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Structure and Properties of the Condensed Phosphates. XVIII. Ring-Chain and Other Equilibria in Organic Solvents

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Phosphoric acids in the range from the pyro- to the metaphosphate composition were equilibrated in selected mixtures of tetramethylurea and tri-*n*-butylamine and the resulting molecular distributions were measured by ^{31}P nmr. Cyclic molecules were found in much larger proportions than in any other phosphate system at the same cation:phosphorus ratio. Values of the equilibrium constants interrelating the variously sized ring and chain molecules are calculated and discussed.

Introduction

Although molecular equilibria involving the interconversion of cyclic structures of different sizes and the relation of these cyclic molecules to the noncyclics have been extensively studied both theoretically¹⁻³ and experimentally,⁴⁻⁸ little is known about this behavior for solutions of the condensed phosphoric acids and their salts, since most of the work reported for them has been done in water, which is a sufficiently reactive solvent so that hydrolysis competes with molecular reorganizations.⁹ It is true that the equilibria between phosphate molecule ions occurring in molten salts^{9,10} as well as in concentrated acids¹¹ have been profitably studied¹ using analytical procedures conducted in aqueous solution under conditions where hydrolysis was inconsequential. In the solvent-free systems where these equilibrations occurred, however, the close packing of the molecules involved in the redistribution reactions ensured the amount of cyclic phosphates was always quite small.

Attempts to conduct scrambling reactions to equilibrium do not work in aqueous solution because of the relatively

rapid hydrolysis of the condensed phosphates. By finding an appropriate nonaqueous solvent system for the condensed phosphate anions (using tertiary ammonium counterions to obtain reasonably high solubilities), it has been possible to carry out the work reported herein in which equilibrium with respect to phosphate scrambling was achieved in a nonreactive solvent at sufficient dilution so that cyclic molecules ought to predominate.

Experimental Section

Chemical Manipulations. Tetramethylurea from Eastman Organic Chemicals Co. was purified and carefully dried as previously described.¹² All of the other solvents were purified where necessary and rendered anhydrous by accepted procedures.¹³ The tri-*n*-butylamine which was used to make the ammonium phosphates in solution was also purified and dried according to the literature.¹² Although various combinations of phosphoric acids were occasionally employed as precursors in the equilibration studies, the usual procedure was to achieve the proper degree of condensation,¹² *D*, by adding water to commercial phosphorus pentoxide. To do this, the organic solvent containing the desired amount of amine was added to a 40-ml Teflon-capped centrifuge tube containing a weighed amount of P_2O_5 . After magnetic stirring to disperse the P_2O_5 , the amount of water needed to give the proper degree of condensation was added dropwise. Note that in order to determine the proper amount of added water, it was necessary to establish the water content of the P_2O_5 and this was achieved by precisely determining the degree of condensation of an equilibrated test mixture. Freshly opened bottles of phosphorus pentoxide were found to vary extensively in water content (from 0.01 to 5 wt % H_2O); however, if care is taken in dispensing (without use of drybox or drybag in the winter or with air conditioning), we find no change in the water content of the P_2O_5 in a 1-lb bottle being consumed over a period of several months.

All of the measurements reported in this paper correspond to equilibration at 62° for at least 4 weeks. Several studies of the rate of equilibration indicated that at this temperature there were no detectable changes in the ^{31}P nuclear magnetic resonance (nmr) patterns after 1 week in the slowest case. For those cases where phos-

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phate branch groups were detected in the ^{31}P nmr spectrum at equilibrium, it was always found that the rate of equilibration was extremely rapid, being complete in less than 2 hr. For all of the equilibration rate studies, quantitative spectra were taken over a period in the range of 2–4 months in order to look for any unusually slow steps in the reactions. In several cases, mixtures of different members of the family of condensed phosphoric acids were employed to achieve the same final degree of condensation and it was then found that the resulting ^{31}P nmr patterns were the same and independent of the reagents used.

