent reviews of acidic solvolyses can be found in (a) E. Cherbuliez, *Chimia*, **15**, 327 (1961); (b) C. A. Bunton, *Accounts Chem. Res.*, **3**, 257 (1970).

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TABLE I

^{31}P AND ^{1}H NMR SPECTRAL PARAMETERS OF PROTONATED PHOSPHORUS OXYACIDS, TRIALKYL (ARYL) PHOSPHATES, TRIALKYL (ARYL) PHOSPHITES, AND DIALKYL PHOSPHONATES (−60°)

			δ_H					
	$\delta_{^{31}P}$ (85% H_3PO_4 = 0)		PH proton ($^1J_{PH}$, Hz)		α-Alkyl protons ($^3J_{POCH}$, Hz)		Other protons	
Phosphonium ion	Ion	Precursor	Ion	Precursor	Ion	Precursor	Ion	Precursor
$P(OH)_4^+$	−2.3[a]	0.0[b]	...	...	...	...	...	...
$HP(OH)_3^+$	−19.0	−5.4[b]	7.62 (825)	7.55 (683)[b]	...	...	...	...
$H_2P(OH)_2^+$	−36.1	−12.3[b]	7.64 (687)	7.47 (567)[b]	...	...	...	...
$HOP(OCH_3)_3^+$	−2.0[a]	−2.3	...	...	4.42 (11.5)[a]	4.15 (11.2)	...	...
$HOP(OC_2H_5)_3^+$	+1.6[a]	+1.0	...	...	4.73 (8.5)[a]	4.42 (8.6)	Methyl: 1.72[a]	1.65
$HOP(O\text{-}i\text{-}C_3H_7)_3^+$	+4.5	+3.4	...	...	5.19 (5.8)	4.86 (7.1)	Methyl: 1.66	1.59
$HOP(O\text{-}n\text{-}C_4H_9)_3^+$	+1.2[a]	+0.6	...	...	4.76 (7.4)[a]	4.32 (7.5)	Methyl: 1.30[a]	1.28
$HOP(OC_6H_5)_3^+$	+16.0[a]	+17.9[c]	...	...	...	...	Aryl: 7.45[a]	7.55[c]
$HP(OCH_3)_3^+$	−24.7	−139.7	7.47 (827)	...	4.34 (12.1)	3.66 (10.8)	...	...
$HP(OC_2H_5)_3^+$	−19.7	−137.6	7.46 (811)	...	4.72 (7.4)	4.00 (8.5)	Methyl: 1.67	1.40
$HP(O\text{-}i\text{-}C_3H_7)_3^+$	−15.7	−137.5	7.44 (796)	...	5.23 (5.3)	4.53 (8.8)	Methyl: 1.64	1.37
$HP(O\text{-}n\text{-}C_4H_9)_3^+$	−20.4	−137.8	7.47 (812)	...	4.65 (5.5)	4.07 (7.7)	Methyl: 1.15	1.20
$HP(OC_6H_5)_3^+$	−11.7	−126.9	8.32 (875)	...	...	...	Aryl: 7.24, 7.42	7.05
$HP(O\text{-}n\text{-}C_3H_7)_2^+$	−19.4	−7.3	7.49 (820)	7.03 (686)	4.60 (7.1)	4.25 (9.0)	β-Methylene:	
|							2.01	1.94
HO							Methyl: 1.18	1.20
$HP(O\text{-}n\text{-}C_4H_9)_2^+$	−19.3	−7.2	7.47 (819)	7.03 (686)	4.62 (6.6)	4.32 (8.8)	Methyl: 1.12	1.21
|								
HO								

[a] At room temperature. [b] In H_2O. [c] In CCl_4.

solutions have been obtained.[13b,d] Such chemical shifts have also been very recently obtained for chlorosulfuric acid solutions and oleum solutions with varying sulfur trioxide content.[13d] Gillespie and his coworkers have cited conductometric and cryoscopic measurements as evidence for the generation of protonated phosphoric acid, $P(OH)_4^+$, from several precursors in sulfuric acid[13c] and disulfuric acid solution.[14] Their measurements indicated that triethyl phosphate is protonated in sulfuric acid solution but that phosphorus oxyfluoride is not.[13c] The conductivity of triphenyl phosphate in sulfuric acid has been explained by protonation.[9] Moedritzer observed changes in the ^{31}P chemical shifts of several phosphoric, phosphonic, and phosphinic acid derivatives upon addition of strong acids such as perchloric and hydrochloric acids.[15] Sheldrick[16] and Haas and Gillman[17] have studied the protonation of phosphonic acid and phosphinic acid in sulfuric and perchloric acid solutions by measuring the nmr coupling constant, $^1J_{PH}$, between phosphorus and the proton(s) bound directly to it. McFarlane and White have quite recently observed by nmr the protonation at phosphorus of several phosphites in 100% sulfuric acid.[18]

