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[CONTRIBUTION FROM MONSANTO CHEMICAL CO., RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION, ST. LOUIS 66, MO.]

Principles of Phosphorus Chemistry. XI. The Polyphosphate Esters

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Reorganization between structural building units takes place in the family of polyphosphate esters. For the ethyl polyphosphates, the equilibrium constant for formation of an end and a branching group from two middle groups is 0.02, and the equilibrium constant for formation of a middle group and the orthophosphate ester from two end groups is 0.06. The nuclear magnetic resonance peak for the branching group in the family of polyphosphate esters and in the family of polyphosphoryldimethylamides occurs at 41 p.p.m. upfield from that of the reference standard, orthophosphoric acid; whereas, in the family of polyphosphoryl halides, this resonance peak appears at +50 p.p.m. This anomaly is discussed.

Since Hall and Jacobson² demonstrated that the "hexaethyl tetraphosphate,"³ which Schrader formulated as the *iso* molecule, was a mixture of triethyl orthophosphate, tetraethyl pyrophosphate and a so-called "ethyl metaphosphate," chemists have been at least vaguely aware of the fact that the esters of the condensed phosphoric acids may be mixtures. However, this concept has not been treated quantitatively until now. It is the purpose of this paper to show that the system of normal phosphate esters obeys the general principles of structural reorganization, with equilibria between the various structural building blocks following the principles outlined previously in this series of papers.

Experimental Details

Mixtures of normal esters of polyphosphoric acids exhibiting various average degrees of condensation were made by combining⁴ triethyl orthophosphate (or, in one case, trimethyl orthophosphate) with various proportions of phosphorus pentoxide. The mixtures were heated at 110° in rocking, sealed glass tubes for a month, even though pilot experiments showed that equilibrium for $R = (\text{C}_2\text{H}_5\text{O})/\text{P} = (\text{C}_2\text{H}_5)_2\text{O}/\text{P}_2\text{O}_5 \geq 1.5$ was achieved in a matter of hours. These pilot experiments clearly indicated that equilibrium at 110° occurs immediately upon dissolution of the phosphorus pentoxide in the liquid phase, so that the rate-determining step is the dissolution process. Even at 110°, the rate of dissolution of the phosphorus pentoxide is very low at R values below 1.2, because of the high viscosity of the liquid phase. In spite of the fact that equilibrium was first established at 110°, it is believed that the reported equilibria correspond to room temperature (26°), because of rapid re-equilibration during and after cooling. This conclusion is based on the finding that pure tetraethyl pyrophosphate obtained by molecular distillation reverts to the equilibrium reorganization mixture within a matter of hours at room temperature. Furthermore, there was no change in the proportions of structural building units after the sample for which $R = 1.5$ had been allowed to stand at room temperature for 3 months.

The acid-catalyzed formation of ethylene was an undesirable side reaction in this investigation. In order to minimize this reaction the phosphorus pentoxide was kept scrupulously dry, and the triethyl orthophosphate was doubly distilled to avoid acidic contaminants. Even with these precautions, it was found that the rate of ethylene formation became so rapid at temperatures much above 115° that the thick-walled

Pyrex tubes were shattered by pressure build-up. On the other hand, at temperatures much below 100°, the rate of dissolution of the phosphorus pentoxide, especially in the more viscous systems corresponding to values of R below 1.5, was inconveniently slow. This limited the P_2O_5 -dissolution process to 100–115°.

³¹P nuclear magnetic resonance (n.m.r.) measurements were carried out according to the techniques previously described.⁵ Numerous attempts were made to find a good solvent with which the polyphosphate esters would not react. Unfortunately, all of the solvents which did not react with the esters (such as benzene, dioxane and carbon tetrachloride) dissolved only such a small amount of the higher molecular weight esters that it was impossible to apply the methods of polymer physics.

Results and Conclusions

³¹P N.m.r. Data.—The n.m.r. results for the distribution of the various structural units^{6,7}—orthophosphate, ends, middles and branches—are presented for the family of ethyl phosphates, in Fig. 1, from which it can be seen that the maximum amount of end groups (at $R = 2.00$) is 67% of the total phosphorus and the maximum amount of middle groups (at $R = 1.00$) is 78%. Even though the experimental measurements did not extend beyond the value of $R = 1.2$, it is believed that the extrapolation on the basis of the structural equilibrium constants to the value of $R = 1.00$ and below is reasonably precise.

