JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 78 AUGUST 6, 1956 NUMBER 15

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY, THE STATE UNIVERSITY OF NEW JERSEY]

Degradation of Polyphosphates in Solution. I. Kinetics and Mechanism of the Hydrolysis at Branching Points in Polyphosphate Chains[1]

BY ULRICH P. STRAUSS AND THEODORE L. TREITLER

RECEIVED FEBRUARY 27, 1956

Previous kinetic studies of the rapid hydrolysis of branching points in sodium polyphosphate have been extended. From the first-order rate constants, measured both titrimetrically and viscosimetrically at 0, 25 and 45°, an activation energy of 18.9 kcal. per mole was calculated. Lowering the polarity of the aqueous solvent by the addition of organic solvents had no significant effect on the rate. Several conceivable hydrolysis mechanisms are examined and, of these, only the mechanism involving a nucleophilic attack of a water molecule on the branch point phosphorus atom followed by a breakdown of the transition state into two polyphosphate chains is consistent with the known experimental data. Consequences of a similar nucleophilic mechanism operating in the case of the degradation of linear portions of polyphosphate chains are discussed and found to be in qualitative accord with published results. Further conclusive evidence is presented that the rapid initial hydrolysis of Graham's salts occurs at branch points in the polyphosphate chains.

The hydrolytic degradation of the linear inorganic polyphosphates has been widely studied. Published reports of such studies show that the rate of degradation is significantly affected by a great number of experimental variables such as temperature,[2–6] *p*H,[2,3,5–8] ionic strength,[6] concentration of sodium ion[3,6] and other uni- and multivalent cations[9] which are complexed by the polyphosphates. The relations between the degradation rate and most of these variables are complicated, and therefore little progress has been made in correlating the experimental data with a suitable reaction mechanism.

In a recent study, aimed at proving the existence of chain branching in Graham's salts with Na/P ratios slightly greater than unity, it was discovered that the rate, measured at 25°, of the rapid degradation at branching points was constant over the *p*H range 3.4–8.1 and independent of the ionic strength and sodium ion concentration.[10] Since these results indicated relatively simple kinetics, it seemed promising to extend these rate studies, with the aim of obtaining some experimental evidence which would point to one out of a variety of conceivable mechanisms.

This knowledge might then furnish a clue toward a better understanding of the slower, but apparently much more complex degradation occurring in the linear portions of the polyphosphate chains. The understanding of this degradation mechanism may suggest methods of slowing down the degradation of commercially important polyphosphates during use and throw light on the splitting of phosphate bonds in biological systems where such processes are essential intermediate steps in the conversion of chemical to mechanical energy.

Experimental

Preparation and Characterization of Polymer.—Sodium polyphosphate (our sample No. 249P) was prepared by fusing 250 g. of $NaH_2PO_4 \cdot H_2O$ (Eimer and Amend, C.P. grade) for 14 hr. at 970° and quenching between cold steel plates. The polymer was characterized by the methods described in a previous paper.[10] The Na/P ratio was 0.998.

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[1] The contents of this paper are contained in a thesis submitted by T. L. Treitler to the Graduate School of Rutgers University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(30-1)1018. Presented at the Symposium on "Phosphorus and Its Compounds" before the Division of Physical and Inorganic Chemistry, 129th meeting of the American Chemical Society, Dallas, Texas, April 9, 1956.

(2) R. N. Bell, *Ind. Eng. Chem.*, **39**, 136 (1947).

(3) S. L. Friess, THIS JOURNAL, **74**, 4027 (1952).

(4) R. Pfanstiel and R. K. Iler, *ibid.*, **74**, 6059 (1952).

(5) D. O. Campbell and M. L. Kilpatrick, *ibid.*, **76**, 893 (1954).

(6) J. R. Van Wazer, E. J. Griffith and J. F. McCullough, *ibid.*, **77**, 287 (1955).

(7) J. P. Crowther and A. E. R. Westman, *Can. J. Chem.*, **32**, 42 (1954).

