[CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Complexes of Triphosphate Ion with Alkali Metal Ions[1]

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The stabilities of the complexes of triphosphate ion with sodium, potassium and lithium ions have been calculated from the *p*H lowering during titrations of triphosphate ion with hydrogen ion. In one *M* tetramethylammonium chloride at 25°, formulas of the complexes and the values of their formation constant are: $KP_3O_{10}^{4-}$, $10^{1.39 \pm 0.06}$; $NaP_3O_{10}^{4-}$, $10^{1.64 \pm 0.06}$; $LiP_3O_{10}^{4-}$, $10^{2.87 \pm 0.06}$. Sodium and lithium ions also form acidic complexes with $HPO_3O_{10}^{4-}$, having the following formulas and values for their formation constants: $Na(HPO_3O_{10})^{3-}$, $10^{0.77 \pm 0.06}$; and $Li(HP_3O_{10})^{3-}$, $10^{0.88 \pm 0.06}$.

Introduction

Since Huber's[2] preparation and investigations, sodium triphosphate has become an important commercial product. Triphosphate ion forms complexes with most metal ions including those of the alkali group. As a consequence of the biological and commercial importance of triphosphates, several authors[3-5] have studied the lowering of *p*H of triphosphate buffers by the addition of alkali and particularly alkaline earth metal ions. In most of the studies the effect was ascribed to complex formation, but no quantitative evaluations of the stability constants were made. Recently, Martell and Schwarzenbach[6] have evaluated the stability constants of magnesium and calcium complexes with triphosphate by treating the data obtained in the titration of triphosphoric acid in a manner similar to that used in this study.

Schendewolf and Bonhoeffer[7] in a study of polyphosphates by membrane potentials observed that the order of increasing stability for the alkali metal complexes was $K^+ < Na^+ < Li^+$ and that the stability increased with polyphosphate chain length. On the basis of conductivity measurements Monk[8] obtained a value of $10^{2.5}$ for the first formation constant of the sodium complex. Van Wazer and Campanella[9] obtained a somewhat smaller complexity constant for sodium with several condensed polyphosphate glasses. They also investigated the complexes of other metal ions.

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 *p*H. 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,[6] $K_5'_{-n}$, for this stepwise addition of hydrogen ion as

$$K'_{5-n} = \frac{[H^+]\,\Sigma\, q(M_m(H_nP_3O_{10})_q{}^{(5q-nq-m)-})}{\Sigma q(M_m(H_{n+1}P_3O_{10})_q{}^{(4q-nq-m)-})} \qquad (1)$$

where *m*, *n* and *q* indicate the number of metal, hydrogen and triphosphate ions in any particular species. In this paper parentheses indicate concentrations and brackets indicate activities. *n* has a single value from zero to five 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 triphosphate ion and the corresponding acidity constant are

$$H^+ + H_nP_3O_{10}{}^{(5-n)-} \rightleftharpoons H_{n+1}P_3O_{10}{}^{(4-n)-} \qquad (2)$$

$$K_{5-n} = \frac{[H^+](H_nP_3O_{10}{}^{(5-n)-})}{(H_{n+1}\ P_3O_{10}{}^{(4-n)-})}$$

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

$$mM^+ + qH_nP_3O_{10}{}^{q(5-n)-} \rightleftharpoons M_m(H_nP_3O_{10})_q{}^{(5q-nq-m)-} \qquad (3)$$

$$\beta_{M_mH_nL_q} = \frac{(M_m(H_nP_3O_{10})_q{}^{(5q-nq-m)-})}{(M^+)^m(H_nP_3O_{10}{}^{(5-n)-})^q}$$

where the subscript L indicates the ligand $P_3O_{10}{}^{5-}$.

