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Structure and Properties of the Condensed Phosphates. X. General Structural Theory

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RECEIVED MAY 9, 1955

A theory has been developed to aid in the prediction of the structures to be expected in the various systems of inorganic phosphates. Equations are given for calculating (1) the number of P–O–P linkages in any phosphate and (2) the compositions at which pure species may be found. A general formula which includes all phosphates from phosphoric oxide to the orthophosphates is also presented. This formula is $M_{nR}P_nO_{n(R+5)/2}$, where M stands for one equivalent of the cations and/or organic radicals present and $R = M_2O/P_2O_5$.

Introduction

The phosphates may be defined as structures in which the anions consist of PO_4 tetrahedra which may be linked together by the sharing of corners. There is a continuous range of phosphates going from the orthophosphate to pure P_2O_5 which, for the purposes of this discussion, is defined as a phosphate in the limiting case. If we let M stand for one equivalent of a cation or of an organic radical, we can restate the above composition range by saying that for the phosphates[1] $0 < M_2O/P_2O_5 \leqslant 3$. Following standard practice,[2] we shall call the composition range for which $1 < M_2O/P_2O_5 \leqslant 3$ the polyphosphate region, the composition for which $M_2O/P_2O_5 = 1$ the metaphosphate composition, and the composition range for which $0 < M_2O/P_2O_5 < 1$ the ultraphosphate region.

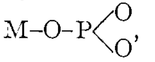
It has been demonstrated[2,3] that in the polyphosphate region, there is a series of straight chain compounds exhibiting the formula $M_{n+2}P_nO_{3n+1}$. The first member of this series is the orthophosphate, M_3PO_4, and the second member is the pyrophosphate, $M_4P_2O_7$. The metaphosphate corresponds to rings, $(MPO_3)_n$, and extremely long chains, $\mathop{\mathrm{L}}_{n \to \infty} M_{n+2}P_nO_{3n+1} = (MPO_3)_n$. In the ultraphosphate region there must be some PO_4 groups which share three of their oxygen atoms, and the quantity of these groups is equal to $(P_2O_5 - M_2O)/P_2O_5$ in terms of the fraction of the total number of PO_4 groups. As has been previously stated,[2,3] it is to be expected that, in any environment in which reactions involving the degradation of condensed phosphates can occur, one of the three P–O–P linkages to the PO_4 group sharing three oxygen atoms will be broken at an unusually fast rate.[4]

Theory

If we either neglect ionization or consider a M^+, $^-O–P$ as an ionic linkage, we can compute the total number of linkages in a given phosphate composition. A linkage may be of two kinds: a P–O–P linkage or an M–O–P linkage. The two bonds making up such a linkage are then either (1) a δ-bond irrespective of its polarity or π-bond character or (2) the coulombic attraction between a plus and minus charge. It is apparent that, if N_t is the total number of linkages in a phosphate structure containing P phosphorus atoms and M cations (or organic radicals), the following equation is true.

$$N_t = (M + 3P)/2 \qquad (1)$$

N_t must be an integer and, if it is not, one must double the number of atoms in the proposed compounds in order to obtain the simplest structure which can exist. For example, there is no phosphate in which there is only one phosphorus atom and two cations ($R \equiv M/P = 2/1 = 2$), but there is a known compound containing two phosphorus and four cations ($R = 4/2 = 2$). This point is demonstrated easily by substituting the values into equation 1.

It may be seen that the number of phosphorus atoms in the simplest phosphate structure having a given M_2O/P_2O_5 ($= M/P$) ratio, R, is found when the sum of the numerator and denominator of R is an even number. When the sum is odd, the numerator and denominator of R must be doubled in order to get the simplest structure. This is apparent when equation 1 is rewritten as $2N_t = M + 3P$, in which N_t is a whole number and hence $M + 3P$ must be an even number. Since multiplying an odd number by three gives an odd number, and multiplying an even number by three gives an even number, the sum of the denominator and numerator of R must be even, for the minimum number of phosphorus atoms in a structure of a given ratio to be the same as the denominator of the ratio. The sole exception to this rule occurs for the ratio $R = 1/1$. Here this formula is incapable of distinguishing between one linkage and two half-linkages. Thus, in the non-existent $NaPO_3$ monomer, , the P–O bonds are half-linkages. Equation 1 is not particularly useful, but it may be employed to derive other equations which are useful.

