The Complexes of Pyrophosphate Ion with Alkali Metal Ions

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The stabilities of the complexes of pyrophosphate ion with sodium, potassium and lithium ions have been calculated from the pH lowering during the titration of pyrophosphate ion with hydrogen ion. The acidity constants of pyrophosphoric acid have been obtained in the absence of alkali metal ions and compared with those of ortho- and triphosphoric acid. The following complexes and their corresponding complexity constants were obtained at 25° using tetramethylammonium chloride to adjust the ionic strength to unity. $K(P_2O_7)^{3-}$, $K_{KPY} = 10^{0.8)} \pm 0.06$; $Na(P_2O_7)^{3-}$, $K_{NaPY} = 10^{1.00} \pm 0.06$; Li$(P_2O_7)^{3-}$, $K_{LiPY} = 10^{2.39} = 0.06$. Only lithium ions formed an acidic complex with the ligand $(HP_2O_7{}^{3-})$; Li$(HP_2O_7)^{2-}$, $K_{LiHPY} = 10^{1.03} \pm 0.06$. The successive acidity constants of pyrophosphoric acid at 25° and unity ionic strength were $10^{0.82}$, $10^{1.81}$, $10^{6.13}$, $10^{8.93}$. No complexes of the alkali metal ions with orthophosphate ion were detected.

Introduction

This is the third paper of a series on the acidity and complexes of polyphosphates.[3,4]

The existence of alkali metal complexes with pyrophosphate ion was not considered before Monk,[5] during a conductance study of the acidity of pyrophosphoric acid, found evidence of complex formation with sodium ion and calculated a dissociation constant of $10^{-2.45}$ for the complex, $NaP_2O_7{}^{3-}$. Complex formation of pyrophosphate with alkali metal ion is of considerable importance since alkali metal ions usually are added to adjust ionic strength or as a source of pyrophosphates.

The classic conductivity measurements of Abbott and Bray[6] yielded reliable values for the acidity constants of pyrophosphoric acid, particularly the first and second constants, while Kolthoff and Bosch[7] obtained excellent values for the third and fourth ionization constants extrapolated to infinite dilution. The tendency of pyrophosphate to form complexes with many metals through chelate ring formation has been the subject of numerous studies.[8-16]

In the present study the acidity constants of pyrophosphoric acid were evaluated at various ionic strengths in the presence of tetramethylammonium chloride with alkali metal ions absent. As in the second paper of this series[4] on triphosphate complexes with alkali metal ions the lowering of the apparent acidity constants of pyrophos-

(1) Abstracted from the Ph.D. thesis of Sheldon M. Lambert submitted in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1957.

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(3) J. I. Watters, E. D. Loughran and S. M. Lambert, THIS JOURNAL, 78, 4855 (1956).

(4) J. I. Watters, S. M. Lambert and E. D. Loughran, ibid., 79, 3651 (1957).

(5) C. B. Monk, J. Chem. Soc., 423 (1949).

(6) G. A. Abbott and W. C. Bray, THIS JOURNAL, 31, 729 (1909).

(7) I. M. Kolthoff and W. Bosch, Rec. trav. chim., 47, 826 (1928).

(8) I. M. Kolthoff and J. I. Watters, Ind. Eng. Chem., Anal. Ed., 15, 8 (1943).

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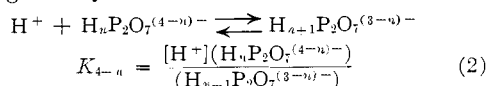(16) J. A. Davis, Dissertation Abstracts, Vol. XV, No. 12, 2403 (1955).

phoric acid in the presence of an excess of various alkali metal ions was used as a means of evaluating the extent of complex formation.

Theoretical

If an acid can be titrated in the presence of a relatively large excess of metal ion without precipitate formation, it is possible to investigate complex formation by the lowering of the pH. When the inflections at the various equivalence points persist for the stepwise addition or removal of hydrogen ions, the calculations are greatly simplified. In this case, it is evident that each ligand adds one hydrogen ion in a stepwise manner even though the ligand may also be bound to a metal ion. Under these conditions it is expedient to define a function which is called the apparent acidity constant,[11] K'_{4-n}, for this stepwise addition of hydrogen ion as

$$K'_{4-n} = \frac{[H^+] \Sigma q(M_m(H_nP_2O_7)_q{}^{(q(4-n)-m)-})}{\Sigma q(M_m(H_{n+1}P_2O_7)_q{}^{(q(3-n)-m)-})} \quad (1)$$

