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Phosphorus Nuclear Magnetic Resonance Studies of Ortho and Condensed Phosphates

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The P^{31} nuclear magnetic resonance spectrum of the tetrapolyphosphate ion, $P_4O_{13}^{-6}$, is presented under conditions of very high resolution with previously unobserved details of spin–spin splitting being resolved. The spectrum is analyzed to yield precise values of the phosphorus spin coupling constants by trial and error fit with computed theoretical spectra. P^{31} chemical shifts for ortho, pyro, tripoly, tetrapoly, trimeta, and tetrametaphosphate also have been measured in concentrated aqueous solutions over the pH range 0 to 12. Changes in the chemical shifts and phosphorus spin coupling constants with pH are discussed in terms of dynamic changes in the anionic structures with increasing acidity. Evidence is presented which suggests that the weakly acidic protons in the species $HP_3O_{10}^{-4}$, $H_2P_3O_{10}^{-3}$, $HP_4O_{13}^{-5}$, and $H_2P_4O_{13}^{-4}$ may, on the average, spend a larger fraction of their time associated with the middle phosphate groups in these short chain polyanions than previously assumed on the basis of pH titration data.

Introduction

Early phosphorus n.m.r. studies of condensed phosphates[1] showed well resolved chemical shifts for isolated, end, and middle phosphate groups. Details of fine structure due to phosphorus–phosphorus spin coupling were observed later for tripolyphosphate, $P_3O_{10}^{-5}$, and tetrapolyphosphate, $P_4O_{13}^{-6}$, although the spectrum of the latter could not be analyzed due to limitations of resolution.[2] It also was observed previously that increasing the acidity of phosphate solutions increased the shielding of the phosphorus nucleus, causing a shift of the P^{31} resonances to higher field by several parts per million.[3] Jones and Katritzky[4] examined this shift in some detail for orthophosphate and plotted a smoothly varying function as $H_3PO_4 \rightarrow PO_4^{-3}$. No detailed study of this pH effect has been reported previously for the condensed phosphates. The present work was undertaken to determine the precise nature of the change in shift with acidity for the lower condensed phosphates and to determine the magnitude and direction of any associated changes in phosphorus spin coupling constants. Improvements in instrumentation allowed these measurements to be made with much greater precision than formerly was possible for phosphorus spectra. During the work, the spectrum of the tetrapolyphosphate anion was obtained for the first time under very high resolution. Previously unobserved fine structure in this spectrum was completely resolved, and the spectrum was analyzed to obtain the phosphorus coupling constants for end-to-middle and middle-to-middle phosphate linkages. Changes in the chemical shifts and coupling constants with pH are discussed in terms of the dynamic structures of the condensed phosphate anions in solution.

Experimental Details

Apparatus and Procedure.—Measurements were made on a Varian Associates high resolution spectrometer system using a Model V-4311 fixed frequency R-F unit operating at 24.288 Mc. in a magnetic field of 14,092 gauss. The magnet was equipped with temperature-controlled cooling water, Super Stabilizer, field homogeneity shim coils, field trimmer, magnet yoke insulation, and air temperature control. The field was trimmed with the shim coils at the beginning of each set of runs to achieve 1.0 c.p.s. or better resolution, as measured by the peak widths at half height of the eight observable peaks in the trimethylphosphite multiplet. Phosphate samples were examined as concentrated aqueous solutions in 5.0 mm. o.d. thin-wall precision tubes without spinning; probe temperature was 27°. R-F power level was chosen as the best compromise between satisfactory signal-to-noise ratios and minimum saturation levels. Sweep rates in the range of 0.5 to 2.0 c.p.s. per second normally were used to record the absorption mode spectra on a Sanborn Model 151 recorder. Referencing was done by an audio side-band modulation technique using, as an external reference, 85% H_3PO_4 in a sealed 1.0 mm. o.d. capillary tube inserted in the sample. When the best precision was desired, referencing was done in triplicate. Peak positions measured in this way could be reproduced on the same sample to within ±0.1 c.p.s.

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(1) J. R. Van Wazer, C. F. Callis, and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 4945 (1955).

(2) C. F. Callis, J. R. Van Wazer, J. N. Shoolery, and W. A. Anderson, *ibid.*, **79**, 2719 (1957).

(3) J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *ibid.*, **78**, 5715 (1956).

(4) R. A. Y. Jones and A. R. Katritzky, *J. Inorg. Nucl. Chem.*, **15**, 193 (1960).

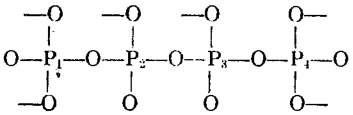
(±0.004 p.p.m.). The data are presented as obtained with no corrections for bulk susceptibility differences or extrapolations to infinite dilution being attempted.