The calculations are further simplified if the maximum values of *m* and *q* are unity. This assumption can be tested by calculations based on varied concentrations and ratios of metal ion and triphosphate ion. In this case eq. 3 reduces to

$$M^+ + H_nP_3O_{10}{}^{(5-n)-} \rightleftharpoons MH_nP_3O_{10}{}^{(4-n)-} \qquad (4)$$

$$K_{MH_nL} = \frac{(MH_nP_3O_{10}{}^{(4-n)-})}{(M^+)(H_nP_3O_{10}{}^{(5-n)-})}$$

A high concentration of an essentially non-complexing electrolyte such as tetramethylammonium chloride and relatively low concentrations of metal ion and triphosphate ion are used in order to minimize the effect of the varied concentrations of the reacting species on the various activity coefficients. Under these conditions a lowering of the *p*H in the titration curve indicates complex formation since the presence of metal ion in an acid enhances its acidity. In regions where no *p*H lowering occurs, one may conclude that complex formation does not occur to an appreciable extent. Since no *p*H lowering occurred in the triphosphate curves for *n* values larger than 2, when the concentrations of the reactants were relatively small

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(1) Presented before the Division of Physical and Inorganic Chemistry, 131st Meeting of the American Chemical Society, Miami, Florida, 1957.

(2) H. Huber, *Angew. Chem.*, **50**, 323 (1937).

(3) L. Frankenthal, THIS JOURNAL, **66**, 2124 (1944).

(4) H. Rudy, *Angew. Chem.*, **54**, 447 (1941).

(5) M. Bobtelsky and S. Kertes, *J. Appl. Chem.* (*London*), **4**, 419 (1954).

(6) A. E. Martell and G. Schwarzenbach, *Helv. Chim. Acta*, **39**, 653 (1956).

(7) U. Schendewolf and K. F. Bonhoeffer, *Z. Elektrochem.*, **57**, 216 (1953).

(8) C. B. Monk, *J. Chem. Soc.*, 427 (1949).

(9) J. R. Van Wazer and D. Campanella, THIS JOURNAL, **72**, 655 (1950).

the following equations were derived by substituting equations having the forms of (2) and (3) into (1) with m and q equal to unity in the metal complex.

$$K'_4 = \frac{[\mathrm{H^+}][(\mathrm{HP_3O_{10}{}^{4-}}) + (\mathrm{MHP_3O_{10}{}^{3-}})]}{(\mathrm{H_2P_3O_{10}{}^{3-}})} = K_4 + K_{\mathrm{MHL}}K_4(\mathrm{M^+}) \quad (5)$$

$$K'_5 = \frac{[\mathrm{H^+}][(\mathrm{P_3O_{10}{}^{5-}}) + (\mathrm{MP_3O_{10}{}^{4-}})]}{(\mathrm{HP_3O_{10}{}^{4-}}) + (\mathrm{MHP_3O_{10}{}^{3-}})} = \frac{K_5 + K_{\mathrm{ML}}K_5(\mathrm{M^+})}{1 + K_{\mathrm{MHL}}(\mathrm{M^+})} \quad (6)$$

K_4 and K_5 are the acidity constants of triphosphoric acid, while K_{ML} and K_{MHL} are the formation constants of the form in eq. 4 for the complexes $\mathrm{M(P_3O_{10})^{4-}}$ and $\mathrm{M(HP_3O_{10})^{3-}}$.