where m, n and q indicate the number of metal, hydrogen and pyrophosphate ions in any particular species. In this paper parentheses indicate concentrations and brackets indicate activities. The number of bound hydrogen ions, n, has a single value from zero to four if the addition of hydrogen ion is stepwise while m and q may have several values if several complex species, and the uncomplexed ligand, as well, are in equilibrium. The general equation for the stepwise addition of hydrogen ion to pyrophosphate ion and the corresponding acidity constant are

$$H^+ + H_nP_2O_7{}^{(4-n)-} \rightleftharpoons H_{n+1}P_2O_7{}^{(3-n)-}$$

$$K_{4-n} = \frac{[H^+](H_nP_2O_7{}^{(4-n)-})}{(H_{n-1}P_2O_7{}^{(3-n)-})} \quad (2)$$

The general equation for the formation of any complex ion and the corresponding complexity constant, $\beta_{M_mH_nL_q}$, are

$$mM^+ + qH_nP_2O_7{}^{q(4-n)-} \rightleftharpoons M_m(H_nP_2O_7)_q{}^{(q(4-n)-m)-}$$

$$\beta_{M_mH_nL_q} = \frac{(M_m(H_nP_2O_7)_q{}^{(q(4-n)-m)-})}{(M^+)^m(H_nP_2O_7{}^{(4-n)-})^q} \quad (3)$$

where the subscript L indicates the ligand $P_2O_7{}^{4-}$.

The equations used to calculate the complex formation constants were derived by substituting equations having the forms of (2) and (3) into (1) with m and q assumed to be equal to unity.

$$K_3' = \frac{[H^+][(HP_2O_7{}^{3-}) + (MHP_2O_7{}^{2-})]}{(H_2P_2O_7{}^{2-})} =$$
$$K_3 + K_{MHL}K_3(M^+) \quad (4)$$

$$K_4' = \frac{[H^+][(P_2O_7{}^{4-}) + (MP_2O_7{}^{3-})]}{(HP_2O_7{}^{3-}) + (MHP_2O_7{}^{2-})} =$$

$$\frac{K_4 + K_{ML}K_4(M^+)}{1 + K_{MHL}(M^+)} \quad (5)$$

K_3 and K_4 are the acidity constants of pyrophosphoric acid, while K_{ML} and K_{MHL} are the formation constants for the complexes $M(P_2O_7)^{3-}$ and $M(HP_2O_7)^{2-}$.

From these equations it follows that the apparent acidity constants are constants if the concentration of unbound metal ion is constant, provided precautions are taken to avoid changes in activity coefficients. A high concentration of an essentially non-complexing electrolyte and relatively low concentrations of metal ion and pyrophosphate ion were used for this purpose. For the titration of pyrophosphate ion with hydrogen ion in the absence of metal ions the acidity constants can be calculated by the following form of eq. 1. In the presence of metal ions K_{4-n}' is calculated by the same equation

$$K_{4-n} = \frac{[H^+][(n + 1 - a)C_p - K_w/[H^+]f + H^+/f]}{(a - n)C_p + K_w/[H^+]f - [H^+]/f} \quad (6)$$

where a is the number of moles of hydrogen ion per mole of pyrophosphate ion present in any form. The symbol f indicates the activity coefficient of a univalent ion. If the acid is not too dilute the constants have the same value as the pH at $a = n + 1/2$.

Experimental

The source of pyrophosphate ion for most of the experiments was $Na_4P_2O_7 \cdot 10H_2O$, Mallinckrodt analytical reagent grade. The pyrophosphoric acid was prepared from sodium pyrophosphate by the use of the acid form of the ion-exchange resin Dowex 50-X12, 100–200 mesh, low porosity in a manner exactly analogous to that described for the preparation of triphosphoric acid.[3] Potassium pyrophosphate was prepared by heating anhydrous dipotassium hydrogen phosphate at 500 to 700° for 3 hr.[8] Lithium pyrophosphate was prepared in the same manner as lithium triphosphate in the previous study using the exchange resin Dowex 50-X12 charged with lithium ions. All other reagents and the general experimental procedure are described in the previous paper.[4]

The titrations were performed in an aqueous thermostat adjusted to 25 ± 0.1° using the Beckman model G pH meter equipped with a "general purpose" glass electrode.