In continuation of our work on protonation of phosphines in strong acid solution,[1a] we extended our studies to the protonation and cleavage reactions of phosphates and phosphites in FSO_3H and FSO_3H–SbF_5 solutions. We have found that phosphoric acid, trialkyl (aryl) phosphates, phosphonic acid, trialkyl (aryl) phosphites, dialkyl phosphonates, and phosphinic acid form in fluorosulfuric acid (at sufficiently low temperatures) stable protonated species which can be observed by nuclear magnetic resonance spectroscopy. ^1H and ^{31}P nmr spectra of the neutral starting compounds and of the corresponding protonated species in excess fluorosulfuric acid were obtained. We were particularly interested in the effect of protonation upon the phosphorus chemical shifts, as well as the nmr spectral parameters of protons bound directly to phosphorus. Another goal of our studies was to be able to identify the sites of protonation, and to follow subsequent cleavage reactions spectrally, as such information would be relevant to many important reactions in organophosphorus chemistry.

Results and Discussion

The nmr data for protonated phosphorus oxy acids trialkyl (aryl) phosphates, trialkyl (aryl) phosphites, and dialkyl phosphonates in fluorosulfuric acid solution, at −60° unless otherwise indicated, are listed in Table I. The phosphorus precursors, except those which were dissolved in the indicated solvents, were examined as neat liquids. Room-temperature spectra of solutions of inorganic phosphates [KH_2PO_4, $(NH_4)_2HPO_4$] and the trialkyl (aryl) phosphates (except for triisopropyl phosphate) in excess fluorosulfuric acid were indicative of the protonated species. The 60-MHz proton spectra of the acid solutions were similar to those of the starting compounds, except for changes in peak positions and separations and the presence of a new, sharp singlet at δ 10.9 to 12.1 (ppm from external capillary tetramethylsilane). The 24.3-MHz phosphorus spectra likewise showed changes only in peak positions and separations.

Since sulfuric acid itself is sufficiently strong to protonate phosphoric acid and triethyl phosphate,[13c] the phosphates we have studied should be fully protonated in the stronger[19] fluorosulfuric acid. The ^{31}P chemical shift of phosphoric acid is practically the same when it is dissolved in aqueous sulfuric acid of H_0 −8.6 (−2.5 ppm relative to 85% H_3PO_4)[13b] as when it is dissolved in fluorosulfuric acid (−2.3 ppm) where H_0 is −13.9.[19] Dillon and Waddington have also recently expressed the opinion that the limiting value of the ^{31}P chemical

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shift of $P(OH)_4^+$ is −2.1 ppm.[13d] Protonation is assumed to take place on the phosphoryl oxygen atom, but no proton coupling with phosphorus is exhibited, nor is a new proton absorption observed directly. Exchange with excess solvent fluorosulfuric acid is evidently very rapid, so that only a single averaged acid peak is seen. This phenomenon is characteristic of hydroxyl groups bonded to phosphorus. Attempts to slow exchange through low-temperature experiments at 100 MHz were made. However, solutions of diammonium phosphate in fluorosulfuric acid at −50° or in fluorosulfuric acid–sulfuryl chlorofluoride at −90° exhibited only the usual singlet acid peak and an additional minor peak at δ 10.2 [attributed to hydronium ion (H_3O^+) impurity].[20] Phosphonic acid, phosphinic acid, and dialkyl phosphonates, which also are tetravalent phosphoryl compounds, similarly show no signal observable separately from the solvent acid peak when protonated on the phosphoryl oxygen atom.