(8) J. D. McGilvery and J. P. Crowther, *ibid.*, **32**, 174 (1954).

(9) J. Green, *Ind. Eng. Chem.*, **42**, 1542 (1950).

(10) U. P. Strauss and T. L. Treitler, THIS JOURNAL, **77**, 1473 (1955).

$M_{W\infty}$, the weight average molecular weight, determined after degradation of all the branches from the intrinsic viscosity in 0.035 N NaBr,[11] was 15,500. Potentiometric titrations and viscosity measurements were carried out by the same methods and with the same instruments as previously described.[10]

Branching Point Degradation Rates.—The degradation rates were followed at 0, 25 and 45° in the absence of CO_2 both by titration for hydrogen ions and by viscosity measurements, essentially following the procedures employed earlier.[10] However, while previously the polyphosphate samples had been allowed to dissolve completely, in the experiments reported here the dissolution was allowed to proceed for only 10 to 15 minutes; during this time the solution was stirred violently while nitrogen bubbled through it. After the dissolution period the pH was brought up to 7.1 with NaOH, and the polymer solution was separated from any undissolved polymer by decantation. In this way measurements could be begun before the degradation had become appreciable. The purpose of the pH adjustment was to avoid any possible interference from hydrolysis of linear portions of the chains. The polyphosphate concentration was determined by analysis of an aliquot of the solution for total phosphate, carried out by a potentiometric titration between the first and second neutralization points of the orthophosphate solution resulting from acid hydrolysis of the aliquot.[12] Samples intended for the 25 and 45° runs were dissolved at these temperatures. However, the dissolution at 0° was so slow that the samples intended for the 0° runs were dissolved at approximately 5°. During the 10 minutes which were allowed for dissolution, the temperature usually rose to about 15° even though the solution was kept in an ice-bath.

If the degradation follows first-order kinetics, the results can be expressed by the relation

$$\log b = -0.434kt + \log b_0 \qquad (1)$$

where b is the number of meq. of branches per g. of polymer, t is the time in min. and k is the rate constant in min.$^{-1}$. The symbol b_0 refers to b at $t = 0$, and with the proper choice of zero time it is a rough measure of the initial number of branches in the samples. The details of the extrapolation procedure have been discussed.[10] The value of b may be obtained either from h and h_∞ or from M_n and $M_{n\infty}$,[13] where h is the number of meq. of titratable hydrogen ions per g. of polymer, M_n is the number average molecular weight, and the subscript ∞ refers to the measurements made after the branch point degradation is complete. The value of M_n was assumed to be one-half M_W, the weight average molecular weight, which was determined viscosimetrically, as previously described.[10] Whenever made necessary by the use of polymer concentrations, solvent media or temperatures different from those previously employed, new empirical relationships between the reduced viscosity and the molecular weight were first established.

Completion of the branch point degradation took less than 2 hr. after dissolution at 45° and less than 24 hr. at 25°; but at 0° the degradation was so slow that there were still some branches left after 5 days. Therefore, in order to save time, the branches remaining after all the desired data in a given 0° run had been obtained were decomposed at room temperature for at least 7 hr., and h_∞ or $M_{n\infty}$ were determined.

Results and Discussion

Effect of Temperature.—The results obtained in aqueous solution at three temperatures are shown graphically in Fig. 1. Three features are noteworthy: first, the titration and viscosity methods give closely agreeing results; second, the rates are first order at all three temperatures and third, the rates increase with rising temperature. In order to fit the 0° data on the graph, an expanded time scale was used. The slowness of the degradation near 0° also made it possible to demonstrate for the first time that for every two titratable hydrogen ions only one end-group was produced. This is the most direct proof yet that the degradation under age study occurs at branch points, since for every cleavage in the linear portion of the chain two end-groups would be formed.[14] The details of this demonstration are given in the Appendix.