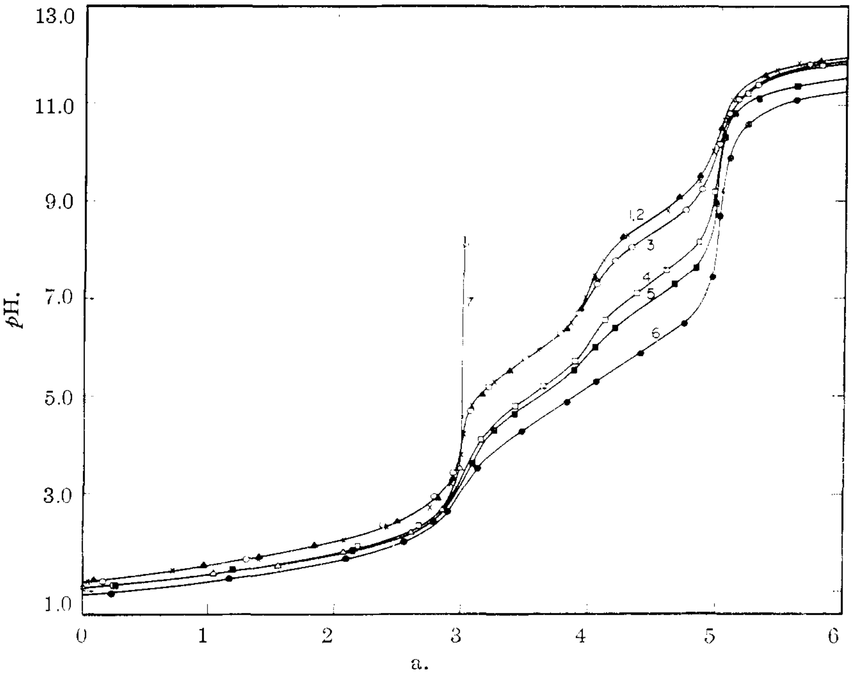

Fig. 1.—A comparison of the effects of potassium, sodium and lithium ions on titration curves of triphosphoric acid with tetramethylammonium hydroxide: curve 1, 0.0393 M $\mathrm{H_5P_3O_{10}}$ titrated with 0.1326 N $\mathrm{(CH_3)_4NOH}$; curve 2, 0.0396 M $\mathrm{H_5P_3O_{10}}$ with 0.0868 N $\mathrm{(CH_3)_4NOH}$, $\mu = 1.0$ M with $\mathrm{(CH_3)_4NCl}$; curve 3, 0.0399 M $\mathrm{H_5P_3O_{10}}$ with 0.1108 N KOH; curve 4, 0.0396 M $\mathrm{H_5P_3O_{10}}$ with 0.0961 N KOH, $\mu = 1.0$ M with $\mathrm{KNO_3}$; curve 5, 0.0379 M $\mathrm{H_5P_3O_{10}}$ with 0.1194 N NaOH, $\mu = 1.0$ M with $\mathrm{NaNO_3}$; curve 6, 0.0415 M $\mathrm{H_5P_3O_{10}}$ with 0.0960 N KOH, $\mu = 1.0$ M with $\mathrm{LiNO_3}$; curve 7, 0.1162 M HCl with 0.1004 N $\mathrm{(CH_3)_4NOH}$, $\mu = 1.0$ M with $\mathrm{(CH_3)_4NCl}$.

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. The apparent constants can be calculated by the following form of eq. 1 for the titration of the triphosphate ion with hydrogen ion

$$K'_{5-n} = \frac{[\mathrm{H^+}][(n + 1 - a)C_\mathrm{p} - K_\mathrm{w}/[\mathrm{H^+}]f + [\mathrm{H^+}]/f]}{(a - n)C_\mathrm{p} + K_\mathrm{w}/[\mathrm{H^+}]f - [\mathrm{H^+}]/f} \quad (7)$$

where "a" is the number of moles of hydrogen added per mole of triphosphate ion present in any form. The symbol f indicates the activity coefficient of a univalent ion. If the acid is not too dilute pK'_{5-n} has the same value as the pH at $a = n + {}^1/_2$.

Experimental

The sodium triphosphate, tetramethylammonium chloride and tetramethylammonium hydroxide were prepared according to a procedure described in a previous paper.[10] Carbonate-free potassium and sodium hydroxide solutions were prepared from Baker Analyzed pellets and stored in paraffin-lined bottles. All water used in preparing solutions and washing the columns was demineralized, doubly distilled, and purged with nitrogen to remove the dissolved carbon dioxide. Mallinckrodt reagent grade salts were used.