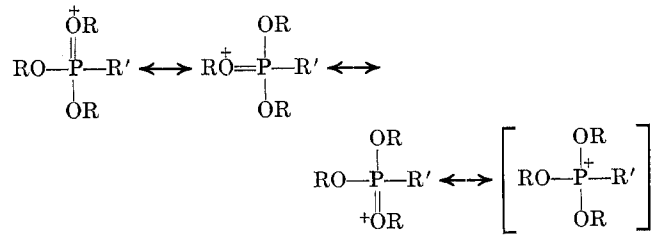
The ^{31}P chemical shifts of the protonated phosphates are comparable to values which have been reported for tetraalkoxy- and tetraphenoxyphosphonium ions. The first reported values for $P(OCH_3)_4^+$ and $CH_3OP(OC_2H_5)_3^+$ of −51.5 and −50 ppm[21] are in disagreement with subsequent shifts given for similar ions: −5,[22] −1.9,[23] −1.6,[24] and 0 ppm[25] for $P(OCH_3)_4^+$, and −3,[22] +2.4,[23] and +5 ppm[25] for $P(OC_2H_5)_4^+$. The more recent values are considered correct (in the early studies, the absorptions of the tetraalkoxyphosphonium ions may have been hidden by the reference peak[23b]). ^{31}P shifts of +18[26] and +24 ppm[25] have been found for $P(OC_6H_5)_4^+$. In certain cases the tetraalkoxyphosphonium ions were prepared by direct alkylation of the appropriate phosphates—the phosphoryl oxygen atom is clearly reactive toward sufficiently strong electrophiles.

Supplementing the nmr spectroscopic studies, it might be expected that protonated phosphoric acid, which should possess full tetrahedral symmetry, would produce a distinctive Raman spectrum. Laser Raman spectra of concentrated solutions of anhydrous phosphoric acid in fluorosulfuric acid led to no definite conclusions, for only lines due to the solvent fluorosulfuric acid and the major phosphoric acid lines observed by Simon and Weist[12d] in mixtures of phosphoric acid (which itself gives a spectrum characteristic of a tetrahedral environment) and perchloric acid were obtained.

In general, the protonated phosphorus compounds other than the phosphates are less stable, requiring their observation in solutions at −60°. The proton spectra of phosphonic acid, phosphinic acid, and dialkyl phosphonates showed sizable deshielding effects in fluorosulfuric acid solution. The coupling constants between a directly bound phosphorus and proton, $^1J_{PH}$, show large increases upon protonation. From a study of $^1J_{PH}$ obtained from solutions of phosphonic acid and phosphinic acid in aqueous sulfuric acid of variable acid strength, Sheldrick has calculated a value of 809–810 Hz for $^1J_{PH}$ in fully protonated phosphonic acid, $HP(OH)_3^+$, and a value of 675–681 Hz for $^1J_{PH}$ in fully protonated phosphinic acid, $H_2P(OH)_2^+$.[16] Haas and Gillman feel that their observed values of 804 and 671 Hz for $^1J_{PH}$ of phosphonic acid and phosphinic acid in 98% sulfuric acid are representative of the fully protonated species.[17] We obtained values of 819 to 825 Hz for phosphonic acid and the dialkyl phosphonates, and 687 Hz for phosphinic acid, when dissolved in fluorosulfuric acid (indicative of observation of the protonated compounds).

The tervalent trialkyl (aryl) phosphites are protonated at phosphorus in excess fluorosulfuric acid, yielding species similar to intermediates thought to occur in the Arbuzov reaction of organo phosphites.[27] The proton bound to phosphorus appeared in pmr spectra as a characteristic widely separated doublet, distinguishable from the strong low-field singlet due to excess fluorosulfuric acid. In all cases, this doublet was utilized to obtain the ^{31}P chemical shift by the internuclear double resonance (INDOR) method.

The ^{31}P chemical shifts of phosphoric acid and phosphates change very little upon protonation (and alkylation, as indicated before), whereas the α-alkyl protons in trialkyl phosphates become noticeably more deshielded. These protons exhibit chemical shifts which are comparable to values reported for $P(OCH_3)_4^+$ (δ 4.1,[25b] 4.32,[24] 4.37[23a]) and $P(OC_2H_5)_4^+$ (δ 4.5,[25b] 4.65[23a]). The ^{31}P shifts of the trialkyl (aryl) phosphites demonstrate startlingly large shielding effects upon protonation, moving upfield to values like that of protonated phosphonic acid and protonated dialkyl phosphonates. We conclude from these observations that in these hydroxy and alkoxy (aryloxy) phosphonium ions the positive charge is largely shifted from phosphorus to the oxygen atoms through the contribution of five-bond, phosphoryl-like structures in which the oxygen atoms donate nonbonded electron pairs to the formation of $d\pi$–$p\pi$ bonds.



