$$\mathrm{CuCNS\ (adsorbed)} \rightleftarrows \mathrm{Cu^+ + CNS^-} \quad (12)$$

Then the concentration of cuprous ions at the electrode surface is given by

$$[\mathrm{Cu^+}]^0 = \frac{Ka_{\mathrm{ad}}}{[\mathrm{CNS^-}]f_{\mathrm{Cu^+}}f_{\mathrm{CNS^-}}} \quad (13)$$

where K and a_{ad} are, respectively, the dissociation constant and the activity of adsorbed cuprous thiocyanate. Relations 4 and 5 should be valid both on the second and the third waves, and hence from 4, 5 and 13 we obtain

$$E = E^0 - \frac{RT}{F}\ln\frac{f_{\mathrm{a}}f_{\mathrm{CNS^-}}}{a_{\mathrm{Hg}}k_{\mathrm{a}}Ka_{\mathrm{ad}}} - \frac{RT}{F}\ln\left(i - \frac{i_{\mathrm{d}}}{2}\right) - \frac{RT}{F}\ln\,[\mathrm{CNS^-}] \quad (14)$$

In this expression a_{ad} varies with potential along the third wave. Therefore, the third wave cannot be analyzed simply by plotting E *vs.* $\log[i - (i_{\mathrm{d}}/2)]$.

At the half-wave potential, however, a_{ad} should be constant and independent of copper(II) concentration, corresponding to a half coverage of the mercury surface. The current at the half-wave potential $(E_{1/2})_{\mathrm{III}}$ is given by

$$i = i_{\mathrm{d}} - (i_{\mathrm{a}}/2) \quad (15)$$

From 14 and 15 we obtain

$$(E_{1/2})_{\mathrm{III}} = E_{\mathrm{III}}'' - \frac{RT}{F}\ln\,(i_{\mathrm{d}} - i_{\mathrm{a}}) - \frac{RT}{F}\ln\,[\mathrm{CNS^-}] \quad (16)$$

where

$$E_{\mathrm{III}}'' = E^0 - \frac{RT}{F}\ln\frac{f_{\mathrm{a}}f_{\mathrm{CNS^-}}}{2a_{\mathrm{Hg}}k_{\mathrm{a}}Ka_{\mathrm{ad}}} = \mathrm{Constant} \quad (17)$$

The shift of half-wave potential of the third wave with i_{d} and hence with copper concentration is then given by

$$\Delta(E_{1/2})_{\mathrm{III}} = -0.059\,\Delta\log(i_{\mathrm{d}} - i_{\mathrm{a}}) \quad (18)$$

Observed and calculated values of $\Delta(E_{1/2})_{\mathrm{III}}$ are compared in Table III. The agreement was only approximate. It is predicted from eq. 16 that the half-wave potential of the third wave should be shifted by 0.059 volt in the negative direction with a tenfold increase in thiocyanate concentration. The half-wave potentials of the third waves observed with 10^{-3} M copper(II) in 0.01 and 0.1 M potassium thiocyanate were −0.485 and −0.540 volt, respectively. The difference of 0.055 volt is in satisfactory agreement with the theoretical value.

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND]

The Acidity and Complexes of Peroxydiphosphoric Acid[1]

BY MARVIN M. CRUTCHFIELD[2] AND JOHN O. EDWARDS

RECEIVED DECEMBER 4, 1959

The third and fourth acid dissociation constants of peroxydiphosphoric acid were measured at 25° by *p*H titrations of the tetramethylammonium salt with hydrochloric acid at a series of ionic strengths. Extrapolation to infinite dilution yielded the values $K_3 = 6.6 \pm 0.3 \times 10^{-6}$ and $K_4 = 2.1 \pm 0.1 \times 10^{-8}$. Approximate values for the first and second acid dissociation constants, which could not be obtained from the *p*H titration, were estimated from the trend observed in other tetravalent acids of similar structure to be $K_1 \simeq 2$ and $K_2 \simeq 3 \times 10^{-1}$. Formation constants for complex ions of peroxydiphosphate ion and the cations—$\mathrm{Li^+}$, $\mathrm{Na^+}$, $\mathrm{K^+}$ and $\mathrm{Mg^{+2}}$—were measured at 25° and unit ionic strength by the *p*H lowering technique and compared with known constants for pyrophosphate. Structural implications are discussed.