Analytical Procedures. The dominant analytical technique employed in this work consisted of ^{31}P nmr measurements carried out under signal-averaging conditions on a Bruker HFX-5 spectrometer operating at 90 MHz for the ^1H lock and 36.4 MHz for the ^{31}P samples.^{14,15} To ensure the accuracy as well as the precision of the spectral area measurements, the spectra were recorded under classical slow-passage¹⁶ conditions and these were checked by measuring samples of known constitution. In order to confirm the nmr results, a differential phosphorus analysis was carried out on some of the samples using a thin-layer chromatographic technique developed^{17,18} for the separation of the condensed phosphate anions. In certain cases, it was also found advisable to employ controlled hydrolysis¹⁹ of a sample for additional verification of its molecule-anion composition. Since the chromatographic and hydrolytic data were found to agree well with the ^{31}P nmr results, only the latter are reported below.

When there was sufficient tri-*n*-butylamine present in the amine-tetramethylurea solvent mixture to neutralize completely the condensed phosphoric acids, the solutions were found to exhibit quite different nmr patterns from what there was with an insufficient amount of the amine. All of the nmr peaks in these patterns were quantitatively accounted for by the compounds listed in Table I, which shows the ^{31}P chemical shifts observed for the completely neutralized (*basic solutions*) and partially neutralized (*acidic solutions*) phosphoric acids at equilibrium. Note that the ^{31}P nmr pattern of each of the cyclic metaphosphates (R_i) is a single sharp peak¹⁸ and that the nmr patterns and the respective nmr parameters have been obtained²⁰ for the sodium polyphosphates (C_i) up to the decapolypophosphate. The ^{31}P spectra of the two molecules (A and B) involving branch phosphates have also been described.^{19,21} The spectral assignments for the various chain and ring phosphates observed in the equilibrated mixtures were checked by the addition of authentic samples.^{18–22}

Results and Interpretation

Although the lore of phosphate chemistry suggests that there are no good solvents other than water for the full series of phosphoric acids and their salts, we thought it worthwhile to retest this premise in order to find a solvent which would not react chemically with the phosphates as does water. Since we hoped to maximize the variety and amounts of the simple ring phosphates, the metaphosphate composition was an obvious choice for the solubility studies, which were carried out by combining P_2O_5 and H_2O as described in the Experimental Section. Except for mixtures involving tetramethylurea and tri-*n*-alkylamine, no appreciable dissolution was observed for the following aprotic solvents, alone or as mixtures: tri-*n*-alkylamine for *n* ranging from 1 through 5, pyridine, acetonitrile, dimethylformamide, tetramethylurea, acetone, dioxane, chloroform, benzene, and cyclohexane.

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Table I. ^{31}P Nmr Chemical Shifts (ppm) of the Observed Compounds in the Solvent Systems Employed

Compd	e ^a	em	mmm	b
C_1	(−0.1) ^{b,c}			
C_2	9.8			
C_3	9.6	26.7		
C_4	10.2	25.5		
C_6	12.3	24.2	24.6	
	14.3 ^c	26.4	26.9	
C_7	13.0	24.2	24.6	
R_3			21.5	
			25.6 ^c	
R_4			24.2	
			26.7	
R_5			25.4	
R_6			27.3	
R_7			26.1	
R_8			27.6	
A	14.4	26.7		
	15.3	23.0 ^d	36.0	
B		26.2 ^e	38.1	
		26.5 ^e	35.5	
		27.1 ^f	38.1	
		28.3 ^f		

^a The symbols heading the columns of chemical shifts have the following meanings: e, phosphate end group; em, a phosphate middle group next to an end group; mmm, a phosphate middle group lying between two other middle groups; b, a phosphate branch group. ^b To save space the chemical shift of the orthophosphate moiety is listed incorrectly in the end group column. ^c The numbers shown in italics refer to the partially neutralized phosphoric acids, i.e., the acidic solutions of Table II, whereas the other numbers refer to the tri-*n*-butylammonium polyphosphates, the basic solutions of Table II. ^d This lower value of the chemical shift for R_8 as compared to R_4 – R_7 , has been previously observed and rationalized.¹⁸

^e This chemical shift corresponds to mmb rather than to mmm.

^f This chemical shift corresponds to bmb rather than to mmm.