R = H, alkyl, aryl; R′ = H, alkoxy, aryloxy, hydroxy

When R′ is an alkoxy, aryloxy, or hydroxy substituent, an additional contributing structure containing a phosphorus–oxygen double bond can be written. With hydroxy substitution going from the dihydroxyphosphonium ion [$H_2P(OH)_2^+$] to the tetrahydroxyphosphonium ion [$P(OH)_4^+$], the ^{31}P chemical shifts show

(20) A referee's inquiry prompted us to consider the concentration dependence of the chemical shift of the acid proton. In mixtures of trimethyl phosphate and fluorosulfuric acid, where the mole fraction of phosphate ranged from 0 to 0.9, the position of the acid peak varied correspondingly from δ 10.6 to 15.0.

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the expected increasing shielding, indicating the degree of charge delocalization on oxygen. Protonation of phosphine oxide (H_3PO) would be expected to yield the monohydroxyphosphonium ion, but the instability and ease of oxidation of phosphine oxide[28] has so far prevented observation of the ion.

Protonated triisopropyl phosphate and phosphite, protonated tri-*tert*-butyl phosphate and phosphite, and protonated di-*tert*-butyl phosphonate cleave so rapidly at room temperature that nmr spectra of these species could not be obtained. For example, the ^{31}P spectrum of the fluorosulfuric acid solution of triisopropyl phosphate showed only a singlet at -2.3 ppm [$P(OH)_4^+$]. However, the isopropoxyphosphonium ions have limited stability at $-60°$, allowing their proton spectra to be obtained at that temperature.

Protonated tri-*n*-butyl phosphate and phosphite also cleave with time at room temperature. Two days after preparation of the fluorosulfuric acid solution of the phosphate, the ^{31}P spectrum showed only a singlet at -2.5 ppm [$P(OH)_4^+$]. When dissolved in the super acid, 1:1 FSO_3H–SbF_5, the proton spectra of the phosphate and phosphite showed primarily singlets at δ 10.9 to 11.4 (rapidly exchanging acid protons) and δ 4.37 to 4.43 (*tert*-butyl cation). It was found that formation of *tert*-butyl cation from the phosphate could be followed kinetically by nmr spectroscopy at $-60°$ in an excess of 5.5:1 FSO_3H–SbF_5, but that the data could not be interpreted according to a simple rate law, probably because the three *n*-butyl substituents are cleaved off (and rearrange to *tert*-butyl cations) sequentially.

$$HOP(OC_4H_9)_3^+ \xrightarrow[-C(CH_3)_3^+]{+H^+} (HO)_2P(OC_4H_9)_2^+ \xrightarrow[-C(CH_3)_3^+]{+H^+}$$

$$(HO)_3POC_4H_9^+ \xrightarrow[-C(CH_3)_3^+]{+H^+} (HO)_4P^+$$

By varying the FSO_3H/SbF_5 ratio (changing the acid strength) and temperature, a direct qualitative correlation of the rate of formation of *tert*-butyl cation with acid strength and temperature was observed.

It seems clear that carbon–oxygen bond cleavage in protonated trialkyl phosphates and phosphites is facilitated by the ability of the alkyl substituents to leave as carbonium ions. Thus the order tri-*n*-butyl < triisopropyl < tri-*tert*-butyl was observed for ease of cleavage, in accordance with the relative stabilities of the corresponding alkyl cations. The instability of the protonated tri-*tert*-butyl compounds is especially to be expected: *tert*-butyl phosphate is known to hydrolyze by an SN1 process, even at pH 4.[29]

Any warming of the protonated triisopropyl phosphate and phosphite solutions above Dry Ice temperature resulted in the pmr signal of the methine proton changing from a doublet of septets to a single septet: the coupling between phosphorus and the methine proton disappeared. The new methyl and methine resonances (δ 1.73–1.74 and 5.54–5.55, respectively; $^3J_{HCCH}$ = 6.2 Hz), as well as the appearance in the fluorine nmr spectrum of a new singlet at -37.6 to -37.7 ppm (relative to external CCl_3F), suggest that isopropyl fluorosulfonate is formed in solution. In the case of the triisopropyl phosphite–fluorosulfuric acid solution, the nmr parameters of the phosphorus species remaining after isopropyl group cleavage (^1H shift δ 7.61, ^{31}P shift -18.8 ppm, $^1J_{PH}$ = 822 Hz) are indicative of protonated phosphonic acid. At certain times in a 60-MHz field (at $-60°$), it was possible to observe four different protons bound directly to phosphorus (there is some overlap of the absorptions at 100 MHz). We propose that the resonances arise from a mixture of all the possible ions of the type $HP(O\text{-}i\text{-}C_3H_7)_n(OH)_{3-n}^+$ (n = 0, 1, 2, 3) which would result from sequential cleavage of the isopropyl substituents from protonated triisopropyl phosphite. This proposal is supported by the fact that from a combination of 60- and 100-MHz ^1H spectra, and ^{31}P INDOR spectra, we were able to obtain directly or calculate nmr parameters for each of the ions (see Table II). Unlike the corresponding phosphate, protonated trimethyl phosphite also demonstrates some instability. The pmr spectrum showed a new singlet in the O-methyl region (δ 4.47) which increased with time. In the fluorine spectrum a new singlet appeared at -30.6 ppm. In this case also it is suggested that the methyl groups are cleaved off to form methyl fluorosulfonate (literature values for FSO_3CH_3: ^1H shift δ 4.12, ^{19}F shift -31.2 ppm[30]). These observations are similar to the finding that methyl and ethyl fluorosulfonate can be prepared from fluorosulfuric acid and the corresponding dialkyl sulfates.[30]