Since one P–O–P linkage is prevented by each cation (or organic radical) in a phosphate structure, it is seen that, if one linkage is subtracted for each cation in equation 1, the following results for the number of P–O–P linkages, N_p, in a phosphate structure.

$$N_p = (3P - M)/2 \qquad (2)$$

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(1) Salts—such as $4CaO\ P_2O_5$, Hilgenstockite, sometimes called tetracalcium phosphate—must be considered as double salts, *e.g.*, $(3CaO \cdot P_2O_5)CaO$. The calcium ions of three of the CaO counterbalance the charge of two separate $PO_4^{\equiv}$ groups in the crystal, so that an extra CaO is left to be fitted into the lattice. In this paper only the PO_4 groups and their counter ions are considered, and other ions in complicated crystal structures are ignored. For information about $4CaO \cdot P_2O_5$, see J. Tromel, H. I. Harkcort and W. H. Hotop, *Z. anorg. Chem.*, **256**, 253 (1948); and J. R. Rait and H. J. Goldschmidt, *J. Iron Steel Inst.* (*London*), 68 (April, 1945).

(2) J. R. Van Wazer, "Encyclopedia of Chemical Technology" (Kirk and Othmer, Editors), Vol. X, Interscience Publishing Co., New York, N. Y., 1953, pp. 403–444, 461–476.

(3) J. R. Van Wazer, THIS JOURNAL, **72**, 639 (1950).

(4) U. P. Strauss, E. H. Smith and R. L. Wineman, *ibid.*, **75**, 3935 (1953); U. P. Strauss and T. L. Treitler, *ibid.*, **77**, 1473 (1955).

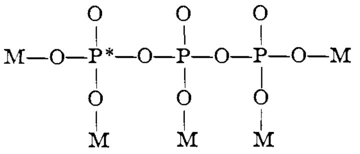
TABLE I

SMALLEST POSSIBLE[a] NUMBER OF ATOMS IN A GIVEN M_2O/P_2O_5 COMPOSITION

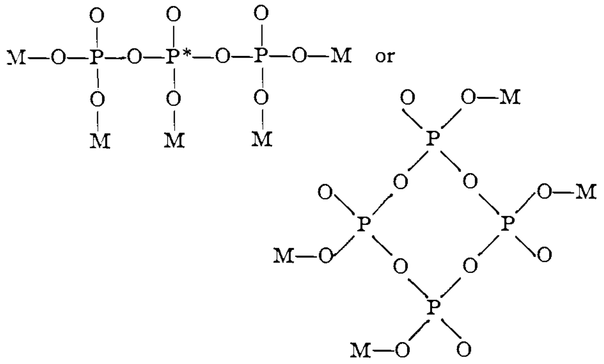
M_2O/P_2O_5	Min. values of M	P	O	Corresponding values of N_t	N_p	N_x	Min. no. of separate structures	Probable structures
5	5	1	5	4	..	..	2	$M_2O + M_3PO_4$
3	3	1	4	3	0	..	1	M_3PO_4
5/2	10	4	15	11	1	..	3	$M_4P_2O_7 + 2M_3PO_4$
2	4	2	7	5	1	..	1	$M_4P_2O_7$
9/5	9	5	17	12	3	..	2	$M_5P_3O_{10} + M_4P_2O_7$
7/5	7	5	16	11	4	..	1	$M_7P_5O_{16}$
6/5	12	10	31	21	0	..	1	$M_{12}P_{10}O_{31}$
1	1	1	2 + 2 (1/2)	1 + 2 (1/2)	2 (1/2)	0	1	$[(MPO_3)_2]$
2/3	4	6	17	11	7	1	1	$(M_2P_3O_8)_2O$
1/2	2	4	11	7	5	1	1	$M_2P_4O_{11}$
1/3	1	3	8	5	4	1	1	MP_3O_8
0	0	2	5	3	3	1	1	P_2O_5 monomer
Polyphosphate $2 > (n + 2)/n > 1$	$n + 2$	n	$3n + 1$	$2n + 1$	$n + 1$	..	1	$M_{n+2}P_nO_{3n+1}$
Metaphosphate $n/n = 1$	n	n	$3n$	$2n$	n	0	1	$M_nP_nO_{3n}$
Phosphorus pentoxide $0/n = 0$	0	n	$5n/2$	$3n/2$	$3n/2$	$n/2$	1	$(P_2O_5)_{n/2}$

[a] This includes highly strained structures and those showing steric hindrance, *i.e.*, all structures being made up from interlinked PO_4 groups.