The greatest concentration (ca. 6 M) of phosphoric acid at the metaphosphate composition is found to dissolve in a mixture of 2.5 volumes of tetramethylurea to 1 of tri-*n*-butylamine. Moving away from this solvent ratio on either side leads to decreased solubility until, for the metaphosphoric acid in either of these pure solvents, the solubility becomes nil. The next best solvent mixture was seen to be tetramethylurea plus tri-*n*-propylamine, and this combination exhibited similar but lower solubilizing characteristics. Obviously the amine acts to neutralize the acidic hydrogens from the phosphoric acids thereby forming tri-*n*-butylammonium ions. However, the overall mechanism of the dissolution process must be considerably more complex, since only 20% of the available hydrogens are neutralized at the maximum metaphosphate solubility in this mixture and since only this solvent pair is at all effective.

In a series of preliminary experiments in which metaphosphate compositions were equilibrated in various proportions of the amine and the urea, it was observed that the ^{31}P nmr patterns of the equilibrated products lay in two different groups, with one group corresponding to the mole ratio of amine to total phosphorus being greater than unity and the other less. Furthermore, when there was more than 1 mol of amine to each mole of phosphorus (i.e., the acid functions were fully neutralized), the nmr pattern corresponding to a given degree of condensation was found to be quite independent of the amine:phosphorus ratio.

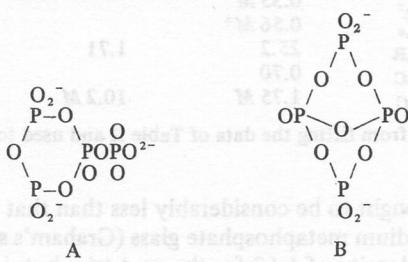
Experimental data are shown in Table II for equilibrated molecular mixtures corresponding closely to the metaphosphate composition for which the degree of condensation,¹² D , is exactly equal to 2. The degree of condensation, which is defined in footnote *a* of Table II is zero for the orthophosphate, 1 for the pyrophosphate, 2 for the metaphosphate,

Table II. Equilibrium Molecular Distributions from ^{31}P Nmr at the Metaphosphate Composition ($D = 2$)

Overall soln			Molecular concn, M									
Total P (M) from reagents	Amine (M) per P (M/M)	D^a from nmr	C_6^b	C_7	R_3	R_4	R_5	R_6	R_7	R_8	A^c	B^d
Basic Solutions (Tri-n-butylammonium Phosphates)												
1.00	1.0	1.999	0.0104	0.0074	0.1119	0.0547	0.0261	0.0124	0.0053	0.0013	0.0018	0.0181
0.50	2.5	1.996	0.0068	0.0046	0.0572	0.0260	0.0118	0.0047	0.0020	0.0004	0.0013	0.0105
0.25	5.1	1.980	0.0052	0.0030	0.0276	0.0119	0.0056	0.0021	0.0006			0.0057
0.10	10.0	1.95	0.0024	0.0019	0.0104	0.0055	0.0015	0.0007				0.0019
0.05	25.0	2.00			0.0096	0.0038	0.0012					
Acidic Solutions (Half-Neutralized Phosphoric Acids)												
1.00	0.5	2.008	0.0069		0.2575	0.0198	0.0025	0.0007		0.0117	0.0110	
0.50	0.5	2.011	0.0032		0.1302	0.0110	0.0013			0.0040	0.0059	
0.25	0.5	2.020	0.0013		0.0650	0.0052				0.0029	0.0038	
0.10	0.5	2.04			0.0262	0.0029				0.0008	0.0016	
0.05	0.5	2.00			0.0143	0.0018						

^a D is the degree of condensation which equals $3 - R$ where $R = [\text{H}_2\text{O}_{\text{compr}}]/[\text{P}_2\text{O}_5]$ mole ratio. By definition, $R = 2e + m$ when $e + m + b$ is normalized to unity. ^b C_n stands for the straight-chain phosphate based on n phosphorus atoms, whereas R_n stands for the simple ring phosphate based on n phosphorus atoms. When written as the acid, $C_n = \text{H}_{n+2}\text{P}_n\text{O}_{3n+1}$ and $R_n = \text{H}_n\text{P}_n\text{O}_{3n}$. ^c The orthophosphatyltrimetaphosphate anion (the acid of which is written $\text{H}_2\text{P}_3\text{O}_9 \cdot \text{PO}_3\text{H}_2$) is denoted by A. ^d The 1,5- μ -oxo-tetrametaphosphate (the acid of which exhibits the formula $\text{H}_2\text{P}_4\text{O}_{11} = \text{P}_4\text{O}_{10} \cdot \text{H}_2\text{O}$) is denoted by B.