The value of the structural equilibrium constants for the homologous series of normal ethyl phosphates are:

$$K_1 = \frac{[\text{end groups}][\text{branching groups}]}{[\text{middle groups}]^2} = 0.02 \quad (1)$$

$$K_2 = \frac{[\text{orthophosphate}][\text{middle groups}]}{[\text{end groups}]^2} = 0.06 \quad (2)$$

From one experiment at $R = 1.47$, it was found that the values of K_1 and K_2 for the methyl phosphates are very close to those for the ethyl system.

For the methyl or ethyl esters, the n.m.r. chemical shifts measured from 85% H_3PO_4 as a standard (with a positive shift being upfield) were found to be in accord with our previous publications.⁸ The ortho esters exhibited a shift of +1 p.p.m.; the middle and end groups +13 and +28 p.p.m.,

(5) L. C. D. Groenweghe, J. H. Payne and J. R. Van Wazer, *THIS JOURNAL*, **82**, 5305 (1960).

(6) J. R. Van Wazer, "Phosphorus and Its Compounds," Interscience Publishers, Inc., New York, N. Y., 1958, Vol. I, Chapt. 12.

(7) J. R. Parks and J. R. Van Wazer, *THIS JOURNAL*, **79**, 4890 (1957); also see J. R. Van Wazer, *ibid.*, **72**, 644 (1950).

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

(1) On leave of absence during 1959 from Göttingen University, Germany.

(2) S. A. Hall and M. Jacobson, *Ind. Eng. Chem.*, **40**, 694 (1948).

(3) G. Schrader, "Die Entwicklung neuer Insektizide auf der Grundlage organischer Fluor- und Phosphor-Verbindungen," Monographien Angew. Chem., Nr. 62, Verlag Chemie, Weinheim, 1952.

(4) This type of preparative procedure is reported by D. Balarev, *Z. anorg. Chem.*, **88**, 145 (1914), and by W. H. Woodstock in U. S. Patent 2,402,703 (1946).

respectively; and the branch group, +41 p.p.m. By combining an equimolar mixture of triethyl phosphate and phosphoryl chloride with varying amounts of phosphorus pentoxide under conditions where the reorganization leading to condensed species progressed considerably but reorganization between the phosphoryl chloride and the triethylphosphate was not much advanced, the branching-point resonance was found to lie at +45 p.p.m., halfway between the values of +41 p.p.m. which would have been obtained if only $(C_2H_5O)_3PO$ were employed and +50 p.p.m. if only $POCl_3$ were used.⁵

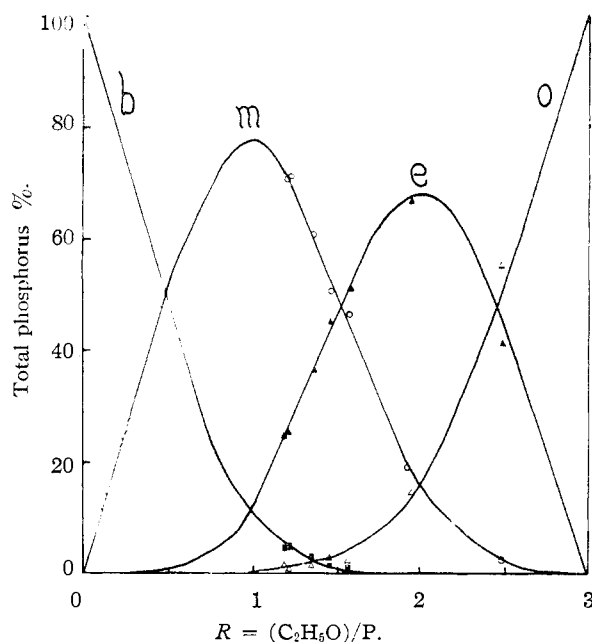


Fig. 1.—Experimental equilibrium distribution at 26° of structural building units in the system of completely esterified ethyl phosphates as a function of the $(C_2H_5O)/P$ mole ratio, R . The symbol b = branching groups, $OP(O_{1/2})_3$; m = middle groups, $(C_2H_5O)(O)P(O_{1/2})_2$; e = end groups, $(C_2H_5O)_2(O)PO_{1/2}$; and o = orthophosphate, $(C_2H_5O)_3PO$.

Discussion.—For the completely ionized phosphates⁶ (sodium, potassium, lithium and calcium phosphate glasses), $K_1 = K_2 = 0.0$; whereas for the phosphoric acids,⁶ which are only partially ionized, $K_1 = 0.001$ and $K_2 = 0.08$. For the unionized esters, $K_1 = 0.02$ and $K_2 = 0.06$ as shown above. It is apparent from this sequence that K_1 and K_2 increase as the degree of ionization of the building blocks decreases. However, the completely random value of $K_1 = K_2 = 0.33$ is not achieved by the polyphosphate ester system.