The first-order rate constants, obtained from the slopes of the lines in Fig. 1 according to equation 1, are given in Table I. Also included in this table are the maximum and minimum estimates of b_0, which are obtained as previously described.[10,15] These estimates agree within the precision of the method, as would be expected.

TABLE I

EFFECT OF TEMPERATURE ON RATE OF BRANCH POINT HYDROLYSIS

Temp., °C.	$k \times 10^3$ (min.$^{-1}$) Titn.	Visc.	$b_0 \times 10^2$ (meq./g.) Titn.	Visc.
0	0.45	0.42	1.6–1.7	2.0–2.5
25	8.0	9.3	1.6–2.6	2.5–3.3
45	59	65	1.3–4.2	1.5–5.8

The energy of activation, E_a, was determined from a conventional log k against $1/T$ plot to be 18.9 kcal. The plot was linear indicating that E_a was constant over the temperature range from 0 to 45°. The entropy of activation, defined by the Eyring equation[16]

$$k = \frac{KT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \qquad (2)$$

was −15 e.u. In equation 2, K is the Boltzmann constant and h is Planck's constant. The value of $\Delta H^\ddagger$ was obtained from the solution kinetics approximation, $\Delta H^\ddagger = E_a - RT$.[17]

Effect of Variations in Nature of Solvent.—As has already been mentioned, we have previously shown that the rate of degradation of branch points at 25° is constant over the pH range 3.4–8.1 and that it is the same in water as in 0.035 N NaBr solution.[10] These ranges have now been extended to pH 11 and to a sodium bromide normality of 0.35, respectively. Moreover, several runs were made, in which the polarity of the aqueous solvent was changed by the addition of organic solvents. Since the polymer was insoluble in these solvents, they could be added only in limited amounts if precipitation of the polymer was to be avoided. The results of these experiments are compared with those obtained in water in Table II. As can be seen, these variations in solvent composition have no significant effect on the rate constant of the branch point degradation.

Reaction Mechanism.—There are several conceivable simple mechanisms for the branch point degradation. In view of the expected weakness

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[11] Using equation 1 of reference 10.

[12] J. R. Van Wazer, THIS JOURNAL, **72**, 644 (1950).

[13] See equations 3 and 4 of reference 10.

[14] Only one measurable end-group would be formed if an orthophosphate group were to split off the end of a chain. However, this process could not explain an initial effect which ceased while the polymer still had a high molecular weight.

[15] In the 0° case, the extrapolation to zero time was made somewhat more difficult by the fact that the samples were dissolved between 5 and 15°. In making the estimates of the upper limit of b_0, the calculated value of k at 15° was used for the extrapolation.

[16] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 196.

[17] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 97.

TABLE II

EFFECT OF VARIATIONS IN SOLVENT COMPOSITION ON RATE OF BRANCH POINT HYDROLYSIS

Solvent[a]	Temp., °C.	Dielectric const.	Method	$k \times 10^3$ (min.$^{-1}$)[d]
Water	25	82[b]	Av. of titn. and visc.	8.6
13.1% Methanol	25	76[b]	Titn.	9.5
11.8% 2-Butanone	25	75[b]	Titn.	9.2
10.3% Dioxane	25	70[c]	Visc.	8.6
0.35 *N* NaBr	25	..	Titn.	9.0
Water	28	..	Calcd.	11.5
0.001 *N* NaOH	28	..	Titn.	9.8
Water	45	75[b]	Visc.	66.1
10.3% Dioxane	45	64[c]	Visc.	66.8

[a] All solvents have water as their main constituent. Percentages are by weight. [b] "International Critical Tables," Vol. VI, McGraw-Hill Book Co., New York, N. Y., 1929, pp. 100–102. [c] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 544. [d] Possible effects of the small changes in water concentration resulting from the addition of organic solvents have been ignored in the calculation of these first-order rate constants.