Analysis of the spin coupling constants for tetrapolyphosphate was carried out by trial and error fit against electronically computed[5] theoretical spectra using an A_2X_2 approximation[6] to obtain initial trial parameters. These were refined until the calculated and observed spectra for all peaks agreed to within ±0.15 c.p.s.

Sample Preparation.—All of the phosphates were either commercial reagent grade materials or laboratory preparations of high purity. Initial measurements were made on each compound as a saturated aqueous solution of the sodium salt, with the exception of tetrapolyphosphate which was examined as the ammonium salt. No large peaks were observed in the n.m.r. spectra other than for major species. Saturated solutions of Na_3PO_4, $Na_4P_2O_7$, $Na_5P_3O_{10}$, $Na_3P_3O_9$, $Na_4P_4O_{12}$, and $(NH_4)_6P_4O_{13}$ were treated separately with either concentrated HCl or concentrated NaOH to obtain a series of samples over the pH range 0 to 12. A Beckman Zeromatic pH meter with a glass and calomel electrode assembly, standardized against buffer at pH 4, 7, and 10, was used to measure pH. N.m.r. measurements were made immediately, before any significant hydrolytic degradation could occur. The small dilution introduced by the pH adjustment was found to have a minor effect on the resulting chemical shifts, but this was small compared with the large shifts produced by the pH change. These small effects due to dilution and change of alkali metal ion or its concentration were usually less than 0.5 p.p.m., while the changes due to pH were approximately tenfold larger. Titration curves were run on some of the concentrated solutions to determine the number of equivalents of acid per mole of polyphosphate present at the pH of the observed inflection points in the n.m.r. chemical shift data.

Results and Discussion

The P^{13} N.m.r. Spectrum of Tetrapolyphosphate.—The tetrapolyphosphate anion, $P_4O_{13}^{-6}$, is thought to have the following structure,[7] where the oxygens are arranged tetrahedrally around the phosphorus atoms.



$$\mathrm{O{-}P_1{-}O{-}P_2{-}O{-}P_3{-}O{-}P_4{-}O}$$

The P^{31} n.m.r. spectrum at 24.3 Mc. for a concentrated aqueous solution of the ammonium salt, shown in Fig. 1, is in complete agreement with this structure. The chemical shifts and spin coupling constants for this spectrum were determined by trial and error fit to electronically computed theoretical spectra using the method of Bothner-By and Naar-Colin.[5] The final constants, as well as detailed data for the theoretical and observed spectra, are given in Table I. Although the spectrum is completely symmetrical, the band at lower field may be assigned to the end phosphorus nuclei on the basis of the known chemical shifts of other polyphosphate end groups. The band at higher field results from the middle phosphorus nuclei. The chemical shifts of the end and middle groups change with decreasing pH as the acid–base equilibria

$$P_4O_{13}^{-6} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} HP_4O_{13}^{-5} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} H_2P_4O_{13}^{-4} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \text{etc.}$$

shift in response to increases in the concentration of free hydronium ion in solution. These data are included in Fig. 2 and will be discussed later. Spin coupling constants, $J_{12} = J_{34}$ for end-to-middle P–O–P bonds and J_{23} for middle-to-middle bonds also change with pH, as shown in Table II, which, in addition, contains data for tripolyphosphate. It is assumed that coupling constants are of like sign. $|J_{12} = J_{34}|$ is always greater than $|J_{23}|$, but the difference is less as the solution becomes more acidic. This is best seen in the ratio J_{23}/J_{12}. Decreased coupling of the phosphorus nuclei apparently results from the formation of H–O–P bonds of some covalent character in the acidic solution. Since the end groups bear a doubly negative charge, the probability of forming an H–O–P linkage is greater for an end group than for a singly changed middle group, and the larger decrease in $|J_{12}|$ with increasing acidity thus is not surprising. It is interesting to note that in the early work on this anion, even though resolution was not sufficient to resolve the fine structure within the end and middle bands of the spectrum, Callis, *et al.*,[2] were able to estimate from the width of the bands that J_{23}/J_{12} must be less than *ca.* 1.2. The observed ratios reported here range from 0.84 ± 0.02 at pH 8 to 0.95 ± 0.02 at pH 0. Coupling constants $J_{13} = J_{24}$ are assumed to be negligible. With the degree of resolution obtained, values between 0 and 0.5 c.p.s. would be undetectable.