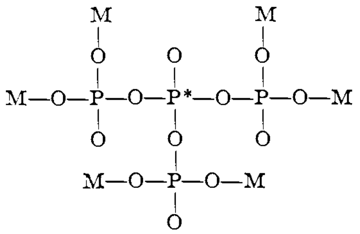
Three types of P–O–P linkages exist. A phosphorus atom may be linked to a single phosphorus atom as in an end group of a chain phosphate,



or it may be linked to two other phosphorus atoms as in the middle of a chain or in a ring



A phosphorus atom may also be linked to three other phosphorus atoms as in a branched or crosslinked structure.



As has been stated previously,[3,4] reaction involving scission of linkages occurs at unusually high rates at triply linked phosphorus atoms which are not protected by steric hindrance. Therefore, we single out one of the P–O–P linkages at a branching point and refer to it as a linkage in excess of the metaphosphate composition. These excess linkages, N_x, may be calculated by the equation

$$N_x = \frac{P - M}{2}, \text{ for } P > M \qquad (3)$$

Existence of branching points outside of the ultraphosphate region will be considered below in the discussion section.

The number of oxygen atoms in a phosphate structure can be computed from the following equation based on stoichiometry.

$$O = M/2 + 5P/2 \qquad (4)$$

We are now able to use equations 1 through 4 as existence theorems to compute the smallest possible number of atoms in a phosphate structure corresponding to a given R; and results of such calculations are shown in Table I. For some values of R, single phosphate structures cannot be found. An example is $R = 7/3$. To determine quickly whether or not a single phosphate structure exists for a given R, the following inequality was developed.

$$P > N_p + 1 \qquad (5)$$

When P is greater than $N_p + 1$, at least two phosphate structures are required to satisfy the ratio R, except for $R = 3$.

Now we shall derive chemical formulas for the various types of phosphates. In chain phosphates, there must be one more phosphorus atom than the number of P–O–P linkages; hence, $N_p = P - 1$. By substituting $P - 1$ for N_p in equation 2, we find that $M = P + 2$; and by substituting this value of M in equation 4, we find that $O = 3P + 1$. By letting $P = n$, one obtains the polyphosphate formula, $M_{n+2}P_nO_{3n+1}$, which is thus seen to fit any chain structure, either straight or branched.

In a simple ring, the number of phosphorus atoms equals the number of P–O–P linkages; and this is also true if any number of straight or branched chains of any size are attached to the ring, as long as the chains do not connect rings to each other or join together to form fused rings. For the rings, $N_p = P$. Substitution of this value in equation 2 and then equation 4 as was done for the chain compounds leads to the formula for the ring phosphates, $M_nP_nO_{3n}$, thereby showing that such structures can only exist at the metaphosphate composition, $R = n/n = 1$. If $P + N_x$ is substituted for N_p in equation 2, and further substitution is made in equation 4 to obtain the number of oxygen atoms in terms of the number of phosphorus atoms, the formula for ultraphosphates—which turns out to be the general formula for all phosphates—is obtained $M_{n-2N_x}P_nO_{3n-N_x}$. Since this formula is not in a convenient form, we substitute the value nR for M (which comes from the definition $R = M/P$ with substitution of n for P) and equate that to its equivalent value $n - 2N_x$. This means that N_x in the general formula can be substituted by $n(1 - R)/2$, and the general formula reduces to its useful form[5] which may be employed for all phosphates ranging from phosphoric oxide to the orthophosphates

$$M_{nR}P_nO_{n(5+R)/2} \tag{6}$$

When $R = 0$, this formula reduces to $P_nO_{5n/2}$. When $R = 1$, the formula reduces to $M_nP_nO_{3n}$; and when $R = (n + 2)/n$, we have the polyphosphate formula, $M_{n+2}P_nO_{3n+1}$, which for $n = 1$ reduces to the orthophosphate, M_3PO_4.

In any phosphate structure, the constituent atoms must naturally be present in whole number amounts. In the general formula (equation 6), this means that nR, n and $n(5 + R)/2$ must be whole numbers. It is sometimes difficult to make $n(5 + R)/2$ an integer. This is particularly true in the ultraphosphate system. If, however, we let

$$n(5 + R) = j, \text{ where } j = 10, 12, 14, 16, \ldots, \infty \tag{7}$$

$n_{\text{min.}}$ occurs for the smallest possible value of j, which is $j_{\text{min.}}$ In other words, when j is the smallest possible even whole number, the resulting value of n gives the minimum number of phosphorus atoms needed to form a single ultraphosphate structure having the given value of R. It is immediately obvious that the smallest values of n in the ultraphosphate composition range occur at $R = 0$, $^1/_3$, $^1/_2$ and 1. For $R = 0$, we find that $n = 2$ corresponding to the formula P_2O_5. For $R = {}^1/_3$, we find that $n = 3$, and the resulting formula is MP_3O_8; and for $R = {}^1/_2$, we find that $n = 4$, and the resulting formula is $M_2P_4O_{11}$. For $R = 1$, we find that $n = 2$, and the resulting formula is $(MPO_3)_2$, the dimetaphosphate.