Introduction

Although peroxydiphosphoric acid, $\mathrm{H_4P_2O_8}$, and its salts have been known for many years,[3] they have received little attention compared with other oxyacids of phosphorus and with the peroxyacids of other elements, such as sulfur. The present investigation of the acid dissociation constants of $\mathrm{H_4P_2O_8}$ was carried out as part of a general study of the aqueous chemistry of this acid and its salts.[1] During the course of the measurements, it was found that aqueous peroxydiphosphate ion forms complex ions with alkali metal cations similar to those which have been reported for pyrophosphate.[4] It was, therefore, necessary to carry out the measurement of the acid dissociation constants in the absence of alkali metal ions. The tetramethylammonium salt was employed, and negligible complexing was assumed for this large cation.

Peroxydiphosphate ion, $\mathrm{P_2O_8^{-4}}$, is quite stable in neutral or basic solution at room temperature but undergoes rapid hydrolysis to form peroxymonophosphoric acid in acidic solution

$$\mathrm{H_4P_2O_8 + H_2O \longrightarrow H_3PO_5 + H_3PO_4}$$

The titrations were, therefore, carried out by adding acid to the salt form in order to minimize the hydrolysis.

Experimental

Impure $\mathrm{K_4P_2O_8}$ was prepared electrolytically by the method of Fichter and Gutzwiller[5] and purified by conversion to crystalline $\mathrm{Li_4P_2O_8 \cdot 4H_2O}$ according to the procedure of Chulski.[6] After two recrystallizations from water–methanol, a product was obtained which was 99.5% pure, as determined by iodometric titration for total active oxygen and by gravimetric determination of total phosphorus by precipitation of phosphate with magnesia mixture. The lithium peroxydiphosphate was converted to the tetramethylammonium salt by ion exchange using a column containing a ten-fold excess of Dowex 50-x4, 100–200 mesh cation exchange resin. The ion exchange procedure was shown in separate experiments to result in no measurable decomposition of the peroxide. The tetramethylammonium chloride used to charge the column and to adjust the ionic strength during the titrations was either the East-

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[1] Abstracted from the Ph.D. Thesis submitted by M. M. C. at Brown University, 1960. Presented in part before the Division of Physical Chemistry at the 135th American Chemical Society Meeting, Boston, Mass., April, 1959.

[2] Monsanto Fellow 1958–1959.

[3] J. Schmidlin and P. Massini, *Ber.*, **43**, 1162 (1910).

[4] S. M. Lambert and J. I. Watters, THIS JOURNAL, **79**, 4262, 5606 (1957).

[5] F. Fichter and G. Gutzwiller, *Helv. Chim. Acta*, **11**, 323 (1928).

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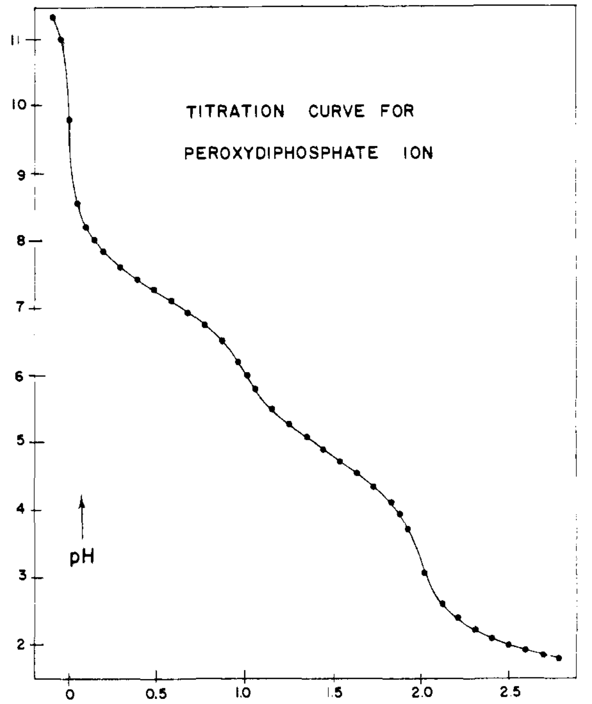


