CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY,
THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO

The Acidity of Tetraphosphoric Acid

BY JAMES I. WATTERS, PETER E. STURROCK, AND R. E. SIMONAITIS

Received November 7, 1962

Two hydrogen ions in linear tetraphosphoric acid are essentially quantitatively dissociated. With the ionic strength adjusted to unity with tetramethylammonium chloride, at 25°, the pK values of the remaining acidity constants are pK_3 = 1.36, pK_4 = 2.23, pK_5 = 6.63, and pK_6 = 8.34. At infinite dilution pK_5 = 7.38 and pK_6 = 9.11. The values of pK_5 and pK_6 are appreciably decreased in the presence of sodium, potassium, or guanidinium ion due to complex formation. There is no appreciable inflection in the acidimetric pH titration curve between the addition of the first and second hydrogen ions to the anion, $P_4O_{13}^{6-}$.

Introduction

Although the existence of the linear tetraphosphate ion has been conclusively established, relatively few papers have been published concerning its properties as a base and complexing agent. Contributing factors to this delay have been its tendency to remain in solution as a viscous liquid without forming crystals in the presence of alkali metal ions, its rapid rate of hydrolysis in acidic solutions, and its tendency to form complex ions even with alkali metal ions. The tetraphosphate ion usually is prepared by alkaline hydrolysis of cyclic tetrametaphosphate to open the ring. This procedure was first used by Thilo and Ratz,[1] who obtained a quantitative conversion to tetraphosphate ion by heating a solution containing sodium tetrametaphosphate and sodium hydroxide in a mole ratio of 1:2 for 100 hr. at 40°. They did not succeed in crystallizing the sodium salt from the viscous solution. Westman and Scott[2] obtained a 60% conversion in 2 hr. at 70°. Quimby[3] observed that in the presence of an excess of NaOH exactly 2 moles of hydroxide ion was used for each mole of tetrametaphosphate in 3 weeks but only an additional 0.15 mole was used in the next 6 months. This indicates that the alkaline hydrolysis of tetrametaphosphate proceeds specifically to linear tetraphosphate but that further hydrolysis to products such as pyrophosphate proceeds much more slowly in strongly alkaline solutions.

Attempts by Quimby to purify the product by crystallizing the salts of sodium, potassium, lithium, or hexaamminecobalt(III) were unsuccessful. However, he finally succeeded in crystallizing the salt hexaguanidinium tetraphosphate, having a purity of at least 98% from formamide-rich solutions.

Crystalline salts of tetraphosphate ion with cations of large ionic radii, namely, lead, barium, and bismuth, have been prepared by thermal decomposition of acidic solutions and have been confirmed by X-ray analysis.[4-6]

Mixtures of polyphosphates including tetraphosphates have been separated by means of paper chromatography[7-14] and by ion-exchange resins using varied proportions of KCl, NH_4Cl, and NH_4OH, and sodium maleate as the eluent.[15-17] The polarographic waves of tetraphosphate complexes of Zn, Cd, and Pb have been investigated and found to be irreversible.[18]

Experimental

In the present study the tetraphosphate was prepared by the hydrolysis of the commercial product "Cyclophos" manufactured by the Victor Chemical Works, and hexaguanidinium tetraphosphate was recrystallized from formamide-rich solutions according to a slight modification of Quimby's procedure[3] in which about 700 ml. of formamide was added to 100 ml. of the sirupy 44% solution obtained after the addition of ethanol. Precipitation from the formamide solution was induced by adding 5 ml. of water and was complete after stirring for 1 hr. The guanidinium salt then was recrystallized by dissolving 45 g. of it and 5 g. of guanidinium chloride in 75 ml. of water. About 70 ml. of formamide was added to produce a permanent turbidity. The crystals were separated by filtration and washed with absolute ethanol. Stock solutions of the guanidinium salt were converted to the tetramethylammonium salt and to the acid through the use of Dowex 50 cation exchange resins according to the procedures described in earlier papers on the acidity of triphosphoric acid[19a] and the complexes of alkali metals with triphosphate[19b] and pyrophosphate.[19c] The solutions and the exchange resins were kept near 0°. The titrations were performed immediately after warming the solutions to 25°.