The potassium and lithium triphosphate solutions were prepared by passing a 0.03 M solution of the recrystallized sodium salt[10] through a 90 cm. by 2 cm. column filled to a height of 50 cm. with Dowex 50-x12 cation-exchange resin, 100–200 mesh, low porosity, supported on a Pyrex glass wool plug. The resin was in the potassium or lithium form, depending upon the triphosphate salt desired. The column was fitted with a Pyrex water jacket, 4 cm. in diameter, through which ice-water was circulated constantly. The column resembled a Liebig condenser, differing in that it had a stopcock on the lower end and a rubber stopper fitted with an ascarite bulb and a tube to facilitate the entry of nitrogen at the top. The eluted solution was warmed to 25 ± 0.1°, diluted to the desired concentration and immediately titrated with standardized hydrochloric acid containing the same concentration of triphosphate as the solution titrated. The inclusion of the triphosphate in both solutions eliminated the dilution of the triphosphate during the titration.

In order to prevent any hydrogen ion leakage, the resin which was originally in the acidic form was charged with potassium or lithium ions by passing through it a 10% solution of KCl or LiCl containing enough KOH or LiOH to make the solution slightly basic. Then a 15% solution of KCl or LiCl was passed through the column which was finally rinsed with water. The titrations were performed in a stoppered Berzelius beaker, placed in a water thermostat at 25 ± 0.1°, with a stream of nitrogen flowing over the solution. pH measurements were made with the Beckman model G pH meter with the Beckman All Purpose Glass electrode and the Beckman reference electrode inserted directly in the solution.

Results and Discussion

Figure 1 illustrates the pH lowering effect due to the presence of large concentrations of sodium, potassium and lithium nitrate in the titration of approximately 0.04 M $\mathrm{H_5P_3O_{10}}$ with approximately 0.1 N $\mathrm{(CH_3)_4NOH}$. Curve 1 was obtained in the absence of extraneous electrolytes while curves 2 and 3 were obtained with sufficient $\mathrm{(CH_3)_4NCl}$ to produce an ionic strength of 1.0. Curve 3 was obtained for the titration of 10 ml. of 0.0339 M triphosphoric acid with 0.1108 N potassium hydroxide. At "a" values below 4 this curve coincides with curve 1 for the titration using tetramethyl-

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[10] J. I. Watters, E. D. Loughran and S. M. Lambert, THIS JOURNAL, **78**, 4855 (1956).

ammonium hydroxide in the absence of metal ions. Above this "a" value the pH is lower, indicating the presence of a complex ion since any activity coefficient effect should have appeared at lower "a" values also. Curves 4, 5 and 6 illustrate the effect of one M potassium, sodium and lithium nitrate on the titration curve for triphosphoric acid. At "a" values below 3 there is a small pH decrease due to the different effects of the various alkali salts on the activity coefficients. At "a" values above 3 the pH drop is much larger due to complex formation. The increasing complex stability in the order $K^+ < Na^+ < Li^+$ is quite evident from curves 4, 5 and 6 of Fig. 1. The necessity of using a constant large concentration of a non-complexing electrolyte and relatively low concentrations of complexing species is evident from these curves for there is a pH lowering when the mean number of bound hydrogen ions exceeds 2 where no complex formation occurs. This conclusion was based on results such as those in Fig. 2. The effect did not occur for $n > 2$ with lower total concentrations but the same ratios of triphosphate and metal ion with sufficient tetramethylammonium chloride present to adjust the ionic strength to unity.

Curve 1, Fig. 2, was obtained for the titration of 0.00919 M $((CH_3)_4N)_5P_3O_{10}$ with a solution containing 0.0543 M HCl and exactly the same concentration of $H_5P_3O_{10}$ as the solution titrated. Curves 2, 3, 4 and 5 were obtained in titrations of solutions containing approximately 0.01 M $Na_5P_3O_{10}$ and different concentrations of NaCl. The acid solution contained approximately 0.05 M HCl and the same concentrations of NaCl and triphosphate as the solution titrated. Since no complex formation was observed between any of the metal ions and triphosphate ions containing two or more hydrogen ions, eq. 5, 6 and 7 were sufficient to calculate the formation constants. The data and results are given in Table I.