Changing the value of R very slightly from the rational fractions at which low numbers are found for $n_{\text{min.}}$ gives extremely large values for $n_{\text{min.}}$ Thus, if R is increased from $^1/_2$ to 0.501, $n_{\text{min.}}$ jumps from 4 to 2,000. A similar decrease in R also gives large values of $n_{\text{min.}}$ This means that low molecular weight compositions in the ultraphosphate region will always exhibit values of R in which the numerator, M_2O, and the denominator, P_2O_5, are relatively small whole numbers.

According to the above concepts, the formula $M_8P_{10}O_{29}$ corresponds to $R = {}^4/_5$; $M_6P_8O_{23}$ corresponds to $R = {}^3/_4$; $M_4P_6O_{17}$ corresponds to $R = {}^2/_3$; $M_4P_{10}O_{27}$ corresponds to $R = {}^2/_5$; $M_2P_8O_{21}$ corresponds to $R = {}^1/_4$; $M_3P_7O_{19}$ corresponds to $R = {}^3/_7$ and MP_5O_{13} corresponds to $R = {}^1/_5$.

Discussion

In order to understand clearly the problems of structure in the phosphate system, it is necessary to draw some structural formulas. Examples of such formulas are found for the tetraphosphates—those compositions made up of four PO_4 groups. Structural formulas for all of the possible tetraphosphates are depicted in Table II; and of these only structures A, C and G are known. Structure G and all of the other structures contain branching points and hence would be expected to degrade rapidly when put into solution. Such rapid degradation has been demonstrated by a number of authors for structure G.

In structures E, F, I, J and K, four-membered rings of alternate phosphorus and oxygen atoms are found. This feature, which we call the dimetaphosphate ring, is a point of strain in the molecule and should give rise to a strain energy which is probably no greater than that found for cyclobutane (36 kcal.). In the best configuration (planar) the bond angles in the dimetaphosphate ring add up to 360°, which is considerably smaller than the angles for the sp^3-hybridization of the phosphorus atom and the hybridization of the oxygen atom which is usually between p^2 and sp^3. Since two 90° angles for the p^2-hybridization of oxygen plus two 109° 28′ angles for the sp^3-hybridization of phosphorus equals 398°56′, and since four tetrahedral angles (assuming sp^3-hybridization for oxygen) equals 437°57′, we see that the angular strain in the ring will range from approximately 39 to 78°.

In addition to the dimetaphosphate ring in which two corners of adjacent PO_4 tetrahedra are shared, we have a single case in which three corners of adjacent tetrahedra are shared. This corresponds to the diphosphate : monomeric P_2O_5. In this structure, the O–P–O angle (2α) is related to the P–O–P bond angle (2β) by the equation: $\sin \alpha = \cos 30° \cos \beta$. If the P–O–P and O–P–O angles were equal, this equation gives a value of 83° for the angles, which would correspond to a great deal of strain[6] in the monomeric P_2O_5 molecules.

With present methods of synthesis for phosphates, in which reorganization at high temperatures is involved, it will be impossible to produce structures exhibiting dimetaphosphate rings, since the strain can be relieved by reorganization to another structure. Likewise, branching points will probably not be found in the region where R is sen-

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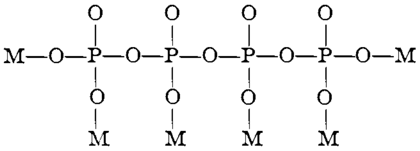
[5] The shortest derivation of this formula is obtained by setting $M_2O/P_2O_5 = R(n/n)$ to get its Berzelius modification, *i.e.*, $(nR)M_2O\cdot(n)P_2O_5$, which can easily be rearranged to the form given above. Similar general formulas can be derived for silicates, borates, sulfates and other salts. Thus, we have $M_{2nR}Si_nO_{n(R+2)}$; $M_{nR}B_nO_{n(R+3)/2}$; $M_{2nR}S_nO_{n(R+3)}$; etc.