The $H_4P_2O_7$ or $((CH_3)_4N)_4P_2O_7$ solutions obtained from the columns were tested for removal of sodium ion.[3] The extent of hydrolysis of $((CH_3)_4N)_4P_2O_7$ was tested by titrations and found to be negligible after periods of one week if the solution was stored in a freezer at −15°. Crowther and his co-workers[17,18] studied the hydrolysis of pyrophosphoric acid and found it to be acid catalyzed but not base catalyzed. In the present study no appreciable hydrolysis was observed if the tetramethylammonium pyrophosphate solution was left at room temperature for one hour.

Results and Discussion

The Acidity of Pyrophosphoric Acid.—Since all previous studies of the acidity of pyrophosphoric acid at large ionic strength were made in the presence of alkali metal ions, the acidity constants were re-evaluated using tetramethylammonium chloride to adjust the ionic strength but with alkali metal ions absent.

Curve 1, Fig. 1, was obtained for the titration

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

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

of 0.02968 $M((CH_3)_4N)_4P_2O_7$ with a solution containing 0.2805 M HCl and the same concentration of $H_4P_2O_7$ as the solution titrated. Curve 5, Fig. 1, was obtained for the titration of 0.04524 M $H_4P_2O_7$ with 0.08901 M $(CH_3)_4NOH$. All solutions contained sufficient $(CH_3)_4NCl$ to produce an ionic strength of unity. The ordinate "a" is the number of equivalents of acid or base added per mole of
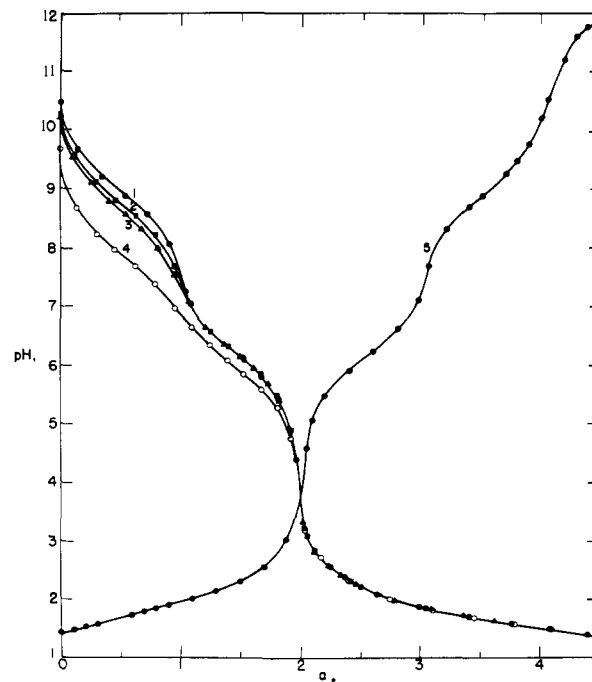

Fig. 1.—Curves for the titration of pyrophosphate ion with hydrochloric acid and the titration of pyrophosphoric acid with tetramethylammonium hydroxide. A comparison of the effects of potassium, sodium and lithium ion on the titration curve of pyrophosphate ion with hydrochloric acid. Curve 1, 0.02968 M $((CH_3)_4N)_4P_2O_7$ titrated with a solution 0.2805 N in HCl and 0.02968 M in $H_4P_2O_7$; curve 2, similar to curve 1, but 0.12 M in K^+; curve 3, 0.12 M in Na^+; curve 4, 0.12 M in Li^{++}; curve 5, 0.04524 M $H_4P_2O_7$ titrated with a solution 0.08901 M $(CH_3)_4NOH$. All solutions adjusted to $\mu = 1$ with $(CH_3)_4NCl$.

pyrophosphate present in any form. The titration curves for pyrophosphoric acid indicate that the first two hydrogen ions are highly dissociated and that the values for their ionization constants are not widely separated. Therefore, Bjerrum's method was used to evaluate these constants in the same manner as for triphosphoric acid.[3] The expression for the stepwise complexity constants is

$$\beta_i = \frac{(H_nP_2O_7{}^{(4-n)-})}{[H^+]^n(P_2O_7{}^{4-})}$$

where parentheses indicate concentrations and brackets indicate activities.