The pH Dependence of Spectra.—The effects of pH on the apparent chemical shifts and coupling constants of the anions PO_4^{-3}, $P_2O_7^{-4}$, $P_3O_{10}^{-5}$, $P_4O_{13}^{-6}$, $P_3O_9^{-3}$, and $P_4O_{12}^{-4}$ are shown in Fig. 2 and Table II. In general, the ring phosphates show little change in shift with pH, while for ortho

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[5] A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961). The authors are indebted to Dr. A. Bothner-By of Mellon Institute for furnishing us with a copy of their "FREQINT III" IBM 704 computer program which was used in the calculation of the theoretical spectra.

[6] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York, N. Y., 1959, p. 140.

[7] J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, New York, N. Y., 1958, p 661.

and chain phosphates the chemical shift becomes more positive with increasing acidity, and P–O–P coupling constants decrease.

TABLE I

OBSERVED AND CALCULATED SPECTRA FOR TETRAPOLYPHOSPHATE[a]

Chemical shifts, c.p.s.	Coupling constants, c.p.s.
$W_1 = 146.4$	$J_{12} = J_{34} = 19.7$
$W_2 = 503.8$	$J_{23} = 16.5$
$W_3 = 503.8$	$J_{13} = J_{24} \simeq 0$
$W_4 = 146.4$	$J_{14} = 0$

Observed spectrum		Calculated spectrum[b]	
Frequency	Intensity	Frequency	Intensity
125.1	0.4	125.1	0.319
136.4	2.0	136.3	1.890
141.8	1.5	141.5	1.597
150.6	1.5	150.7	1.681
156.1	2.1	156.0	2.110
167.3	0.4	167.2	0.403
483.0	0.5	483.0	0.403
494.2	2.1	494.2	2.110
499.6	1.6	499.5	1.681
508.4	1.5	508.7	1.597
513.9	2.0	514.0	1.890
525.1	0.4	525.1	0.319

[a] On a frequency scale with external 85% H_3PO_4 having a chemical shift of 0 c.p.s. [b] Each line of the calculated spectrum is a closely spaced doublet, separated by less than 0.02 c.p.s. The average value is reported here.

TABLE II

THE EFFECT OF PROTON ASSOCIATION ON P–O–P COUPLING CONSTANTS[a]

	Tripoly-phosphate	Tetrapolyphosphate		
pH	J	$\|J_{12} = J_{34}\|$	$\|J_{23}\|$	$\|J_{23}/J_{12}\|$
8	19.4	19.9	16.7	0.84
4	19.2	19.7	16.8	.85
2	18.2	18.7	16.5	.88
0	16.7	16.7	15.9	.95

[a] J values are in c.p.s. and are accurate to within ±0.2 c.p.s.

One finds less change in shift in regions of pH where a single ionic species predominates. Thus, for orthophosphate, inflection points are obtained for PO_4^{-3}, HPO_4^{-2}, and $H_2PO_4^{-}$. Similarly for pyro, tri, and tetrapolyphosphates, flat regions appear for the compositions $P_nO_{3n+1}^{-(n+2)}$ and again for $H_2P_nO_{3n+1}^{-n}$. The ring phosphates, undergoing no weakly acidic hydrogen association, show no changes above pH 2.

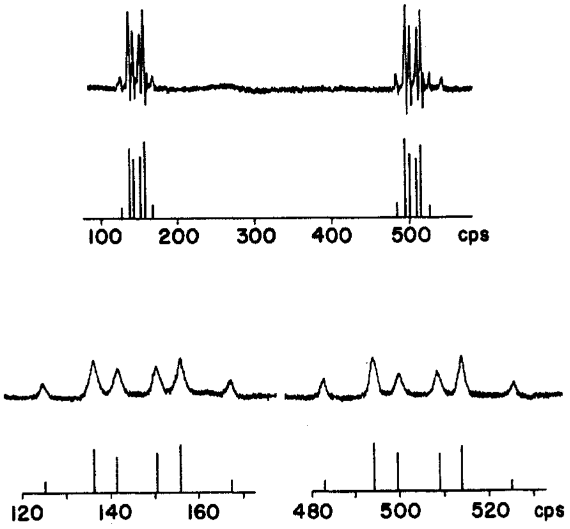

Fig. 1.—Observed and calculated P^{31} n.m.r. spectra at 24.3 Mc. for ammonium tetrapolyphosphate. The peak at 543 c.p.s. is due to a small amount of $P_4O_{12}^{-4}$ present as an impurity.