Fig. 1.—Titration of 100 ml. of 0.02919 *M* tetramethylammonium peroxydiphosphate with 2.868 *M* hydrochloric acid. Tetramethylammonium hydroxide (0.287 meq.) initially present to accentuate the beginning of buffering action by peroxydiphosphate.

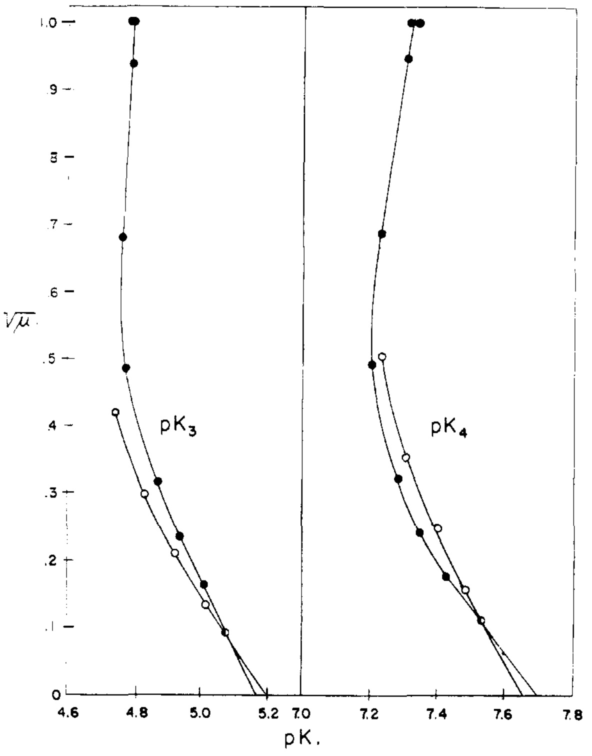


Fig. 2.—*pK* values for third and fourth ionizations of peroxydiphosphoric acid as a function of ionic strength.

man or the Matheson, Coleman and Bell $99^+\%$ product which had been further purified by recrystallization from methanol–acetone solution.

Fifty ml. portions of 0.075 M $Li_4P_2O_8$ were passed through the column, followed by sufficient water to make a total volume of 125.0 ml. Flame tests on the eluate showed that Li^+ was quantitatively removed. Aliquots of these solutions were taken for standardization and titration. Determination of peroxydiphosphate concentration by iodometric titration was impossible in the presence of tetramethylammonium ion. Instead, addition of excess ferrous sulfate, and then back titration with standard ceric sulfate was employed. The tetramethylammonium chloride solutions used to adjust the ionic strength and also the solutions of added metal chlorides were standardized by titration with silver nitrate solution, using dichlorofluorescein indicator.

In each potentiometric titration the initial volume of solution was 100.0 ml. Standard hydrochloric acid was added from a five ml. microburet and the resulting small change in volume was taken into account in the calculation of ionic strength. The titrations were performed under a stream of saturated nitrogen gas in a cell thermostated at 25.00 ± 0.05°. A magnetic stirrer provided efficient mixing. The measurements were made with a Beckman model G *p*H meter and the Beckman All-Purpose Glass and calomel reference electrodes. The meter was standardized before every titration using standard Beckman buffer solutions.

All other chemicals employed were of reagent grade and were used without further purification. All water used in the recrystallizations and in preparing solutions was laboratory distilled and further purified by passing through a mixed-bed ion exchange column of Amberlite MB-1.