and 3 for the phosphoric-anhydride compositions. The data in Table II are divided into two groups, depending on whether the amine:phosphorus ratio is equal or greater than unity (*basic solutions*) or less than unity (*acidic solutions*); and, in both sets of data, the total phosphorus concentration is reduced stepwise from 1.00 to 0.05 M. The first four columns in this table present information concerning the overall solution; whereas the remaining columns give the concentrations of the individual molecules observed. Only two molecules containing branch groups were detected and their concentrations quantitatively measured. These structures are the orthophosphatyltrimetaphosphate and the 1,5- μ -oxo-tetrametaphosphate, shown as the fully ionized molecule ions A and B, respectively.



Viscosity measurements on the solutions for which data are reported in Table I demonstrated that there were inappreciable amounts of macromolecules since all of the viscosities were only 1.5-2.0 times that of water, except for the two samples of highest concentration (1.00 M for P) which exhibited viscosities of 4.7 and 2.1 times that of water for the basic and acidic solutions, respectively. Presumably, the reason that only two sizes of straight chains (C_6 and C_7) are observed is that the total amount of chain molecules is small so that only the species with the highest probability of occurrence may be seen.

According to the principle of Le Chatelier,²³ increasing dilution should lead to more particles in solution so that, as the concentration of total phosphorus is reduced, there should be more rings with respect to chains (see eq 1²⁴) and the distribution of rings should be weighted more highly toward the

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small rings (e.g., see eq 2). Inspection of the data in Table II

$$iR_j \rightleftharpoons jR_i \quad (2)$$

shows that these effects are indeed observed.

In the case of the tri-n-butylammonium phosphates, ten compounds were observed so that ten independent equations are needed to define the system. Only eight of these need be equilibrium-constant expressions, since the remaining two can be used to establish the average degree of condensation of the phosphate mixture and its total phosphorus concentration. These are given by eq 3 and 4 in which [P] stands

$$[P] = \sum_i i[C_i] + \sum_j j[R_j] + 4[A] + 4[B] \quad (3)$$

$$D = 3 - (\sum_i (i+2)[C_i] + \sum_j j[R_j] + 4[A] + 2[B]) / [P] \quad (4)$$

for the molar concentration of the total phosphorus and D is the degree of condensation. Five equilibrium constants of the form of eq 5 may be used to describe the ring-ring equi-

$$K_{3,i}^{00} = [R_3]^i / [R_i]^3 \quad (i = 4-8) \quad (5)$$

libria of eq 2. The additional three equilibrium constants are shown in eq 6-8.

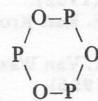
$$K_{AR} = [R_4] / [A] \quad (6)$$

$$K_{RC} = [C_6][R_4] / [C_7][R_3] \quad (7)$$

$$K_{BC} = [R_3]^2[R_4] / [C_6][B] \quad (8)$$

Approximate values of the eight equilibrium constants of eq 5-8 were obtained by putting in individual concentrations from Table I. Then, the best overall value of each constant was found by using the entire set of ten simultaneous equa-

(24) The symbol C_i stands for the straight-chain phosphate based on i phosphorus atoms and R_j for the simple-ring phosphate based on j phosphorus atoms. Thus, C_1 is the orthophosphate ion, PO_4^{3-} ; C_2 , the pyrophosphate ion, $\text{O}_2\text{POPO}_3^{2-}$; and C_6 , the hexapolyphosphate ion, $\text{P}_6\text{O}_{10}^{8-}$, which exhibits the molecular-backbone structure POPOPOPOPOPO . Similarly, R_3 is the trimetaphosphate ion, $\text{P}_3\text{O}_9^{3-}$, which exhibits the molecular backbone



tions to calculate test curves similar to those shown in Figure 1. The best visual fit to the entire set of basic-solution data was obtained for the values of the constants shown in Table III. The concentration curves corresponding to these particular values are presented in Figure 1 where they can be compared with the experimental points. We believe that the values reported in Table III represent the best set of invariant constants which can be fitted to the data for the basic solutions reported in Table II.