Due to the absence of appreciable concentrations of the species $P_2O_7{}^{4-}$ and $HP_2O_7{}^{3-}$ at pH values below 3 the simultaneous solution of Bjerrum's formation equation[3] for β_3 and β_4 in groups of two yielded the values of log $\beta_3 = 1.81 \pm 0.05$ and log $\beta_4 = 2.63 \pm 0.05$. Converting to the usual stepwise acidity constants the values are $pK_2 = 1.81 \pm 0.05$ and $pK_1 = 0.82 \pm 0.05$. Table I shows the

TABLE I

The titration of 20 ml. of a solution of 0.02968 M ((CH_3)$_4$-N)$_4$P$_2$O$_7$ with a solution 0.2805 M in HCl and 0.02968 M in H$_4$P$_2$O$_7$. Both solutions contained sufficient (CH_3)$_4$NCl to produce an ionic strength of 1.0.

a	pH	$\bar{n}_{theory}$	$\bar{n}_{experiment}$
2.10	2.93	2.07	2.06
2.24	2.61	2.14	2.14
2.37	2.42	2.22	2.22
2.50	2.25	2.29	2.32
2.63	2.13	2.35	2.34
3.03	1.89	2.53	2.51
3.41	1.73	2.64	2.68
3.75	1.61	2.75	2.79
4.08	1.52	2.83	2.88
4.93	1.31	3.00	3.00
5.84	1.15	3.05	3.11

agreement between $\bar{n}_{experimental}$ and $\bar{n}_{theoretical}$, where $\bar{n}$ is the mean number of bound H$^+$ ions per pyrophosphate ion.

The acidity constants also were evaluated at infinite dilution. In the previous study of triphosphoric acid an excess of (CH_3)$_4$NCl was present in the dilution solution in order to substitute the known ionic strength of the latter for the less certain effect of the larger dispersed ionic charge of the triphosphate ion. When attempts were made to obtain similar data for pyrophosphoric acid with excess (CH_3)$_4$NCl present to adjust the ionic strength, as was done in the previous study, the graphed data did not approach a straight line before the electrode became poorly poised. Consequently the data were obtained without the extraneous electrolyte, and the ionic strength was calculated on the basis of total pyrophosphate ionic charge.

The values of K_2, K_3 and K_4 at concentrations approaching infinite dilution were calculated using eq. 6 which contains terms for the degree of hydrolysis and dissociation. The activity coefficients of Harned and Ehlers[19] were used. The p values of K_3 and K_4 at an ionic strength of unity were pK_3 = 6.13 and pK_4 8.93. At an ionic strength of 0.1, the value of pK_2, pK_3 and pK_4 were 2.22, 6.36 and 9.11, respectively. The graphic extrapolation to infinite dilution yielded pK_2 = 2.64, pK_3 = 6.76 and pK_4 = 9.42. It is of interest to observe that the last two constants for K_3 and K_4 are quite close to the values pK_3 = 6.679 and pK_4 = 9.391 obtained by Kolthoff and Bosch using a hydrogen electrode with sodium ion added as the pyrophosphate salt. It is evident from the magnitude of the sodium complexes constant that the latter should not affect their result at infinite dilution.

On the basis of these results the dilution experiments for triphosphoric acid were repeated using the same conditions. These revised constants are included in Table II. The agreement of our data for pyrophosphoric acid using the glass electrode with Kolthoff and Bosch's value using the hydrogen electrode supports these values.

pK_1 was determined by Bates,[20] pK_2 by Bates and Acree[21] and pK_3 by Abbott and Bray.[6] Constants

(19) H. S. Harned and R. W. Ehlers, THIS JOURNAL, **55**, 2179 (1933).

(20) R. G. Bates, J. Research Natl. Bur. Standards, **47**, 127 (1951).

(21) R. G. Bates and S. P. Acree, ibid., **30**, 129 (1947).

TABLE II

THERMODYNAMIC IONIZATION CONSTANTS

| Acid	H$_3$PO$_4$[20,21,6]	H$_4$P$_2$O$_7$	H$_5$P$_3$O$_{10}$
pK_1	2.15	$-\infty$	$-\infty$
pK_2	7.20	2.64	$-\infty$
pK_3	12.44	6.76	2.30
pK_4	...	9.42	6.50
pK_5	...	..	9.24

having pK values indicated by $-\infty$ were too large to measure.