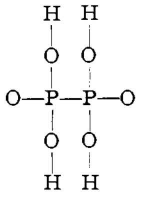
Results and Discussion

Acid Dissociation Constants.—Stepwise titration curves were obtained with definite end points corresponding to the addition of two hydrogen ions to the peroxydiphosphate ion. A sample titration curve is shown in Fig. 1. Values for pK_3 and pK_4 were calculated from these curves using the method of Lambert and Watters.[4] The first and second dissociations, corresponding to pK_1 and pK_2, were so strong that inflection points were not observed. In addition, hydrolysis to peroxymonophosphate and oxidation of the chloride ion by the peroxydiphosphate began to interfere at low *p*H so that only rough estimates for pK_1 and pK_2 could be made.

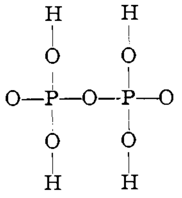
Plots of the measured *pK* values *vs.* the square root of ionic strength are presented in Fig. 2. The two curves in each case represent different methods of adjusting the ionic strength. In the curve drawn through the shaded circles, the same concentrations of peroxydiphosphate and hydrochloric acid were used for every titration, while each time the concentration of added tetramethylammonium chloride was increased. In the second method, represented by the open circles, no tetramethylammonium chloride was added. Instead, the concentrations of tetramethylammonium peroxydiphosphate and hydrochloric acid were increased with each titration, the total ionic strength being calculated on the basis of the theoretical ionic charges of the various species present. With both methods the extrapolation approaches a straight line at low concentrations. The limiting slopes of the two lines for a given *pK* extrapolation are different, but the intercepts at infinite dilution correspond to the same average values of $pK_4 = 7.67$ and $pK_3 = 5.18$ within the experimental error of the *p*H measurements, ±0.02 *p*H unit. It is unknown whether the difference in slopes is due to a slight tendency toward complexing between the peroxydiphosphate and the excess tetramethylammonium ion, despite its large size, or to the uncertain effect of the large ionic charges in calculating the ionic strength of the peroxydiphosphate solutions, or to both.

If one compares the observed limiting slopes with those predicted by Debye–Hückel theory, it is seen that the absolute value of the observed slopes is high. This suggests that the observed *pK* values at infinite dilution may be only lower limits and that the true *pK* values are somewhat higher. On the other hand, the method used in this study is identical in all essential respects to that employed by Lambert and Watters[4] to measure the *pK* values for pyrophosphoric acid, and their extrapolations agree quite well with other values for that acid obtained by conductance measurements in very dilute solutions.[7] It would seem, therefore, that the *pK* values obtained by extrapolation in this study are as accurate as those obtainable for tetravalent acids by other methods.

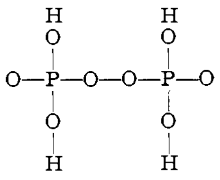
Relation Between Acidity and Structure.—It is informative to consider the *pK* values for peroxydiphosphoric acid in relation to the structure of the acid and to compare it with other acids of similar structure and known dissociation constants. Consider the following series of acids, whose structures are indicated



Hypophosphoric



Pyrophosphoric



Peroxydiphosphoric

The first two structures have been definitely established by physical methods. The structure of peroxydiphosphoric acid is that generally accepted on the basis of its chemical similarity to the persulfates. The evidence has been summarized by Van Wazer.[8] These acids differ, as one proceeds down the list, by an additional one-half oxygen per phosphorus atom. One might qualitatively expect increasing acid strength in the order—hypophosphoric, pyrophosphoric, peroxydiphosphoric acid. The electronegativity of additional oxygens should facilitate the removal of hydrogen ions by decreasing the electron density at the hydrogen atoms. In addition, the inductive effect[9] due to intramolecular charges should decrease as the separation between central atoms increases.

Such a trend in acidities is indeed observed upon comparison of known values for the dissociation constants of these acids. This is represented in Fig. 3. The *pK* values for pyrophosphoric acid are averages of values obtained by several workers.[4,7,10,11] The values for hypophosphoric acid were measured by Treadwell and Schwarzenbach.[12] Since the values for their constants were taken from a titration curve at finite ionic strength, the actual *pK* values may be as much as one-half *p*H unit higher than their reported values. This is indicated in Fig. 3 by arrows pointing in the proper direction. The data for peroxydiphosphoric acid are taken from the present study. The lines are arbitrary lines of identical slope. The closeness of fit of the data for pK_3 and pK_4 shows that to a first approximation this linear relationship is valid. From this plot rough values for K_1 and K_2 for peroxydiphosphoric acid can be estimated, even though they could not be measured from the *p*H titrations. The values $K_1 \simeq 2$ and $K_2 \simeq 0.3$ are thus obtained. These values cannot be exact, since the inductive effect due to ionic charges must depend on the charge separation in a manner for which it is difficult to account accurately. Nevertheless, they are the best estimates available in the absence of other data.