From these considerations, there appears to be an appreciable contribution to the reorganization equilibria from the theoretically treated tendency toward low K values in order to avoid unbalancing the charge distribution in the system by having more than the minimum number of different building blocks exhibiting different charges. However, it is quite obvious that this is not the only factor and that there are contributions due either to mechanical effects (such as steric hindrance) or to as yet not theoretically calculable variations in the

electron distribution⁹ from one molecular building unit to another.

There is an interesting anomaly connected with the n.m.r. peak corresponding to the branching group in those families of compounds having phosphorus pentoxide as the completely branched limiting structure. For the branched phosphate esters described in this paper and for the branched polyphosphoryldimethylamides,¹⁰ the peak corresponding to branching points occurs at +41 p.p.m. of the magnetic field. However, throughout the entire range of measured R values, the branching-point resonance found in the polyphosphoryl halide systems appeared at +50 p.p.m.⁵ As yet, no one has been able to measure the branching-point resonance in the stable liquid form of phosphorus pentoxide, but it must have a fixed value.

It is believed that the difference between the +41 and +50 p.p.m. shifts in the branching-point resonance may reflect variations in electron arrangement, perhaps a change in the unequal distribution of π -bonding between the phosphorus atom and its four oxygens in the branching-point structural unit.⁹ There thus appears to be a close interrelationship between (1) the chemical shift of the n.m.r. peak of the branching points, (2) the atom-center distances as determined from diffraction studies,⁹ and (3) the equilibria between structural building units. In the reports^{6,9} from this Laboratory, variations in these phenomena have been attributed to π -bond effects involving the d-orbitals of the phosphorus.

Study of Previously Reported Preparations.—We have found that "tetraethyl pyrophosphate" made from silver pyrophosphate and ethyl iodide¹¹ at 70–75° gives the correct elemental analysis but consists of the reorganization-equilibrium mixture corresponding to $R = 2.00$. Also the "ethyl metaphosphate" of Hall and Jacobson² and others is seen to be the equilibrium mixture of structural units corresponding to the observed value of the composition parameter R , which can vary depending on preparative or separative details. A commercial sample of tetraethyl pyrophosphate was found to be identical with the reorganization-equilibrium mixture corresponding to its value of $R = 2.00$.

Except for fresh samples very recently distilled at room temperature or below in high vacuum, so-called "pure" tetraethyl pyrophosphate consists of a mixture containing this compound and considerable amounts of higher and lower homologs with the amount of tetraethyl pyrophosphate never being less than that present in the equilibrium mixture. Assuming the "flexible-chain"^{6,7} distribution of molecular sizes, this reorganization-equilibrium mixture for $R = 2.00$ (containing a negligibly small amount of branched groups) is calculated to consist of 16% of the total phosphorus as triethyl orthophosphate, 46% as tetraethyl pyrophosphate, 22% as pentaethyl tripolyphosphate

(9) J. R. Van Wazer, *THIS JOURNAL*, **78**, 5709 (1956).

(10) E. Schwarzmann and J. R. Van Wazer, *ibid.*, **82**, 6009 (1960).

(11) P. de Clermont, *Ann. chim.*, **44**, 330 (1855); J. Cavalier, *Compt. rend.*, **142**, 885 (1906); A. Rosenheim and M. Pritze, *Ber.*, **41**, 2708 (1908).

and 10% as hexaethyl tetrapolyphosphate, with the remainder corresponding to higher straight-chain homologs. There is thought to be an insignificant amount of ring compounds in this reorganization mixture.

Using two different extremely pure samples of sodium tripolyphosphate hexahydrate, amorphous "silver tripolyphosphate" was made and converted to "pentaethyl tripolyphosphate" by reaction with ethyl iodide following the method of Hood and Lange.¹² According to n.m.r. results on two very careful preparations from our laboratory, and a third one from another laboratory, "pentaethyl tripolyphosphate" made by this method consists of a mixture of 11.8% of the total phosphorus as ortho, 75.7% as end groups and 12.5% as middle groups. This quantitative n.m.r. analysis, which does not differentiate⁸ between esterified or unesterified building units of the polyphosphoric or orthophosphoric acids, showed that the parameter R corresponding to this mixture is 1.99, which is close to the pyro composition. This indicates that either we had inadvertent hydrolysis during prep-

(12) A. Hood and W. Lange, *THIS JOURNAL*, **72**, 4956 (1950); also see R. Rätz and E. Thilo, *Z. anorg. u. allgem. Chem.*, **272**, 333 (1953).