Results and Discussion

It is well known that every PO_4 tetrahedron in either chain or ring structures of PO_4 tetrahedra is weakly basic with respect to the association of one hydrogen ion for which the acidity constant is in the order of

---

(1) E. Thilo and R. Ratz, *Z. anorg. Chem.*, **260**, 255 (1949).

(2) A. E. R. Westman and A. E. Scott, *Nature*, **168**, 740 (1951).

(3) O. T. Quimby, *J. Phys. Chem.*, **58**, 615 (1954).

(4) R. K. Osterheld and R. P. Langguth, *ibid.*, **59**, 76 (1955).

(5) R. P. Langguth, R. L. Osterheld, and E. Karl-Kroupa, *ibid.*, **60**, 1335 (1956).

(6) I. Schultz, *Z. anorg. allgem. Chem.*, **287**, 106 (1956).

(7) A. E. R. Westman, A. E. Scott, and J. T. Pedley, *Chem. Can.*, 3, (1952).

(8) A. E. R. Westman and A. E. Scott, *Nature*, **168**, 740 (1951).

(9) J. P. Ebel, *Bull. soc. chim. France*, **20**, 991, 998 (1953).

(10) O. T. Quimby, A. Narath, and F. J. Lohman, *J. Am. Chem. Soc.*, **82**, 1099 (1960).

(11) J. Crowther, *Anal. Chem.*, **26**, 1383 (1954).

(12) E. K. Kroupa, *ibid.*, **28**, 1091 (1956).

(13) M. J. Smith, *ibid.*, **31**, 1023 (1959).

(14) D. N. Bernhart and W. B. Chess, *ibid.*, **31**, 1026 (1959).

(15) T. V. Peters, Jr., and W. Rieman, III, *Anal. chim. acta*, **14**, 131 (1956).

(16) N. Busch, J. P. Ebel, and M. Blanck, *Bull. soc. chim. France*, 486 (1957).

(17) J. P. Ebel, *ibid.*, 981, 1089 (1953).

(18) A. I. Lopushanskaya and A. M. Mandel'eil, *Ukrain. Khim. Zh.*, **26**, 41 (1960); *Chem. Abstr.*, **54**, 15025*i* (1960).

(19) (a) J. I. Watters, E. D. Loughran, and S. M. Lambert, *J. Am. Chem. Soc.*, **78**, 4855 (1956); (b) **79**, 3651 (1957); (c) **79**, 4262 (1957).