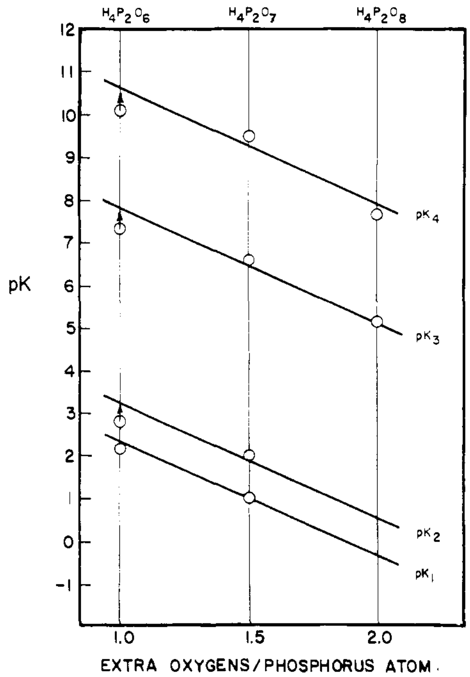


Fig. 3.—The effect of structure on acidity of three related phosphorus acids.

The ratio K_1/K_2 can be shown by statistical considerations to approach the value 4 as a limit as the separation between the acidic groups is increased to the point where intramolecular interaction is negligible.[13,14] The value of this ratio for peroxydiphosphoric acid, therefore, would be expected to fall somewhere between the theoretical limit and the value of 10 to 15 observed for pyrophosphoric acid. For the estimated values of K_1 and K_2, this ratio is approximately 7.

A summary of the dissociation constants for peroxydiphosphoric acid arrived at in this study is given: $K_1 \simeq 2$, $K_2 \simeq 3 \times 10^{-1}$, $K_3 = 6.6 \times 10^{-6}$ and $K_4 = 2.1 \times 10^{-8}$.

Metal Ion Complexes with Peroxydiphosphate.—Examples of the *p*H shift in the titration curves due to the presence of added metal ions are shown

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TABLE I

FORMATION CONSTANTS FOR PEROXYDIPHOSPHATE COMPLEX IONS AT 25°[a]

Complex	"a"	PK'	$C_P \times 10^1$	$C_M \times 10^3$	$K_{M_mH_nP}$	Log formation constant Peroxyphosphate	Log formation constant Pyrophosphate[b]
None	0.50	7.33	1.444	0	..	..	..
None	1.50	4.79	1.430	0	..	..	..
KP	0.50	7.21	1.444	29.93	10.6		
KP	.50	7.14	1.444	59.86	10.7		
KP	.50	7.06	1.444	89.79	9.7		
				Av.	10.3	1.01 ± 0.09	0.80 ± 0.06
KHP	1.50	No detectable complexing					
NaP	0.50	7.22	1.444	30.26	12.3		
NaP	.50	7.25	1.444	36.04	8.0		
NaP	.50	7.16	1.444	66.30	11.2		
				Av.	10.5	1.02	1.00
NaHP	1.50	4.77	1.430	29.97	1.7		
NaHP	1.50	4.77	1.430	35.69	1.4		
NaHP	1.50	4.73	1.430	65.66	2.3		
				Av.	1.8	0.25	..
LiP	0.50	7.31	1.444	5.776	20		
LiP	.50	7.16	1.444	34.17	22		
LiP	.50	6.98	1.444	73.45	25		
				Av.	22	1.34	2.39
LiHP	1.50	4.77	1.430	5.720	10		
LiHP	1.50	4.74	1.430	33.83	4		
LiHP	1.50	4.72	1.430	72.75	2		
				Av.	5	0.70	1.03
MgP	0.50	6.49	1.444	5.024			
MgP	.50	5.83	1.444	25.13	1980		
MgP	.50	6.45	1.541	5.004	2460		
MgP	.50	6.17	1.541	10.01	1920		
MgP	.50	5.80	1.541	25.12	2280		
				Av.	2160	3.33	5.41
Mg_2P	0.50	6.49	1.444	5.025			
Mg_2P	.50	5.83	1.444	25.13	18		
Mg_2P	.50	6.45	1.541	5.004	3		
Mg_2P	.50	6.17	1.541	10.01	37		
Mg_2P	.50	5.80	1.541	25.12	25		
				Av.	21	1.32	2.34
MgHP	1.50	4.70	1.430	4.975	55		
MgHP	1.50	4.50	1.430	24.88	39		
MgHP	1.50	4.66	1.524	4.950	84		
MgHP	1.50	4.60	1.524	9.941	61		
MgHP	1.50	4.45	1.524	24.85	49		
				Av.	58	1.76	3.06