aration or the "silver tripolyphosphate" contained considerable ortho- and pyrophosphate in the same manner that an X-ray diffraction study of "ferric tripolyphosphate" obtained by treating ferric sulfate with sodium tripolyphosphate showed only ferric pyrophosphate, presumably formed by the catalytic action of the immediately precipitated hydrated ferric oxide on hydrolysis of the tripolyphosphate ion.¹³

From the proximate analysis of 22.6% P given by Rätz and Thilo and our R value of 1.99, it appears that the "pentaethyl tripolyphosphate" is only about 90% esterified. This may explain the fact that the value of K_2 calculated for this preparation from our n.m.r. data is lower than that of eq. 2 by a factor of two. Presumably the acid hydrogens make the equilibrium more like an "ionic" type and thus lower the value of K_2 .⁶ In any event, the ester we have prepared from the silver phosphate is not pentaethyl tripolyphosphate but consists of a mixture, presumably at or near reorganization equilibrium, having an over-all composition estimated to be roughly equivalent to $9(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{H}_3\text{O}\cdot 5\text{P}_2\text{O}_5$ in the Berzelius notation.

(13) See p. 659 of ref. 6.

[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALA.]

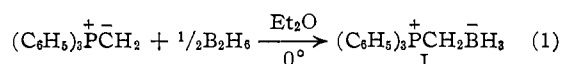
The Reaction of Alkylidene Triphenylphosphoranes with Diborane and Trialkylamine Alkylboranes

BY M. FREDERICK HAWTHORNE

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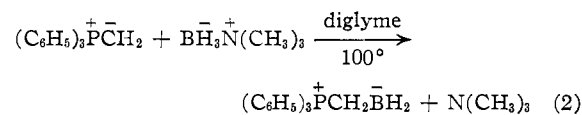
Diborane and a series of alkylidene triphenylphosphoranes combined to produce simple, charge separated complexes of the type $(\text{C}_6\text{H}_5)_3\text{P}^+\text{CHR}\text{B}^-\text{H}_3$. Phenyliminotriphenylphosphorane and diborane gave an analogous product. Methylene triphenylphosphorane readily displaced trimethylamine from a series of trimethylamine alkylboranes and trimethylaminephenyl borane. All complexes of this nature were exceedingly stable toward hydrolysis.

In a previous communication from this Laboratory,¹ the reaction of diborane with alkylidene triphenylphosphoranes² in diethyl ether solution was reported to produce stable adducts.³



Following the first report of these materials, Grim and Seyferth⁴ reported the preparation of methylene triphenylphosphorane trifluoroborane which was successfully alkylated on boron to give trialkylborane analogs of I.⁵ The reaction of methylene triphenylphosphorane with trimethyl-

amine borane also produced I in accordance with eq. 2.⁵



This latter reaction has been employed by us in the preparation of methylene triphenylphosphorane alkyl- and phenylboranes (*vide infra*) from trimethylamine alkyl- and phenylboranes.

(1) M. F. Hawthorne, *THIS JOURNAL*, **80**, 3480 (1958).

(2) The name triphenylphosphine methylene apparently has been superseded by the alkylidene triphenylphosphorane nomenclature in describing Wittig reagents. As an example see S. Trippett and D. M. Walker, *J. Chem. Soc.*, 3874 (1959).

(3) The parent compound I originally was termed triphenylphosphine methylene boron trihydride (ref. 1). A more suitable nomenclature might be constructed in which I is termed methylene triphenylphosphorane borane. This latter concept will be employed throughout this paper. The complicating factor, charge separation, is ignored for simplicity.

(4) S. O. Grim and D. Seyferth, *Chem. and Ind.*, 849 (1959).

(5) D. Seyferth, *XVII Congress of Pure and Applied Chemistry*, Munich, August 30-September 6, 1959. See also *Angew. Chem.*, **72**, 36 (1960).

Reaction of Alkylidene Triphenylphosphoranes with Diborane.—As previously described,¹ alkylidene triphenylphosphoranes rapidly react with diborane in diethyl ether at zero degrees to produce hydrolytically stable adducts (eq. 1). The structures of these adducts were established by their infrared spectra, active hydrogen analyses and C, H and B analyses. Recently a B¹¹ n.m.r. spectrum was obtained with I in methylene chloride solution. The resonance lines formed a quadruplet centered at 620 c.p.s. higher field than methyl borate. This confirms that three hydridic hydrogen atoms are attached to the boron atom in I.

Perhaps the most interesting physical feature of I and of its derivatives is their great solubility in