The Complexes of the Alkali Metals with Pyrophosphate.—Curves 2, 3 and 4, Fig. 1, illustrate the pH lowering effect due to the presence of approximately 0.10 M potassium, sodium and lithium ions in the titration of approximately 0.03 M ((CH_3)$_4$N)$_4$P$_2$O$_7$ with a solution containing approximately 0.28 M HCl and the same concentration of H$_4$P$_2$O$_7$ as the solution titrated. Since curves 1 to 4 coincide at "a" values beyond 2, it is evident that no complex formation occurs between any of the alkali metal ions and H$_2$P$_2$O$_7$$^{2-}$ or H$_3$P$_2$O$_7$$^{1-}$. Furthermore the reactants are sufficiently dilute so there is no measurable effect on the activity coefficients. Consequently the pH lowering at "a" values below 2 must be due to complex formation.

Comparing curve 2 obtained in the presence of potassium with curve 1, a lowering of the pH occurred only for "a" values less than unity proving the absence of detectable concentrations of potassium hydrogen pyrophosphate complexes, so eq. 5 reduced to the form

$$K_4' = K_4 + K_{KL}K_4(K^-)$$

Using the acidity constants of pyrophosphoric acid taken from the previous section and estimating the concentration of the free potassium ion to be the total concentration less the concentration of pyrophosphate ion one obtains a temporary complexity constant. More accurate values of (K^-) were then obtained on the basis of the temporary constant.
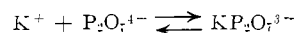
$$K^+ + P_2O_7^{4-} \rightleftarrows KP_2O_7^{3-}$$

$$K_{KL} = \frac{(KP_2O_7^{3-})}{(K^-)(P_2O_7^{4-})} = 10^{0.80} = 6.06$$

As shown in curve 3 obtained in the presence of sodium ion the pH was lowered only for "a" values less than unity proving the absence of detectable concentrations of acidic sodium complexes. Substituting the values of K_4 and the free sodium ion into eq. 7 as before, one obtains
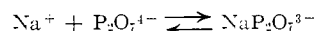
$$Na^+ + P_2O_7^{4-} \rightleftarrows NaP_2O_7^{3-}$$

$$K_{NaL} = \frac{(NaP_2O_7^{3-})}{(Na^-)(P_2O_7^{4-})} = 10^{1.00} = 9.66$$

As shown in curve 4, Fig. 1, obtained in the presence of lithium ions, pH lowering occurred for n or "a" values less than 2 proving the presence of complexes of lithium ion with both P$_2$O$_7$$^{4-}$ and HP$_2$O$_7$$^{3-}$. Substituting the individual values for the apparent constant, K_3, and (Li$^+$) into eq. 5 yields the values of K_{LiHL} given in Table III for the reaction
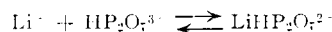
$$Li^- + HP_2O_7^{3-} \rightleftarrows LiHP_2O_7^{2-}$$

$$K_{LiHL} = \frac{(LiHP_2O_7^{2-})}{(Li^+)(HP_2O_7^{3-})} = 10^{1.03} = 6.86$$

TABLE III

| Metal ion	"a"	pH	C_L $\times 10^{3a}$	C_M $\times 10^{3a}$	log K^b
Potassium	0.50	8.71	27.16	109.9	0.78
	.50	8.87	19.87	20.01	.82
	.50	8.72	10.11	100.31	.80
				Av.	.80 ± 0.06
					log K_{NaL}
Sodium	0.50	8.87	2.175	16.20	0.98
	.50	8.84	2.200	28.80	1.02
	.50	8.80	2.180	36.38	0.99
				Av.	1.00 ± 0.06
					log K_{LiL}
Lithium	0.50	8.13	3.667	30.21	2.38
	.50	8.08	3.667	39.80	2.36
	.50	7.98	3.667	50.41	2.43
				Av.	2.39 ± 0.06
					log K_{LiHL}
	1.50	6.00	3.667	30.21	1.02
	1.50	5.97	3.667	39.80	1.00
	1.50	5.91	3.667	50.41	1.06
				Av.	1.03 ± 0.06

^{a} C_L is the total ligand, $P_2O_7^{4-}$, concentration while C_M is the total metal ion concentration. ^{b} Ionic strength adjusted to unity with $(CH_3)_4NCl$, 25°.