[a] All measurements at ionic strength adjusted to 1.0 with $(CH_3)_4NCl$. [b] Lambert and Watters[4] values.

in Fig. 4. Measurements were made in the presence of Li^+, Na^+, K^+ and Mg^{+2} at a total ionic strength of 1.0 maintained by adding tetramethylammonium chloride. At this high ionic strength, activity coefficients may be considered constant. The curve for Na^+ ion is omitted for clarity since it falls between the closely-spaced curves for Li^+ and K^+. The *p*H shift is attributed to the formation of complexes with the metal M of the type

$$mM^{+z} + H_nP_2O_8^{(n-4)} \rightleftharpoons M_mH_nP_2O_8^{(n+zm-4)}$$

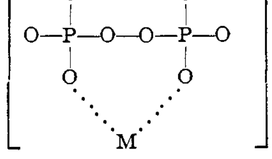
causing a shift in the acid-base equilibria with a resulting decrease in the *p*H. Using methods and analogous to those previously described by Lambert and Watters,[4] formation constants

$$K_{M_mH_nP} = \frac{[M_mH_nP_2O_8^{(n+zm-4)}]}{[M^{+z}]\ [M_{m-1}H_nP_2O_8^{(n+zm-z-4)}]}$$

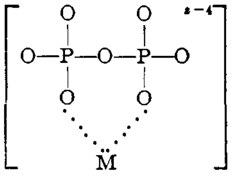
for the complexes were calculated from the *p*H lowering of the stepwise titration curves observed in the presence of the respective metal ions. In Fig. 4 the absence of *p*H lowering for curve 2 after the first end-point indicates that there is negligible complexing of K^+ with $HP_2O_8^{-3}$ ion. It occurs with all the other metal ions, however. There is no evidence for complexing with any of the more acidic forms of peroxydiphosphate. The complexing with Mg^+ is much stronger than for the monovalent cations. In fact, the assumption of the stepwise addition of protons is not strictly valid in this case since the end point inflections practically disappear. Complexing constants were calculated, however, assuming the same species that have been reported for Mg^{+2} with pyrophosphate ion.[4] The values obtained, therefore, allow a comparison of the relative complexing ability of pyrophosphate and peroxydiphosphate for Mg^{+2}. They do not, on the other hand, deny the existence of complexes involving more than one peroxydiphosphate group.

The data and results are summarized in Table I. In this table "a" is the mole ratio of added hydrochloric acid to peroxydiphosphate, pK' is the apparent pK value observed in the presence of metal ion, C_p is the total concentration of peroxydiphosphate in all forms and C_m is the total concentration of added metal ion. The values measured by Lambert and Watters[4] for the corresponding pyrophosphate complexes are included for comparison.