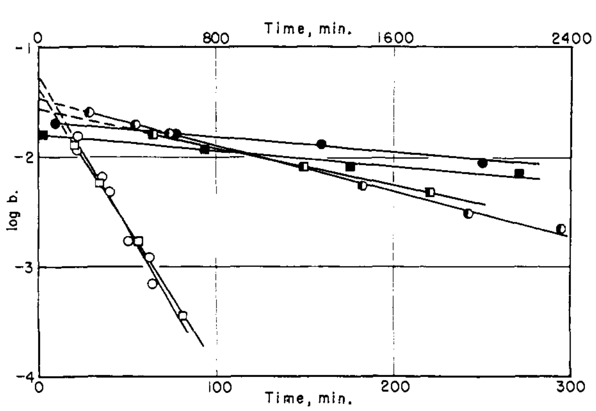
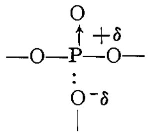


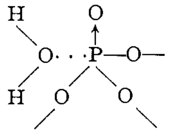
Fig. 1.—Effect of temperature on hydrolytic degradation rate of P–O bonds at branch points in glassy sodium polyphosphate. Upper abscissa applies to 0° runs (shaded squares or circles). Lower abscissa applies to 25° runs (half-shaded symbols) and to 45° runs (open symbols). Squares refer to titration for hydrogen ions ($b = [h_\infty - h]/2$), circles to viscosimetry ($b = 2000/M_{w_\infty} - 2000/M_w$). Time is measured from beginning of dissolution.

of the P–O bonds at branch points,[18] one may, for instance, consider the possibility that the rate-determining step is the splitting off of a branch, followed by the fast addition of water to the fragments. The transition state for this hypothetical SN1 process would have the configuration



A separation of positive and negative charges in the transition state should cause the rate to decrease very strongly with decreasing polarity of the solvent.[19] Since no such polarity effect was found, we consider this ionic mechanism unlikely.

A mechanism which, in its essentials, has been mentioned in connection with the hydrolysis of linear polyphosphates[3,8] and of organic phosphate esters[20,21] involves an attack of the nucleophilic water molecule on the phosphorus and the subsequent breakdown of the transition state



to two polyphosphate chains by the breaking of one of the three equivalent P–O bonds. A substantial lengthening of one or more of these P–O bonds in the transition state, however, would again involve a separation of positive and negative charges and is therefore held unlikely. For these reasons, the formation of the bond between the oxygen of the water molecule and the phosphorus is considered the critical step leading to the transition state. The formation of this bond involves the smearing out of negative charge from the water oxygen to the phosphorus atom. According to Ingold, such a process should be very little affected by a change in solvent polarity,[19] in line with our findings. While it is not necessary to assume that the phosphorus is actually pentacovalent during the transition, such an expansion of the valence shell of phosphorus is a possibility and has been postulated by others[20,22–24] in analogy to similar ideas concerning silicon.[25]

A third conceivable mechanism would be an electrophilic attack of a water molecule on one of the oxygen atoms connecting the phosphorus at a branch point with another phosphorus atom. However, such an attack should be so much easier for an oxonium ion than for a water molecule, that a *p*H effect should be noticeable even though the water concentration is much greater than the oxonium ion concentration.[26] Since no *p*H effect on the rate was observed at as low a *p*H as 3.4,[10] we believe this mechanism to be unlikely.

From these considerations, the nucleophilic attack by a water molecule seems the most likely mechanism for the hydrolysis of P–O bonds at branch points. It is of interest that by assuming a similar mechanism for the hydrolysis of P–O bonds situated in the linear parts of the polyphosphate chain, one can account at least qualitatively for the observed differences in the hydrolytic behavior of the two types of P–O bonds. For the sake of brevity, the hydrolysis at a branch point will be de-

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(18) J. R. Van Wazer and K. A. Holst, THIS JOURNAL, **72**, 639 (1950).

(19) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 347.

(20) S. S. Stein and D. E. Koshland, Jr., *Arch. Biochem. Biophys.*, **39**, 229 (1952).

(21) J. D. Chanley and E. Feageson, THIS JOURNAL, **77**, 4002 (1955).