[6] This discussion in terms of strain corresponds to Pauling's rule that "the presence of shared edges and especially of shared faces in a coördinated structure decreases its stability," which appears on p. 397 of "The Nature of the Chemical Bond," 2nd ed., Cornell Univ. Press, Ithaca, N. Y., 1945.

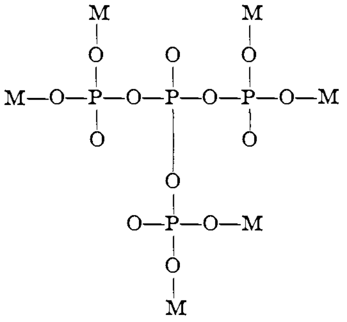
TABLE II

THE TETRAPHOSPHATES

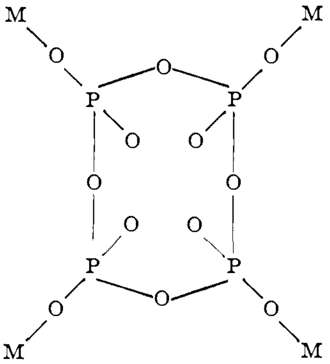


(A) Tetrapolyphosphate, $M_6P_4O_{13}$

(not crystallized; but shown to exist by chromatography, see A. E. R. Westman and A. E. Scott, *Nature*, **168**, 740 (1951); also ref. 7)

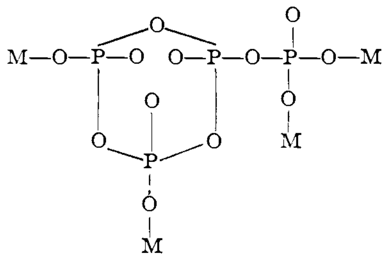


(B) "Iso"-tetrapolyphosphate, $M_6P_4O_{13}$ (not known)

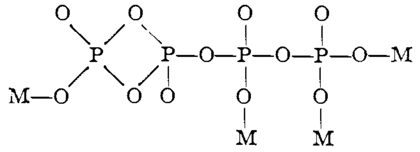


(C) Tetrametaphosphate, $(MPO_3)_4$

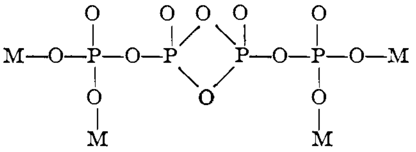
(structure of aluminum and ammonium salts shown by X-ray, L. Pauling and J. Sherman, *Z. Krist.*, **96**, 481 (1937); J. A. A. Ketelaar and C. H. MacGillavry, *Nature*, **164**, 960 (1949))



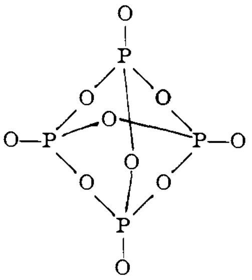
(D) "Iso"-tetrametaphosphate, $(MPO_3)_4$ (not known)



(E) "Iso"-tetrametaphosphate, $(MPO_3)_4$ (not known)

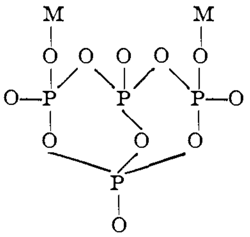


(F) "Iso"-tetrametaphosphate, $(MPO_3)_4$ (not known)



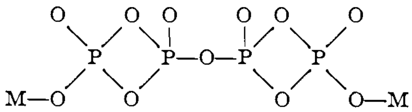
(G) Dimeric phosphorus pentoxide, $(P_2O_5)_2$

(Structure of vapor and hexagonal crystalline forms of phosphorus pentoxide. See H. C. J. de Decker and C. H. MacGillavry, *Rec. trav. chim.*, **60**, 153 (1941); P. C. Hampson and A. J. Stosick, THIS JOURNAL, **60**, 1814 (1939))

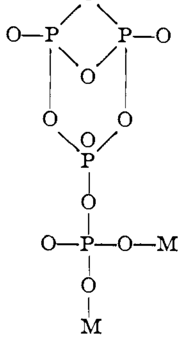


(H) An ultraphosphate, $M_2P_4O_{11}$, $M_2O \cdot 2P_2O_5$

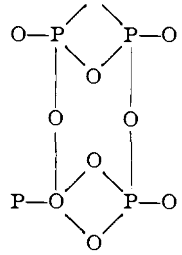
(Must appear as transient intermediate in hydrolysis of P_4O_{10}; see B. Raistrick, *Trans. Faraday Soc.*, **5**, 235 (1949); R. N. Bell, L. F. Audrieth and O. F. Hill, *Ind. Eng. Chem.*, **44**, 568 (1952))