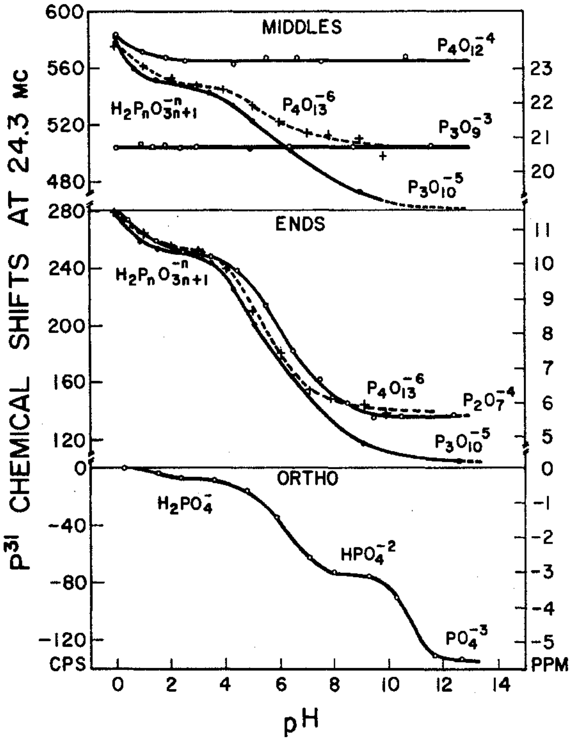

Fig. 2.—Change in P^{31} chemical shifts of ortho and condensed phosphates with pH.

An inflection point in regions of pH where a single ionic species predominates also can be seen in the P–O–P coupling constants. Figure 3 shows detailed data on tripolyphosphate. There is a pronounced inflection at pH 2 for the composition $H_2P_3O_{10}^{-3}$. As the acidity decreases, the coupling constant increases up to pH 5.5, as expected. Here there is a sharp break, and the coupling constant again decreases as the solution becomes more basic. This decrease most likely results from the effect of sodium ion complexing by the tri-

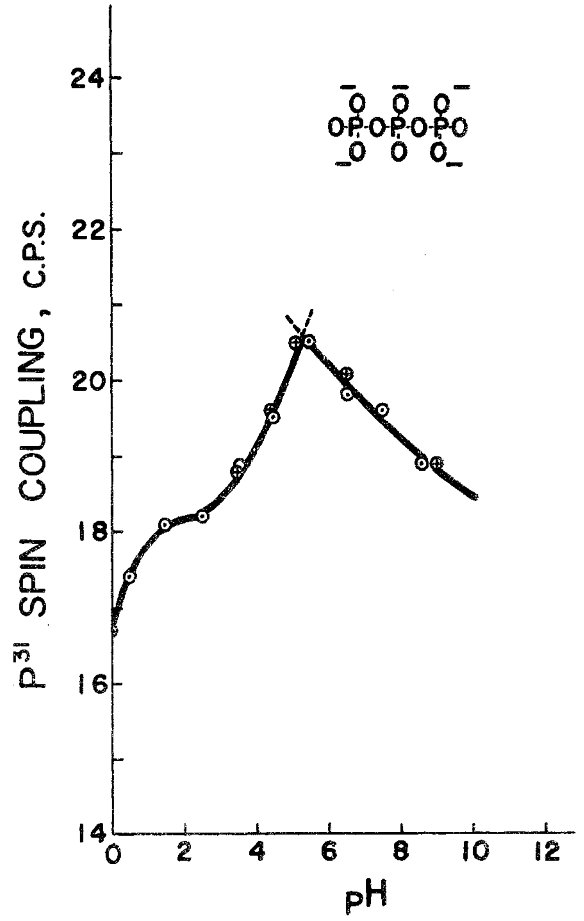

Fig. 3.—The change in the phosphorus spin coupling constant for the tripolyphosphate ion with pH.

polyphosphate anion,[8] which is known to occur with the species $HP_3O_{10}^{-4}$ and $P_3O_{10}^{-5}$.

The addition of each weakly acidic hydrogen increases the chemical shift by 2 to 3 p.p.m. for end phosphate groups and by 1 to 2 p.p.m. for middle groups. Somewhat cruder experiments, not reported here, have shown that in chain phosphates longer than tetra, the average middle group shift is less affected by the addition of the first two protons[9] than in the shorter chains.

The absence of an inflection point in Fig. 2 for the chain phosphate composition $HP_nO_{3n+1}^{-(n+1)}$ is significant, since pH titration curves[10,11] do exhibit inflections for this composition. It should be remembered that titration curves reflect the effect of over-all acid–base equilibria on the concentration of free hydronium ion and show that a second proton becomes associated less readily after the first one has been added to the basic anion. Titration curves do not, however, give *direct* evidence about the location of the *bound* protons. The P^{31} chemical shift, when measured with sufficient precision, is a very sensitive function of the structure and bonding in the polyphosphate anion, and for $P_3O_{10}^{-5}$ and $P_4O_{10}^{-6}$ the end and middle phosphorus atoms within each anion provide, in effect, sensitive probes, by means of which information about the bonding of associated protons may be inferred.