TABLE I

DATA AND RESULTS FOR THE TITRATION OF TRIPHOSPHATE ION WITH HYDROGEN ION IN THE PRESENCE OF VARIOUS ALKALI METAL IONS

The heading "a" is the number of moles of hydrogen ion added per mole of triphosphate ion, $C_L \times 10^3$ is the total triphosphate concentration and $C_M \times 10^3$ is the total concentration of metal ion. The ionic strength was adjusted to unity with $(CH_3)_4NCl$, 25°.

Metal ion	"a"	pH	$C_L \times 10^3$	$C_M \times 10^3$	log K
					log K_{KL}
Potassium	0.50	8.69	2.274	13.87	1.43
	.50	8.61	2.274	28.87	1.36
	.50	8.52	2.274	33.87	1.38
	.50	8.45	2.274	58.87	1.38
				Av.	1.39 ± 0.06
					log K_{NaL}
Sodium	0.50	8.51	10.20	51.00	1.65
	.50	8.30	9.940	99.70	1.64
	.50	8.75	1.040	5.20	1.66
	.50	8.46	2.500	50.00	1.62
				Av.	1.64 ± 0.06
					log K_{NaHL}
	1.50	5.72	10.20	51.00	0.76
	1.50	5.63	9.970	99.90	.77
	1.50	5.42	10.10	250.0	.78
				Av.	.77 ± 0.06
					log K_{LiL}
Lithium	0.50	8.01	3.208	31.04	2.84
	.50	8.24	2.623	13.12	2.84
	.50	8.01	2.223	28.12	2.86
	.50	7.89	3.208	46.04	2.90
	.50	7.87	2.623	42.12	2.89
				Av.	2.87 ± 0.06
					log K_{LiHL}
	1.50	5.29	3.208	31.04	1.90
	1.50	5.19	3.208	46.04	1.87
	1.50	5.13	3.208	61.04	1.86
				Av.	1.88 ± 0.06