(I) An ultraphosphate, ($M_2P_4O_{11}$ $M_2O \cdot 2P_2O_5$) (not known)



(J) An ultraphosphate $M_2P_4O_{11}$ $M_2O \cdot 2P_2O_5$ (not known)



(K) An isomer of dimeric phosphorus pentoxide $(P_2O_5)_2$ (not known)

TABLE III

THE PHOSPHATE FAMILY

P-atoms per unit mol. structure	Total no. of computed structures	No. of isolated known structures	"Polyphosphates" No. of chain compds.		"Metaphosphates" No. of ring compds.			"Ultraphosphates" No. of cross-linked compds.	
			Straight[b, a]	Branched	Simple[a] excepting dimeta rings	Subd. excepting dimeta rings	With dimeta rings	Excepting[a] dimeta rings	With dimeta rings
1	1	1	(1)	0	0	0	0	0	0
2	3	1	1	0	0	0	1	0	1
3	4	2	1	0	1	0	1	0	1
4	11	3	1	1	1	1	2	2	3
5	25	1[b]	1	1	1	3	3	7	9
6	*ca.* 73	1[b]	1	3	1	8	6	*ca.* 18	*ca.* 36

[a] These compositions are to be expected from present methods of synthesis. [b] Unpublished data obtained at Monsanto through chromatography on anion-exchange resins.

sibly less than unity until room-temperature syntheses methods are evolved. There is, of course, no reason why such structures[7] cannot be made—as, say, cyclopropane is made—by positional synthesis methods, such as are employed in organic chemistry. In Table III the multiplicity of structures which can be obtained in the phosphate family are shown for the low molecular weight compounds having six or fewer phosphorus atoms per molecule of molecule-ion. The number of possible structures becomes astronomical for high molecular weights, and it should be remembered that potassium metaphosphates (long chains) have been made with molecular weights[8] as high as *ca.* 10^6.

In the ultraphosphate region, a reasonably large number of relatively simple structures, corresponding to rational fractional values of R, are to be expected, and work is now under way in our laboratory to isolate such structures. For values of R less than unity which are not rational fractions, the only low molecular weight crystalline compositions which can be expected are mixtures of structures, each of which corresponds to a rational fractional value for R. Because of this limitation, it is to be expected that the initial seeding of ultraphosphate melts to give crystalline compounds will be difficult. Previous experience[9] indicates that ultraphosphates readily supercool to form glasses.

In this paper we have shown that a very large number of structures are to be expected in the ultraphosphate region. Moreover, we have pointed out that development of synthesis methods similar to those of organic chemistry should lead to the preparation of numerous compounds (lying in the poly-, meta- and ultraphosphate regions of composition) which cannot now be made because of the strain inherent in the dimetaphosphate ring. In order to produce and study the many thousands of phosphates having branching points and/or dimetaphosphate rings, new experimental techniques are necessary, and the methodology of polymer physics, which has been so successful[10] within the last decade in elucidating the structures of chain and ring phosphates, will probably no longer be applicable because of rapid hydrolysis.

In spite of the difficulties, studies directed toward preparation of ultraphosphates and the measurement of their physical properties are now under way in our laboratory. As predicted in this paper, we have found considerable complexity in this region of composition. In addition, work has been started on room temperature synthesis methods. Results from these various investigations will be reported upon their completion.

DAYTON, OHIO

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(7) It should be noted that either dimetaphosphate rings or branching points will be destroyed immediately upon dissolution in water unless protection of these vulnerable spots can be achieved through steric hindrance. The reports of water-soluble mono and dimetaphosphates which have appeared in the literature are false, as has been demonstrated recently by J. P. Ebel, *Bull. soc. chim. France*, **20**, 1089 (1953).

(8) R. Pfanstiel and R. K. Iler, THIS JOURNAL, **74**, 6059 (1952); R. K. Iler, *J. Phys. Chem.*, **56**, 1086 (1952); Harry Malmgren, *Acta Chem. Scand.*, **2**, 147 (1948); *ibid.*, **6**, 1 (1952).

(9) J. R. Van Wazer, THIS JOURNAL, **72**, 654 (1950); and A. V. Kroll, "Ueber Ultraphosphate," Leipsig, 1912.

(10) C. F. Callis, J. R. Van Wazer and P. G. Arvan, *Chem. Revs.*, **54**, 777 (1954).