(22) E. Blumenthal and J. B. M. Herbert, *Trans. Faraday Soc.*, **33**, 849 (1937).

(23) J. D. Chanley, E. M. Gindler and H. Sobotka, THIS JOURNAL **74**, 4347 (1952).

(24) J. D. Chanley and E. M. Gindler, *ibid.*, **75**, 4035 (1953).

(25) C. G. Swain, R. M. Esteve and R. H. Jones, *ibid.*, **71**, 965 (1949).

(26) Due to the polyelectrolyte nature of the polyphosphate, the electrical potential in the neighborhood of the polymer chain is negative, and consequently the local oxonium ion concentration is considerably greater near the chain than in the bulk of the solution.

noted by *B-hydrolysis* and the hydrolysis in the linear portion of the chain by *L-hydrolysis* in the following comparison.

First of all, we must account for the observation that the B-hydrolysis proceeds at a much greater rate than the L-hydrolysis. Most of this dissimilarity can be attributed to the differences in the energies of activation, which are 18.9 kcal. for the B-hydrolysis and about 25 kcal.[4,6] for the L-hydrolysis. We believe that this difference in activation energy arises for the most part from the fact that, while in both cases the negative oxygen atom of the attacking water molecule is repelled by the negative oxygen atoms surrounding the phosphorus atom, this repulsion is much weaker in the case of a B-phosphate group with an over-all charge of zero than in the case of an L-phosphate group with a net charge of -1. The relative weakness of the P–O bonds at a branch point may also contribute to the lowering of the activation energy. However, in view of the evidence that these bonds are not considerably lengthened in the assumed transition state, we believe this factor to be less important.

We shall consider next the difference in the *p*H dependence of the B- and L-hydrolyses. As the *p*H is decreased from 7 to 3.5,[27] the rate of the B-hydrolysis remains constant,[10] while that of the L-hydrolysis increases sharply.[2,7] Since hydrogen ions may be bound by the negative phosphate groups, they can neutralize the charges of the latter and so facilitate the approach of a water molecule in the case of the L-hydrolysis.[8] On the other hand, the phosphate groups at branch points are neutral to start with and therefore are not altered by hydrogen ions. Consequently one would not expect the approach of water molecules to be influenced by the hydrogen ion concentration in the case of the B-hydrolysis.

Since all these factors are consistent with the mechanism involving as the critical step in the hydrolysis the nucleophilic attack of a water molecule on the phosphorus atom, it is interesting to consider the effect of other nucleophilic agents which may be present in the solution. One such agent which is much more nucleophilic than the water molecule is the hydroxyl ion. It seems then surprising that up to a *p*H of 11 this ion has no measurable effect on the B-hydrolysis rate. However, we can account for this result if we consider that the hydroxyl ion concentration is much smaller than the concentration of the water molecules and that on account of the polyelectrolyte effect, this concentration difference is enhanced in the neighborhood of the negatively charged polyphosphate chain which repels the hydroxyl ions. No observations concerning the effect of hydroxyl ions at *p*H's higher than 11 have been reported for the B-hydrolysis. However, there is considerable evidence that at high *p*H hydroxyl ions increase the L-degradation rate[2,6] and that this increase is enhanced by the addition of excess sodium ions.[8] With the mechanism discussed here, one would expect the sodium ions, which are complexed by the phosphate groups, to heighten the effect of the hydroxyl ions for two reasons. First, they decrease the negative potential near the polyphosphate chain and thus increase the effective local concentration of hydroxyl ions. Second, they neutralize some of the phosphate groups which, no longer possessing a negative charge, can then be attacked more easily by the negative hydroxyl ions.