Present evidence seems to indicate that in metal ion complexes of this type the bonding between anion and cation is primarily electrostatic with some evidence for "specific-site-binding" in the case of the stronger complexes. Van Wazer and Callis[15] have discussed this question in a recent review on metal complexing with phosphates. It is interesting to consider the complexing ability of peroxydiphosphate and pyrophosphate in terms of their respective structures. Table I indicates the same relative order of increasing strength for complexes of K^+, Na^+, Li^+ and Mg^{+2} with both anions. This is in the expected order for electrostatic bonding, *i.e.*, the order of increasing ratio of charge to the square of the ionic radius. For a given cation, however, the respective abilities of the two anions to bind the cation should determine the actual magnitude of the formation constants. Table I shows that for the weakly-held cations, K^+ and Na^+, formation constants with peroxydiphosphate and pyrophosphate are approximately equal, while for the more strongly-bound cations, Li^+ and Mg^{+2}, the pyrophosphate complexes are considerably stronger. The only difference in the anion is an additional oxygen atom between the phosphate groups in peroxydiphosphate. Both anions have a maximum charge of minus four. The slightly decreased electron density on peroxydiphosphate due to the extra atom hardly seems to provide an adequate explanation for the observed differences in the complexing constants. A more likely possibility becomes obvious when one considers three dimensional models for the two complexes.



Peroxydiphosphate complex



Pyrophosphate complex

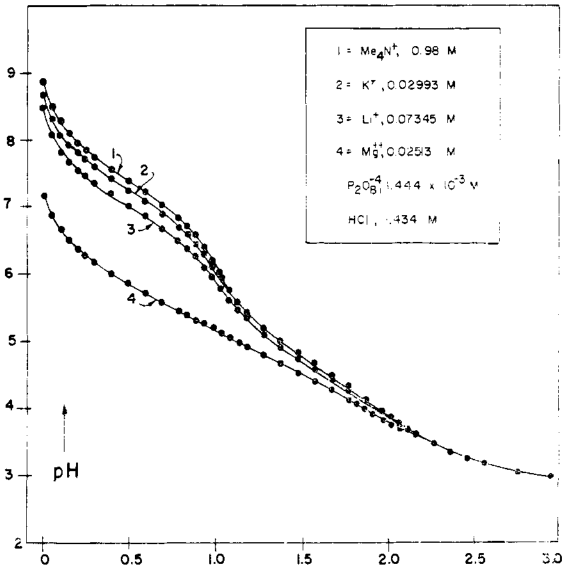


Fig. 4.—Examples of pH lowering of titration curves by added metal cations. The concentrations of the added metal ions were (1) $[(CH_3)_4N^+] = 0.98$ *M*, (2) $[K^+] = 0.02993$ *M*, (3) $[Li^+] = 0.07345$ *M*, (4) $[Mg^{++}] = 0.02513$ *M*. In each case the initial concentration of peroxydiphosphate was 1.444×10^{-3} *M*, the hydrochloric acid concentration was 1.434 *M*, and the ionic strength was adjusted to 1.0 with tetramethylammonium chloride.

The extra oxygen in peroxydiphosphate gives that anion considerably more freedom of motion than pyrophosphate. The non-adjacent oxygen–oxygen distance in pyrophosphate ion is fixed within rather narrow limits, while for peroxydiphosphate the corresponding distance is variable over a rather wide range due to the possibility of internal rotation in the non-linear P–O–O–P chain. The specific-site-binding of small, strongly-bound cations would, therefore, be expected to be accompanied by a less favorable entropy change in the case of peroxydisphosphate, since it would considerably reduce the freedom of motion of the anion. This effect would be less pronounced with larger cations which would produce a less constrained bonding configuration. It is assumed here that effects due to solvation are identical for pyrophosphate and peroxydiphosphate.

It would be interesting to compare the temperature dependence of the formation constants for these two anions with alkali and alkaline earth metal ions. It might be possible in this way to differentiate between ions which are bound at specific sites and those which are only loosely held in the vicinity of the anion, since in the latter case the temperature dependence should be of lesser magnitude.

Acknowledgments.—We are indebted to Mrs. Katalin Polgar and Miss Lois Nyberg for their assistance with the synthetic and analytical tasks. This research was supported by the U. S. Atomic Energy Commission.

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