For the acidic solutions shown in Table II, only seven compounds were observed so that in addition to eq 3 and 4 only five equilibrium constants are necessary. Three of these equilibrium constants are of the form of eq 5 for $i = 4-6$. The equilibrium constants of eq 6 and 8 are also applicable. By carrying out the same operations as were employed in treating the data obtained on the basic solutions, the curves shown in Figure 2 were obtained for the acid solutions reported in Table II. The corresponding equilibrium constants are presented in Table III.

Attempts to measure the effects on the equilibrium constants of varying the degree of condensation for the fully neutralized tri-*n*-butylammonium phosphate mixtures was unsuccessful because of the low solubilities of the short-chain phosphates (including the orthophosphate) in the solvent mixture. However, it was apparent from the data that, as expected, there was a precipitous drop in the average chain length of the polyphosphate constituents as the value of D was lowered much under 2.00. In the case of the partially neutralized phosphoric acids, the solubility was good for both the large and small chain molecules so that the data described in Table IV could be obtained. Note in this table that even at D as large as 1.89 there is an appreciable amount of orthophosphate and at D as small as 1.37 the molar concentration of the trimetaphosphate anion is still relatively large. Obviously the same equilibrium constants as were reported in Table III cannot be evaluated from the data of Table IV since the relevant molecules were present at concentrations too small to be detected. Thus, another set of equilibrium constants was needed to describe the data of Table IV and these constants are given in eq 9-11 with their best-fit experimental

$$K_{C2} = [C_3][C_1]/[C_2]^2 = 4.8 \quad (9)$$

$$K_{C3} = [C_2][C_4]/[C_3]^2 = 0.16 \quad (10)$$

$$K_\alpha = [C_4]/[C_1][R_3] = 0.20 M \quad (11)$$

values.

Discussion

All previous equilibration studies^{9,11,25} of condensed phosphoric acids and their alkali metal salts have of necessity involved coming to equilibrium in an undiluted liquid form. Therefore, only a small number of cyclic molecules have been observed,^{9,26} with the larger rings being present to such small amounts that they were often undetected. Of course, cyclization during hydrolysis²⁷ of aqueous metaphosphate solutions represents an incomplete approach to ring-chain equilibration.

The tri-*n*-butylammonium ion is so large that even in the neat metaphosphate glass the molar concentration of the

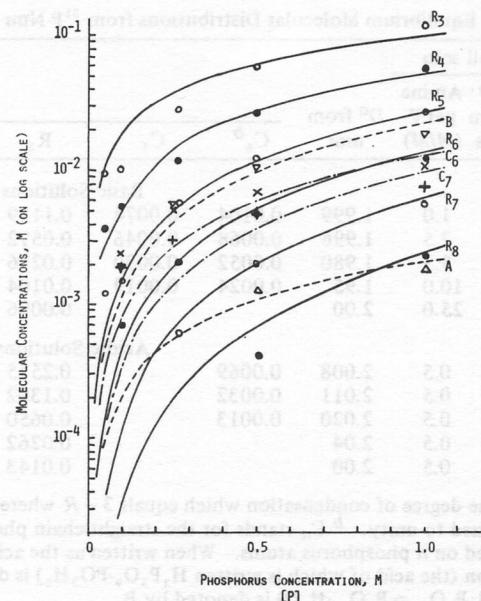


Figure 1. Curves based on the equilibrium constants of Table III showing the variation of the concentrations of the individual molecular species with the total phosphorus concentration for the tri-*n*-butylammonium metaphosphate composition. The solid lines correspond to the cyclic metaphosphates, the dashed lines to the compounds containing branch groups, and the dash-dotted lines to the straight-chain polyphosphates. The experimental points are denoted by \circ for R_3 , R_5 , and R_7 ; \bullet for R_4 , R_6 , and R_8 ; \times for C_6 , $+$ for C_7 , Δ for compound A; and ∇ for compound B.