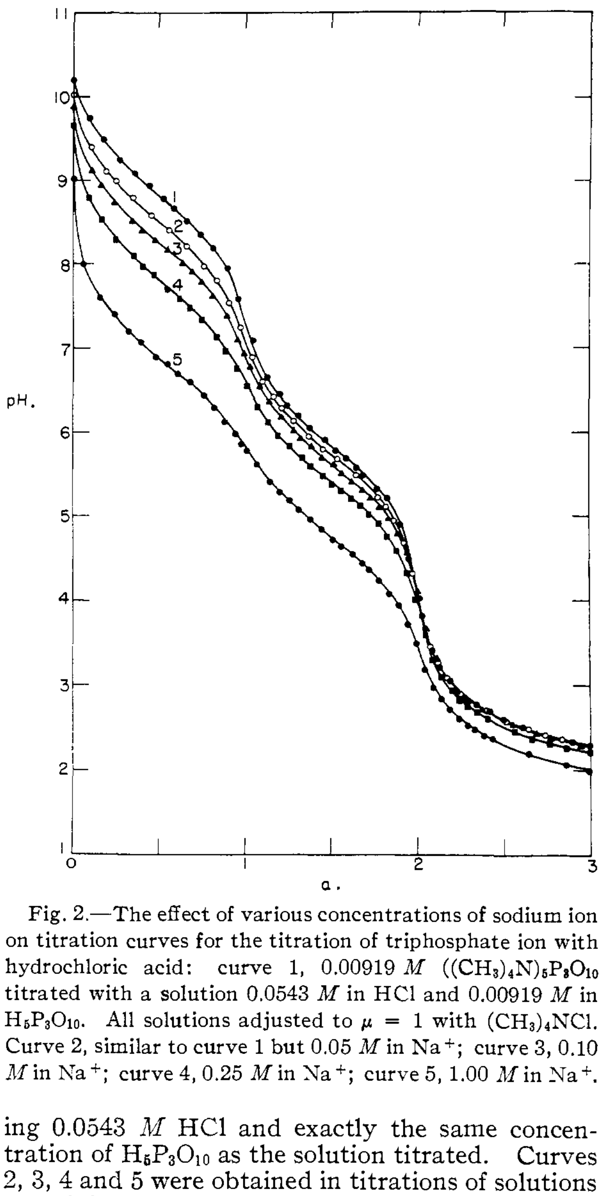


Fig. 2.—The effect of various concentrations of sodium ion on titration curves for the titration of triphosphate ion with hydrochloric acid: curve 1, 0.00919 M $((CH_3)_4N)_5P_3O_{10}$ titrated with a solution 0.0543 M in HCl and 0.00919 M in $H_5P_3O_{10}$. All solutions adjusted to $\mu = 1$ with $(CH_3)_4NCl$. Curve 2, similar to curve 1 but 0.05 M in Na^+; curve 3, 0.10 M in Na^+; curve 4, 0.25 M in Na^+; curve 5, 1.00 M in Na^+.

In the presence of potassium ion a lowering of the pH occurred only for "a" values less than unity proving the absence of detectable concentrations of potassium hydrogen triphosphate complexes, so eq. 6 reduced to the form

$$K'_5 = K_5 + K_{KL}K_5(K^+) \qquad (8)$$

The apparent constant, K'_5, is equal to the pH at the corresponding "a" value of $^1/_2$. The values for the acidity constants of triphosphoric acid in 1 M $(CH_3)_4NCl$ at 25° taken from the previous paper were $10^{-5.83}$ for K_4 and $10^{-8.81}$ for K_5. The total concentration of potassium ion was first used for the value of the free potassium ion. After obtaining preliminary formation constants a correction was applied for metal ion bound in the complex. Substituting these values in eq. 6 yields the formation constant, K_{KL}, for the reaction

$$K^+ + \mathrm{P_3O_{10}}^{5-} \rightleftarrows \mathrm{KP_3O_{10}}^{4-}$$

$$K_{\mathrm{KL}} = \frac{(\mathrm{KP_3O_{10}}^{4-})}{(K^+)(\mathrm{P_3O_{10}}^{5-})} = 10^{1.39 \pm 0.06}$$

In the presence of sodium or lithium ions pH lowering occurred for n or "a" values less than 2 for all of the solutions. In the presence of 0.25 M and 1.00 M salt some pH lowering occurred for larger "a" values as shown in curves 4 and 5, Fig. 2. This lowering of pH at larger "a" values is due to the activity effect resulting from the relatively large amount of sodium or lithium ion present. Consequently all calculations were based on relatively low concentrations of reacting species.

Substituting the individual values for the apparent constant, K'_4, the acidity constant, K_4, and (M^+) into eq. 5 yields the values of K_{LiHL} and K_{NaHL} given in the last column of Table I for the reactions

$$\mathrm{Na}^+ + \mathrm{HP_3O_{10}}^{4-} \rightleftarrows \mathrm{NaHP_3O_{10}}^{3-}$$

$$K_{\mathrm{NaHL}} = \frac{(\mathrm{NaHP_3O_{10}}^{3-})}{(\mathrm{Na}^+)(\mathrm{HP_3O_{10}}^{4-})} = 10^{0.77 \pm 0.06}$$

$$\mathrm{Li}^+ + \mathrm{HP_3O_{10}}^{4-} \rightleftarrows \mathrm{LiHP_3O_{10}}^{3-}$$

$$K_{\mathrm{LiHL}} = \frac{(\mathrm{LiHP_3O_{10}}^{3-})}{(\mathrm{Li}^+)(\mathrm{HP_3O_{10}}^{4-})} = 10^{1.88 \pm 0.06}$$