The negative oxygen atom on a $P–O^-$ group may also be expected to act as a powerful nucleophile. The effect of this nucleophile should manifest itself in different ways depending on whether the phosphorus atom to be attacked is situated on the same or on a different polyphosphate chain than the attacking $P–O^-$ group. In the latter case one would expect the kinetics to be of second order and some of the reaction products to have higher chain length than the starting materials. The reasons that such effects have apparently not been observed are similar to those given for the case of the hydroxyl ion. Under the conditions usually employed, the competing water molecules are present in much higher concentration than the $P–O^-$ groups which are further handicapped by their negative charge. It may be possible that at very high polyphosphate concentrations such effects may be noticeable.[28,29] If the attacking $P–O^-$ group and the attacked phosphorus atom belong to the same polyphosphate chain, one may expect metaphosphate rings as the reaction products. Both trimeta-[30] and tetrametaphosphate[31] rings have been identified as products of the degradation of long chain linear polyphosphates in aqueous solution. The kinetics of the ring formation under these conditions is being investigated in this Laboratory in order to obtain experimental information concerning the reaction mechanism of this interesting process.

Appendix

Relation between Increases in Titratable Hydrogen Ions and in End-groups during Degradation.—In order to determine the initial end-group and hydrogen ion concentration values before the hydrolytic degradation at the branch points had become appreciable, dissolution of the polymer samples was carried out at about 5° for 10 to 15 minutes followed by *p*H adjustment and decantation, as described under Experimental. Final polymer concentrations were between 7 and 9%. End-group[32] and hydrogen ion determinations were performed on separate aliquots as soon as possible. The B-hydrolysis was then allowed to go to completion at room temperature, and the end-group and hydrogen ion titrations were repeated. In the case of sample No. 249P, with a Na/P ratio of 0.998, the increases in end-groups and hydrogen ions were 0.98 and 2.03 meq. per 100 g. of sodium

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[27] The behavior at *p*H's higher than 7 will be discussed below.

[28] The observation by Thilo and Grunze that several days after they had added acetone to aqueous solutions of sodium triphosphate, they found tetra- and pentaphosphate species in the highly concentrated oily layer may be a case in point [mentioned as unpublished results, H. Roux, E. Thilo, H. Grunze and M. Viscontini, *Helv. Chim. Acta*, **38**, 15 (1955)].

[29] This mechanism may also play an important role in the making and breaking of polyphosphate chains in the melt.

[30] E. Thilo, G. Schulz and E. Wichman, *Z. anorg. Chem.*, **272**, 184 (1953).

[31] U. P. Strauss and T. L. Treitler, unpublished results.

[32] End-groups were determined as described in reference 10.

polyphosphate, respectively. For sample No. T-143B, with a Na/P ratio of 1.002,[33] the corresponding figures were 0.66 and 1.48. It is apparent that approximately two titratable hydrogen ions have been produced for every end-group. These results serve as a final proof that the rapid initial hydrolysis actually occurs at branch points.

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(33) For the preparation and properties of this sample, see reference 10.

[CONTRIBUTION FROM CHEMICAL AND RADIOLOGICAL LABORATORIES]

Nuclear Magnetic Resonance Spectra of Phosphorus Compounds

BY NORBERT MULLER, PAUL C. LAUTERBUR AND JEROME GOLDENSON

RECEIVED DECEMBER 15, 1955

Results of chemical shift measurements for sixty-three phosphorus compounds are presented. In general, shielding increases as one passes from trivalent phosphorus compounds to thiophosphoryl compounds, and then to phosphoryl compounds. The chemical shifts depend in a complicated way on the nature of the molecule involved; a modification of the theory of Saika and Slichter is given, in terms of which the main features of the data may be understood.

Introduction

Chemical shifts in the nuclear magnetic resonance (NMR) of P^{31} were discovered by Knight.[1] Subsequent measurements, particularly those by Gutowsky and his co-workers[2,3] indicate that NMR spectroscopy can become a valuable tool for chemical studies involving phosphorus compounds. To extend the usefulness of the method in this direction, we have obtained chemical shift values for a much larger variety of compounds than has previously been investigated.