Table III. Equilibrium Constants^a Measured at the Metaphosphate Composition

Constant	Tri- <i>n</i> -butylammonium phosphates	Half-neutralized phosphoric acids
$K_{3,4}^{00}$	0.67 M	300. M
$K_{3,5}^{00}$	$0.52 M^2$	$4.4 \times 10^4 M^2$
$K_{3,6}^{00}$	$0.35 M^3$	$6.8 \times 10^5 M^3$
$K_{3,7}^{00}$	$0.35 M^4$	
$K_{3,8}^{00}$	$0.56 M^5$	
K_{AR}	25.2	1.71
K_{RC}	0.70	
K_{BC}	1.75 M	10.2 M

^a Obtained from fitting the data of Table II and used to calculate Figure 1.

phosphate ought to be considerably less than that in the corresponding sodium metaphosphate glass (Graham's salt). Thus, assuming a density of 1.63 for the neat tri-*n*-butylammonium metaphosphate glass, we estimate a total phosphorus concentration of 6.2 M for this glass at room temperature. This is to be compared with the corresponding value of 24.4 M obtained for Graham's salt, using its measured room-temperature density of 2.48.

From the eight equilibrium constants given for the tri-*n*-butylammonium phosphates in Table III, we have calculated that the percentage of total phosphorus present as cyclic molecules at equilibrium in a $(C_4H_9)_3HNPO_3$ glass having a density in the range of 1.0-2.5 will remain around 73%. This number is much larger than the value of 8% of the total phosphorus experimentally observed as cyclic molecules in Graham's salt, and it corresponds to an extrapolation of the concentration of the total phosphorus in the tri-*n*-butylammonium metaphosphate glass to the physically impossible value corresponding to Graham's salt. Obviously these calculations are only poor approximations, since all of the pertinent equilibrium constants applicable to the high concentrations surely do not appear in Table III. However, the calculations do indicate that factors in addition to dilution by a

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Table IV. Equilibrium Molecular Distributions of Tri-*n*-butylammonium Phosphates from ^{31}P Nmr for Various Degrees of Condensation at an Amine:Phosphorus Mole Ratio of 2.5 and a Total Phosphorus Concentration of 0.5 M

[P], M	Degree of condensation ^a		Molecular concn, M					
	From reagents	From nmr	C ₁	C ₂	C ₃	C ₄	R ₃	R ₄
0.500	1.90	1.888	0.0250	0.0030			0.1530	0.0025
0.495	1.82	1.823	0.0346	0.0042	0.0051		0.1472	
0.495	1.78	1.774	0.0435	0.0070	0.0055		0.1420	
0.490	1.73	1.773	0.0475	0.0088	0.0075	0.0015	0.1355	
0.488	1.67	1.670	0.0590	0.0105	0.0090	0.0020	0.1285	
0.483	1.60	1.584	0.0700	0.0145	0.0145	0.0015	0.1172	
0.481	1.49	1.480	0.0900	0.0170	0.0170	0.0010	0.1070	
0.481	1.37	1.373	0.1100	0.0205	0.0200		0.0965	

^a The degree of condensation which equals $3 - R$ where $R = [\text{H}_2\text{O}_{\text{compr}}]/[\text{P}_2\text{O}_5]$ mole ratio. By definition $R = 3n + 2e + m$ where $n + e + m = 100\%$ of the total phosphorus. ^b C_n stands for the straight-chain phosphate based on *n* phosphorus atoms, whereas R_n stands for the simple-ring phosphate based on *n* phosphorus atoms. When written as the acid, C_n = H_{n+2}P_nO_{3n+1} and R_n = H_nP_nO_{3n}.