TABLE II

^{31}P AND ^1H NMR SPECTRAL PARAMETERS OF HYDROXYISOPROPOXYPHOSPHONIUM IONS, $HP[OCH(CH_3)_2]_n(OH)_{3-n}^+$ (n = 0–3), AT $-60°$

n	$\delta_{^{31}P}$ (85% H_3PO_4 = 0)	$\delta_{^1H}$ PH proton	$^1J_{PH}$, Hz
0	−18.8	7.61	824
1	−17.3	7.56	821
2	−16.3	7.48	812
3	−15.7	7.44	796

In studying the formation of protonated phosphonic acid by direct ^{31}P nmr spectroscopy (at 24.3 MHz), it was found that protonated phosphonic acid in fluorosulfuric acid undergoes further reaction at room temperature. After 45 min it was completely converted into phosphorus oxyfluoride (^{31}P spectrum a quartet centered at +36.5 ppm, ^{19}F spectrum a doublet centered at +90.5 ppm, $^1J_{PF}$ = 1062 Hz). The nmr parameters are identical with those obtained when phosphorus oxyfluoride was dissolved in fluorosulfuric acid. The protonated phosphonic acid generated from protonated trimethyl phosphite by methyl group cleavage also reacts with fluorosulfuric acid to form phosphorus oxyfluoride (the only product observed after 8 days at room temperature). Protonated phosphinic acid reacts to give phosphorus oxyfluoride, which could be observed in the ^{19}F spectrum of the fluorosulfuric acid solution after 2 days. In these cases the fluorinating ability of fluorosulfuric acid is an important factor.[31]

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(31) For example, phosphorus pentoxide in fluorosulfuric acid produces phosphorus oxyfluoride in good yield: E. Hayek, A. Aignesberger, and A. Engelbrecht, *Monatsh. Chem.*, **86**, 735 (1955).

Experimental Section

Materials.—Potassium dihydrogen phosphate, diammonium hydrogen phosphate, 85% aqueous phosphoric acid, tri-*n*-butyl phosphate, phosphonic acid, trimethyl phosphite, triphenyl phosphite, di-*n*-propyl phosphonate, di-*n*-butyl phosphonate, 50% aqueous phosphinic acid, and phosphorus oxyfluoride were commercially obtained and purified by standard methods. Triethyl phosphite, triisopropyl phosphite, and tri-*n*-butyl phosphite were prepared by reaction of phosphorus trichloride and the appropriate alcohol in the presence of a tertiary nitrogen base[4,32] and distilled under reduced pressure. Trimethyl phosphate, triethyl phosphate, triisopropyl phosphate, and triphenyl phosphate were prepared by nitrogen dioxide oxidation of the corresponding phosphite.[33] The procedure for the preparation of tri-*tert*-butyl phosphite from phosphorus trichloride and *tert*-butyl alcohol[34] initially yielded, as had been reported, a mixture of tri-*tert*-butyl phosphite and di-*tert*-butyl phosphonate, along with a smaller amount of tri-*tert*-butyl phosphate. Commercially available fluorosulfuric acid and antimony pentafluoride were twice distilled before use in the preparation of solutions.