Substituting the values for the apparent acidity constant, K_4', the acidity constant, K_4, the metal concentration, (Li^+), and the above acid complex formation constants into eq. 4 yields the values of the formation constant given in the last column of Table III for the reaction

$$Li^+ + P_2O_7^{4-} \rightleftarrows LiP_2O_7^{3-}$$

$$K_{LiL} = \frac{(LiP_2O_7^{3-})}{(Li^+)(P_2O_7^{4-})} = 10^{2.39 \pm 0.06}$$
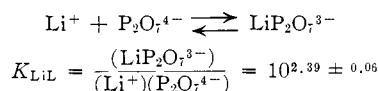
Regarding the structure of the complex, $MP_2O_7^{3-}$, the most pertinent information is the fact that no alkali metal complexes were obtained with orthophosphate ion even though the latter has a greater affinity than pyrophosphate ion for the first associated hydrogen ion. This eliminates the possibility that the metal ion is associated with one or two oxygen atoms of a single phosphorus atom in the pyrophosphate ion. It is possible that the metal ion is a member of a six-membered ring, structure I, which can be formed without strain. However, the bonding with the alkali metal ions is probably essentially electrostatic rather than covalent in nature so the exact position of the metal ion as a part of a chelate ring may be more a function of field strength than of bond direction. If this structure persists for the acidic complex $MHP_2O_7^{2-}$ which forms with lithium ion it seems probable that the hydrogen ion is bonded to one oxygen atom, structure II, possibly with some hydrogen bonding to the other available oxygen atom bonded with the same phosphorus atom, since two six-membered rings involving both phosphorus atoms cannot be formed without some strain. The possibility of strong bonding of a hydrogen ion to one or two oxygen atoms of a single phosphorus

atom is evident from the small second and third acidic dissociation constants of orthophosphoric acid.
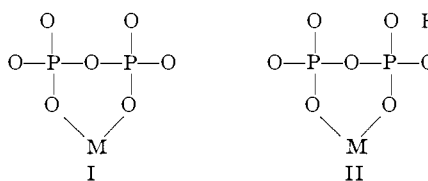
A comparison of the stabilities of the pyrophosphate and triphosphate complexes with alkali metals shown in Table IV is interesting. In gen-

TABLE IV

Metal ion	Ligand	log K^a
K^+	$P_2O_7^{4-}$	log K_{KPy} = 0.80 ± 0.06
K^+	$P_3O_{10}^{1-}$	log K_{KTp} = 1.37 ± 0.06
K^+	$HP_2O_7^{3-}$	Not detected
K^+	$HP_3O_{10}^{4-}$	Not detected
Na^+	$P_2O_7^{4-}$	log K_{NaPy} = 1.00 ± 0.06
Na^+	$P_3O_{10}^{5-}$	log K_{NaTp} = 1.64 ± .06
Na^+	$HP_2O_7^{3-}$	Not detected
Na^+	$HP_3O_{10}^{4-}$	log K_{NaHTp} = 0.77 ± 0.06
Li^+	$P_2O_7^{4-}$	log K_{LiPy} = 2.39 ± 0.06
Li^+	$P_3O_{10}^{5-}$	log K_{LiTp} = 2.87 ± .06
Li^+	$HP_2O_7^{3-}$	log K_{LiHPy} = 1.03 ± 0.06
Li^+	$HP_3O_{10}^{4-}$	log K_{LiHTp} = 1.88 ± .06

^{a} Complex formation constants were obtained at an ionic strength adjusted to unity with $(CH_3)_4NCl$, 25°. Pyrophosphate is designated by Py and triphosphate by Tp.

eral, the constants of the triphosphate complexes are $10^{0.56 \pm 0.1}$ larger than those of pyrophosphate. As suggested by Martell and Schwarzenbach[11] for the calcium complex this may be due to a tridentate structure involving two six-membered rings containing oxygens bound to all three phosphorus atoms. However, the following factors also may be responsible. The statistical probability of complex formation with triphosphate ion with one metal ion is greater by a factor of 2 if the metal ion enters at a chelating position or by a factor of 8/6 if the metal enters the complex at a single oxygen. Thus the statistical factor may account for $10^{0.3}$ or about half of the difference. Furthermore, the triphosphate ion has a total negative charge of 5 while pyrophosphate has a total negative charge of 4 which may be partially localized in the vicinity of the metal ion. Consequently there is a possibility that the structure of triphosphate complexes with alkali metals may be similar to those of pyrophosphate complexes.

The formation constants of the acidic complexes with either $HP_2O_7^{3-}$ or $HP_3O_{10}^{4-}$ are about $10^{1.2 \pm 0.2}$ smaller than those with hydrogen ion absent. This is consistent with our finding no detectable concentrations of the acid complexes of potassium with either $HP_2O_7^{3-}$ or $HP_3O_{10}^{4-}$ and sodium with $HP_2O_7^{3-}$ since their constants would probably be of the order of unity or smaller.

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