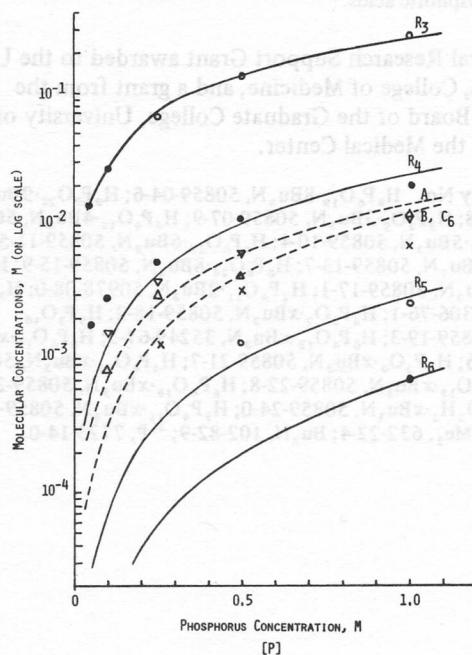


Figure 2. Curves based on the equilibrium constants of Table III showing the variation of the concentrations of the individual molecular species with the total phosphorus concentration for the half-neutralized metaphosphoric acid composition. The solid lines correspond to the cyclic metaphosphates and the dotted lines to the other species. The experimental points are denoted by O for R₃ and R₅; • for R₄ and R₆; X for C₆; Δ for compound A; and ▽ for compound B. Note that in this system exactly the same curve applies to compounds B and C₆.

solvent favor cyclization in the tri-*n*-butylammonium phosphate system.

In addition to the much larger proportion of cyclic molecules, the tri-*n*-butylammonium metaphosphates exhibit a much sharper distribution of straight-chain molecules than is found for their sodium analogs. As pointed out by Meadowcroft and Richardson,²⁸ large cations should lead to sharp distributions of the chain species. These authors have surveyed the values of K_{C_2} and K_{C_3} (which they call K_2 and K_3) for various binary phosphate glasses and concluded that, for K_{C_3} at least, the value should increasingly deviate from the random value of unity with increasing cationic size. Thus, the following series of experimental mean values of K_{C_3} were reported: 0.48 for Li⁺, 0.26 for Na⁺, 0.27 for K⁺, to which should be added from this work the value of 0.16 for (C₄H₉)₃HN⁺.

Table V. Calculation^a of $K_2 = [e][b]/[m]^2$ from the Data of Table II

Total P, M	% of total P as			$10^3 K_2$
	e	m	b	
Basic Solutions (Tri- <i>n</i> -butylammonium Phosphates)				
1.00	3.91	92.30	3.79	1.74
0.50	4.82	90.72	4.46	2.61
0.25	6.55	88.89	4.56	3.78
0.10	9.0	87.0	4.0	4.8
Acidic Solutions (Half-Neutralized Phosphoric Acids)				
1.00	2.55	94.08	3.37	0.97
0.50	2.08	94.76	3.16	0.73
0.25	2.20	93.61	4.19	1.05
0.10	0.0	96.0	4.0	

^a The use of this equilibrium constant involving building units is applicable only when the reorganizational heat order¹ is zero or unity, a situation which is not found to be true for the condensed sodium phosphates but is a reasonable approximation for the condensed phosphoric acids.

Only two of the eight equilibrium constants defined above in eq 5-8 can be evaluated from the data for the sodium phosphate system. These constants are $K_{3,4}^{00} = 1.1$ and $K_{RC} = 1.02$. The values of $K_{3,4}^{00}$ and K_{RC} are not greatly different from those reported in Table III for the tri-*n*-butylammonium phosphates. From the data for the condensed phosphoric acids, $K_{3,4}^{00} = 7$, a value which is considerably smaller than $K_{3,4}^{00} = 300$ reported in Table III for the condensed phosphoric acids half-neutralized by tri-*n*-butylamine. We tentatively ascribe the severalfold increase in magnitude of $K_{3,4}^{00}$, when going from either the sodium phosphates or condensed phosphoric acids equilibrated in a neat melt to the half-neutralized phosphoric acids equilibrated in tetramethylurea, to a solvent effect, which involves a poorer interaction of hydrogen ions with the tetramethylurea molecular matrix than with the presumably hydrogen-bonded assemblage of condensed phosphoric acid molecules. Concomitantly, we envisage that there is a good interaction between tri-*n*-butylammonium cations and the molecular array corresponding to liquid tetramethylurea and between the constituent sodium ions and the molten sodium phosphate system.