Nmr Spectra.—Pmr spectra were recorded with Varian Associates Models A-60, A-56/60A, and HA-100 nmr spectrometers. Proton chemical shifts are reported in parts per million (δ) from external (capillary) tetramethylsilane. Fluorine nmr spectra were taken with the A-56/60A spectrometer operating at 56.4 MHz; fluorine chemical shifts are reported in parts per million relative to external fluorotrichloromethane. Direct phosphorus nmr spectra were obtained with a Varian Associates HA-60IL nmr spectrometer operating at 24.3 MHz and equipped with a Model V4331A probe. Samples were contained in 12- or 13-mm-o.d. thin-walled polished spinning tubes. A 5-mm-o.d. polished tube containing the reference material was inserted in the sample tube and maintained in a concentric position by two specially constructed Teflon inserts. Normally 85% phosphoric acid was used as the reference material; for samples (especially phosphates) whose resonance signals were masked by phosphoric acid, additional spectra using aqueous phosphonic acid (acid mole fraction $^1/_6$) and triphenyl phosphite as references were obtained. All phosphorus chemical shifts are reported in parts per million relative to 85% H_3PO_4. Whenever possible, direct ^{31}P spectra using 85% H_3PO_4 as the reference material were frequency swept under conditions of field-frequency stabilization. Otherwise, field sweep spectra calibrated by audiofrequency side-band modulation were obtained.

For obtaining phosphorus INDOR spectra (which include all of the low-temperature spectra), the HA-100 spectrometer was operated in the internal lock, frequency sweep mode, the first upper side-band of capillary TMS being used for the lock signal. The sweep 40.48-MHz frequency required for ^{31}P irradiation was obtained from the 20-MHz and 480-kHz outputs of a Monsanto Model 3100A Digital frequency synthesizer; the 20-MHz frequency was doubled and added to the 480-kHz output in an NMR Specialties Model SD-60B mixer and amplifier. The resultant frequency was fed to the probe *via* an attenuator and double-probe adapter and was monitored with a Hewlett-Packard Model 5245L electronic counter. The observing frequency (100 MHz) was determined using the same counter equipped with a Model 5253B frequency converter plug-in unit. ^{31}P resonance frequencies to ± 1 Hz were obtained by monitoring a line in the proton spectrum known to arise from proton–phosphorus coupling, and varying the frequency synthesizer output and attenuation until minimum peak height was found. The ^{31}P chemical shifts were calculated with respect to 85% H_3PO_4 as reference using the equation

$$\delta_P = [(\nu_0/2.4703089) - f_i] \times 10^6/(\nu_0/2.4703089)$$

where ν_0 is the sum of the observing frequency (derived from the V4311 unit) and the lock modulation frequency, and f_i is the measured ^{31}P frequency. This equation holds only for upper side-band operation using TMS lock; it was derived from experimentally determined ν_0/f_i ratios for trimethyl phosphate (2.4703029) and 30% (w/w) aqueous phosphonic acid (2.4702969), and from the ^{31}P chemical shifts of these compounds (−2.3 and −5.0 ppm, respectively) determined from direct phosphorus nmr spectra.

Preparation of the Ions.—Phosphorus compounds were dissolved in a (usually) tenfold molar excess of fluorosulfuric acid or fluorosulfuric acid–antimony pentafluoride solution with stirring and cooling to generate the protonated species under conditions similar to those described previously.[1a]

The laser Raman spectrophotometer which was used has been described previously.[35]

Registry No.—$P(OH)_4^+$, 26902-99-8; $HP(OH)_3^+$, 21862-21-5; $H_2P(OH)_2^+$, 21862-20-4; $HOP(OCH_3)_3^+$, 28180-50-9; $HOP(OC_2H_5)_3^+$, 28206-36-2; $HOP(O\text{-}i\text{-}C_3H_7)_3^+$, 28180-51-0; $HOP(O\text{-}n\text{-}C_4H_9)_3^+$, 28180-52-1; $HOP(OC_6H_5)_3^+$, 28180-53-2; $HP(OCH_3)_3^+$, 28206-37-3; $HP(OC_2H_5)_3^+$, 28206-36-2; $HP(O\text{-}i\text{-}C_3H_7)_3^+$, 28206-39-5; $HP(O\text{-}n\text{-}C_4H_9)_3^+$, 28206-40-8; $HP(OC_6H_5)_3^+$, 28206-41-9; $HP(OH)(O\text{-}n\text{-}C_3H_7)_2^+$, 28206-42-0; $HP(OH)(O\text{-}n\text{-}C_4H_9)_2^+$, 28206-43-1; $HP[OCH(CH_3)_2](OH)_2^+$, 28206-44-2; $HP[OCH(CH_3)_2]_2(OH)^+$, 28206-45-3.

Acknowledgments.—Support of this work by a grant from the National Institutes of Health and by a Public Health Service Fellowship from the National Institute of General Medical Sciences (to C. W. M.) is gratefully acknowledged.

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