Chemical shifts may be used simply as empirical constants characteristic of particular materials. In addition it is possible in principle to deduce from them information as to the bond properties of the molecules studied. Phosphorus compounds present a rather complex problem in this regard, but by introducing suitable simplifications we have been able at least to develop a conceptual framework in terms of which the main features of the results may be understood.

Experimental

The basic theory and experimental details of nuclear magnetic resonance are described in several excellent review articles.[4] The apparatus used in this research was a Bloch-type high-resolution NMR spectrometer (model V-4300), purchased from Varian Associates, Palo Alto, California. It consists of a twelve-inch electromagnet (V-4012) with power supply and current regulator (V-2100 and 2101) and the associated radiofrequency circuits. Resonances were observed at a fixed radiofrequency of 17 mc./sec. and fields in the neighborhood of 9850 gauss.

Chemical shifts were measured by applying an audiofrequency signal from a Hewlett-Packard model 202A function generator to a set of coils wound in the same sense as the coils used to sweep the magnetic field for oscilloscope display. With a single resonance, this causes side-bands to appear on either side of the main resonance, just as if the 17 mc. r-f signal had been replaced by a set of frequencies each differing from 17 mc. by integral multiples of the audiofrequency used.[5] Viewing the sample and a standard alternately, one may adjust the audiofrequency until the *n*th side-band of the standard falls in the same place as the resonance to be measured. Then if ν is the audiofrequency, the chemical shift, δ, is given by the equation

$$\delta = \frac{(H_{\text{sample}} - H_{\text{standard}})}{H_{\text{standard}}} \times 10^6 = \frac{\nu n}{17}$$

The audio-oscillator was calibrated using a Hewlett-Packard 100-D low-frequency standard. Results were reproducible to about ±1%. Additional errors result from neglecting the bulk diamagnetic susceptibility corrections[6]; on the basis of available susceptibility data, we conclude that these errors should not exceed one-half unit of δ.

Many of the materials studied were furnished by a number of chemical companies (see Table I), whose kindness we gratefully acknowledge. We should also like to thank the personnel of the Organic Branch of these Laboratories, who furnished other samples, and Dr. G. F. Svatos who helped with a number of the syntheses carried out in our own group. Chemical shifts are not sensitive to the presence of small amounts of impurities, so the samples were used without further purification. In some cases the structures were verified by infrared spectroscopy and proton nuclear resonance spectra. Observations were made using 1 to 2 ml. of material sealed off under vacuum in Pyrex tubes of 8 mm. outside diameter.

The reference signal used in determining chemical shifts was that of Merck reagent grade 85% aqueous H_3PO_4. We also examined a number of samples made by adding various amounts of distilled water to H_3PO_4 purified by fractional crystallization by R. H. Schumm at the National Bureau of Standards. There was no detectable shift between any of these samples.

Results and Discussion

a. Table of Chemical Shifts.—The chemical shifts obtained for sixty-three phosphorus compounds are given in Table I. In those cases where the resonance is split by indirect spin-spin interactions[2] the value given is that for the center of the resonance pattern. The results may be summarized in the following generalizations.

1. With a few exceptions, the chemical shifts of trivalent phosphorus compounds, compounds containing the phosphoryl linkage, and compounds containing the thiophosphoryl linkage fall into distinct ranges.

Thus the trivalent phosphorus compounds usually have δ's below -95 and ranging down to about -230. The exceptions are PH_3, found by Gutowsky and McCall[3] to have $\delta = +241$, and the trialkyl or triaryl phosphites which have δ's slightly above zero.

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(1) W. D. Knight, *Phys. Rev.*, **76**, 1259 (1949).

(2) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(3) H. S. Gutowsky and D. W. McCall, *ibid.*, **22**, 162 (1954).

(4) For example, J. E. Wertz, *Chem. Revs.*, **55**, 829 (1955); also R. E. Andrew, "Nuclear Magnetic Resonance," Cambridge, 1955.

(5) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

(6) W. C. Dickinson, *Phys. Rev.*, **81**, 717 (1951).