The fact that "end group titrations"[12,13] can be used to determine the length of long chains suggests that the first two associated protons must attach on (or near) the ends of the polyanion. For shorter chains, however, there may be a considerable probability for these weakly acidic protons to bond to the middle phosphate group, or be shared by an end and a middle group. Physical means of directly detecting the average location of associated hydrogens in a polyanion has previously been lacking. The P^{31} n.m.r. chemical shift data reported here must contain this information, if it can be properly interpreted. The absence of hydrogen–phosphorus spin coupling and the presence of only single P^{31} resonances in regions of pH where more than one ionic species predominate are consistent with rapid exchange of bound hydrogens with the water solvent, so only time average information about the locations of the hydrogens can be expected.

The fact that chain phosphate middle groups which are adjacent to end groups exhibit relatively large changes in shift over the same pH range as end groups suggests that the two weakly acidic hydrogens may, on the average, spend a significant fraction of their time on the middle groups as well as on the ends of the anions. The effects seem too large to be explained as simply an inductive effect on middle groups, acting through the P–O–P–O–H linkage. If the relative sizes of the shift-changes for end and middle groups are proportional to the amount of time the associated hydrogen spends in each location, one might estimate from Fig. 2 that the probability of finding the single associated proton on the middle group in $HP_3O_{10}^{-4}$ is approximately one half that of finding either of the end groups thus occupied. As the number of middle groups doubles, for $HP_4O_{13}^{-5}$, the observed change in middle group shift decreases by about one half, consistent with a de-

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(8) J. I. Watters, S. M. Lambert, and E. D. Loughran, *J. Am. Chem. Soc.*, **79**, 3651 (1957).

(9) M. M. Crutchfield, unpublished experiments.

(10) J. I. Watters, E. D. Loughran, and S. M. Lambert, *J. Am. Chem. Soc.*, **78**, 4855 (1956).

(11) S. M. Lambert and J. I. Watters, *ibid.*, **79**, 4262 (1957).

(12) J. R. Van Wazer and K. A. Holst, *ibid.*, **72**, 639 (1950).

(13) Reference 7, pp. 459–461.

creased probability of finding a single associated proton on either one of the two middle groups. Good data are lacking for middle groups not directly attached to ends, but the indication is that this diminishing trend continues[9] for longer chains.

Other interpretations of the observed chemical shift data which do not involve part-time residence of the weakly acidic hydrogens on the middle groups can be offered, however. It can be argued that the hydrogens may associate only with the end phosphate groups, and that the resulting decrease in the over-all anionic charge, which may be considerably delocalized, results in increased shielding of the middle as well as the end P^{31} nuclei. Alternatively, coiling[14] of the linear polyanions with decreasing pH as the repelling negative charges are reduced by association of protons might produce a shift of the middle group resonance without direct proton association at the middle groups themselves. The data for ring phosphates is consistent in this respect, since for $P_3O_9^{-3}$, in which the interphosphorus distances are relatively fixed by steric considerations, there is no change in chemical shift over the entire pH range. For $P_4O_{12}^{-4}$, however, which has a greater number of degrees of freedom,[15] the interphosphorus distances can vary over a wider range, and a corresponding chemical shift is indeed observed below pH 2, where proton association would begin for ring phosphates.

Additional light is shed on the question of hydrogen substitution on middle groups by nuclear double resonance experiments in which the dynamic nuclear polarization enhancement[16] of the P^{31} n.m.r. signals from end and middle phosphate groups, respectively, is measured while the proton resonance is simultaneously saturated at high R-F power levels. The results, which will be reported in a separate communication,[17] tend to confirm the initial hypothesis that the associated protons must indeed reside a considerable fraction of the time on middle groups adjacent to ends in polyphosphate anions over the composition range $P_nO_{3n+1}^{-(n+2)}$ to $H_2P_nO_{3n+1}^{-n}$. This does not deny that other factors also may contribute significantly to the chemical shift data reported in this paper. We are aware, for example, of small differences in our data and that of Jones and Katritzky[4] for orthophosphate. We were able to determine that these were due to small anion and alkali metal ion concentration differences resulting from the difference in the way the samples were prepared.

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(14) Reference 7, p. 464.

(15) Reference 7, p. 699.

(16) A. Abragam, "The Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961, p. 333.

(17) M. M. Crutchfield, J. T. Yoder, and C. F. Callis, to be published.