When the heat of formation of a building unit is essentially independent of the placement of this unit in a molecule (*i.e.*, a reorganizational heat order,¹ ρ , of unity), it has been shown¹ that the equilibria between the various molecules may be approximated in terms of equilibria between the building units of various functionalities. This assumption of $\rho = 1$ has been shown to apply reasonably well to phosphoric acids but not to the sodium phosphates.¹ Moreover, it is generally a poor approximation for systems in which an appreciable proportion of the building units are involved in cyclic structures since there is usually a relatively large en-

thalpy for reactions between rings and chains (see eq 1). However, we have calculated such overall equilibrium constants, K_1 and K_2 , from the data of Tables II and IV and the results are shown in Tables V and VI, in which the constants are defined. For the sodium metaphosphates, the equilibrium constants, K_1 and K_2 , seem to be much smaller than the values obtained in Tables VI and V for the tri-*n*-butylammonium system. From tabulated thermodynamic data,²⁹ we estimate that for the sodium phosphates, $K_1 = ca. 10^{-10}$ and $10^{-14} < K_2 < 10^{-10}$. Reported molecular distribution data²⁵ from rapid quenching of mixed alkali metal phosphate melts near the tripolyphosphate composition to give glasses indicate that $K_1 = 10^{-3}$ for these systems.

If the scrambling of the bridging and nonbridging oxygens of the phosphoryl groups making up the condensed-phosphate molecular assemblages were completely random ($\rho = 0$), K_1 and K_2 would be equal to 0.25. The fact that the values shown for these constants in Tables V and VI are considerably closer to the random values than those estimated for the alkali metal phosphates may indicate that in tetramethylurea the trialkylammonium cations effectively shield and hence neutralize the ionic charges on the phosphate anions more than do the alkali metal cations in a neat melt. In other words, it seems that the alkylammonium phosphates serve as a more inert "solvent" for their anions than do the alkali metal phosphates.

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Table VI. Calculation^a of $K_1 = [o][m]/[e]^2$ from the Data of Table IV

D_{obsd}	% of total p as				K_1
	o	e	m		
1.89	5.00	1.20	93.80		325
1.82	6.99	3.76	89.25		44.1
1.77	8.80	5.05	86.15		29.7
1.73	9.70	7.27	83.03		15.2
1.67	12.10	8.82	79.08		12.3
1.58	14.50	12.64	73.86		6.61
1.48	18.71	14.55	66.74		5.90
1.37	22.89	16.86	66.25		4.85

^a The use of this equilibrium constant involving building units is applicable only when the reorganizational heat order¹ is zero or unity, a situation which is not found to be true for the condensed sodium phosphates but is a reasonable approximation for the condensed phosphoric acids.

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Registry No. $H_8P_6O_{19}\cdot 8Bu_3N$, 50859-04-6; $H_9P_6O_{22}\cdot 9Bu_3N$, 50859-06-8; $H_3P_3O_9\cdot 3Bu_3N$, 50859-07-9; $H_4P_4O_{12}\cdot 4Bu_3N$, 50859-08-0; $H_5P_5O_{15}\cdot 5Bu_3N$, 50859-10-4; $H_6P_6O_{18}\cdot 6Bu_3N$, 50859-11-5; $H_7P_7O_{21}\cdot 7Bu_3N$, 50859-13-7; $H_8P_8O_{24}\cdot 8Bu_3N$, 50859-15-9; $H_2P_3O_9\cdot PO_3H_4\cdot 4Bu_3N$, 50859-17-1; $H_2P_4O_{11}\cdot 2Bu_3N$, 50978-08-0; $H_3PO_4\cdot xBu_3N$, 29306-76-1; $H_4P_2O_7\cdot xBu_3N$, 50859-18-2; $H_5P_3O_{10}\cdot xBu_3N$, 50859-19-3; $H_6P_4O_{13}\cdot xBu_3N$, 35249-67-3; $H_8P_6O_{19}\cdot xBu_3N$, 50859-20-6; $H_3P_3O_9\cdot xBu_3N$, 50859-21-7; $H_4P_4O_{12}\cdot xBu_3N$, 50932-74-6; $H_5P_5O_{15}\cdot xBu_3N$, 50859-22-8; $H_6P_6O_{18}\cdot xBu_3N$, 50859-23-9; $H_2P_3O_9\cdot PO_3H_2\cdot xBu_3N$, 50859-24-0; $H_2P_4O_{11}\cdot xBu_3N$, 50859-26-2; $Me_2NCONMe_2$, 632-22-4; Bu_3N , 102-82-9; ^{31}P , 7723-14-0.