Substituting the values for the apparent acidity constant, K'_5, the acidity constant, K_5, the metal concentration, (M^+), and the above metal–hydrogen formation constants into eq. 6 yields the values of the metal formation constant given in the last column of Table I for the reactions

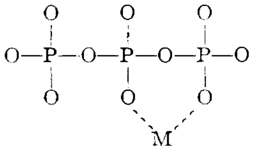
$$\mathrm{Na}^+ + \mathrm{P_3O_{10}}^{5-} \rightleftarrows \mathrm{NaP_3O_{10}}^{4-}$$

$$K_{\mathrm{NaL}} = \frac{(\mathrm{NaP_3O_{10}}^{4-})}{(\mathrm{Na}^+)(\mathrm{P_3O_{10}}^{5-})} = 10^{1.64 \pm 0.06}$$

$$\mathrm{Li}^+ + \mathrm{P_3O_{10}}^{5-} \rightleftarrows \mathrm{LiP_3O_{10}}^{4-}$$

$$K_{\mathrm{LiL}} = \frac{(\mathrm{LiP_3O_{10}}^{4-})}{(\mathrm{Li}^+)(\mathrm{P_3O_{10}}^{5-})} = 10^{2.87 \pm 0.06}$$

These results establish moderately stable complex formation between triphosphate ion and these alkali metals which should be considered in calculating the stabilities of other complexes of triphosphate ions. It is probable that the metal ions are members of at least one chelate ring containing two phosphorus and three oxygen atoms, structure I, as suggested by Kolthoff and Watters[11] for the manganese(III) complex with pyrophosphate and by Van Wazer[9] and his co-workers for complexes of higher phosphates since no complexes were observed in similar experiments with orthophosphate. In these structures the three resonating double bonds and the ionic charges are omitted. It is possible that, in the acidic complexes, the hydrogen ion is bound in the same way. However, the strong bonding of the last hydrogen ion in phosphoric acid relative to its bonding in higher phosphates indicates that the hydrogen ion may be bonded to a single phosphate tetrahedron as shown in structure II. In the next paper of this series it will be shown that the acid triphosphate complexes of lithium are slightly less acidic than the acidic pyrophosphate complexes. This evidence supports a structure for the acidic complex in which the metal ion is not bonded to the same phosphate tetrahedron as the hydrogen ion. Accordingly, structure II seems feasible for the acidic complex. Hydrogen bonding in the same or adjacent tetrahedron probably occurs. Martell and Schwarzenbach[6] have proposed that the triphosphate ion may be tridentate, structures III and IV, in the corresponding complexes with calcium and magnesium. Their structure III for triphosphate is supported by similar experiments with pyrophosphate. These studies indicate that the pyrophosphate complexes with the alkali metals are somewhat less stable than the triphosphate complexes. Hirshfelder–Taylor models indicate that bonding of the metal ion to the two terminal phosphate tetrahedra and to the center tetrahedron as well can occur without strain. However, the bonding with alkali metals is probably essentially electrostatic rather than covalent in nature so the exact position of the metal ion as part of any particular chelate ring may be more a function of field strength than of bonding direction. On this basis it is probable that neither structure I or III uniquely describes the actual situation.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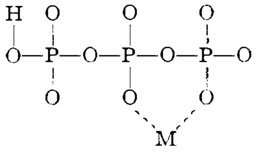
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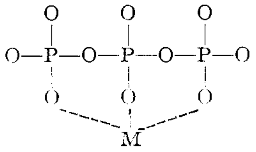
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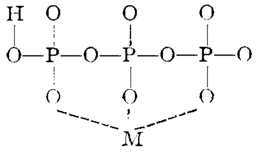
IV

The last four acidity constants of triphosphoric acid and the four acidity constants of ethylenediaminetetraacetic acid are somewhat similar. It is of interest that this similarity persists in the sodium and lithium complexes of these ligands.

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