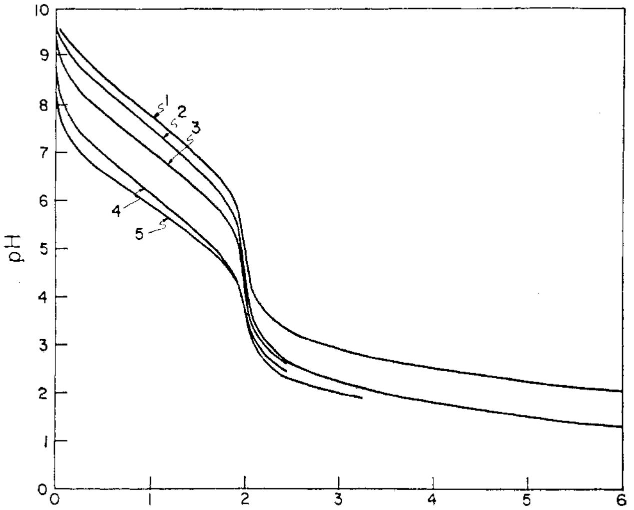

Fig. 1.—Curve 1, 0.00231 *M* $H_6P_4O_{13}$ titrated with 0.0313 *M* $N(CH_3)_4OH$, no supporting electrolyte. Curve 2, 0.02235 *M* $H_6P_4O_{13}$, $\mu = 1$, with $N(CH_3)_4Cl$ titrated with $N(CH_3)_4OH$ without dilution. Curve 3, 0.02 *M* $(N(CH_3)_4)_6P_4O_{13}$ in the presence of 1 *M* $(CH_3)_4NCl$ with 0.12 *M* guanidinium ion also present titrated with 0.0814 *M* HNO_3. Curve 4, like curve 3 but in presence of 1 *M* KNO_3. Curve 5, like curve 3 but in presence of 1 *M* $NaNO_3$.

10^{-2}. Every terminal PO_4 tetrahedron is also strongly basic with respect to the association of another hydrogen ion for which the acidity constant is in the order of 10^{-8}. Thus an aqueous solution of cyclic sodium tetrametaphosphate, $Na_4P_4O_{12}$, is essentially neutral and only the acid, $H_4P_4O_{12}$, can be titrated. In contrast an aqueous solution of linear sodium tetraphosphate, $Na_6P_4O_{13}$, is strongly alkaline. The tetraphosphate ion, $P_4O_{13}^{6-}$, can be titrated as a diacidic base or tetraphosphoric can be titrated as a strong tetrabasic acid and then, less accurately, as a weak dibasic acid.

The concentrations always change slightly upon passing through the resin. However, by assuming that only linear tetraphosphate is present the curves for the titration of various concentrations of the acid, $H_6P_4O_{13}$, and the base, $P_4O_{13}^{6-}$, can be plotted on a single graph. In the titration of $P_4O_{13}^{6-}$ the pH is plotted *vs.* a, the number of moles of acid added per mole of $P_4O_{13}^{6-}$. In the titration of $H_6P_4O_{13}$ the pH is plotted *vs.* $a = 6 - b$, where b is the number of moles of hydroxide added per mole of $H_6P_4O_{13}$. Except for dilution effects during the titration the curves for the titration of the same concentrations of the acid and base, with the same supporting electrolyte present, should coincide provided no other phosphates are present. Titration curves obtained in the presence of several supporting electrolytes are shown in Fig. 1. All titrations were performed in duplicate using at least a tenfold concentration range.

The curves differ from those obtained for similar titrations of pyro- and triphosphates in that there is no appreciable inflection at $a = 1$. This is reasonable because the terminal PO_4 tetrahedra which are responsible for the strongly bound hydrogen ions and, presumably, are primarily involved in the bonding are separated by two internal phosphate tetrahedra. This decreases the inductive effect of the association or dissociation of a hydrogen ion from one terminal PO_4 tetrahedron on the basicity of the other. There is of course a statistical factor of 4 which would be observed even in the absence of inductive effects. This factor depends on the number of equivalent hydrogen ions and the number of sites for hydrogen ion in the various species.

Curve 1, Fig. 1, illustrates the pH change during the titration of a very dilute solution of $H_6P_4O_{13}$, 0.00231 *M*, with 0.313 *M* $N(CH_3)_4OH$ in the absence of any supporting electrolyte. The high pH values in all of the titrations below $a = 2$ are consistent with the expected high values of pK_5 and pK_6. To obtain curve 2, 25 ml. of a solution containing 0.02235 *M* $H_6P_4O_{13}$ and 1 *M* $N(CH_3)_4Cl$ was titrated with a basic solution containing 0.02235 *M* $(N(CH_3)_4)_6P_4O_{13}$ and 0.574 *M* $N(CH_3)_4OH$. In this way the total tetraphosphate was kept constant and the ionic strength was kept close to unity throughout the titration. Data obtained in a typical titration are given in Table I. Within experimental error the same curve was obtained when a solution containing 0.02044 *M* $(N(CH_3)_4)_6P_4O_{13}$ and 0.571 *M* $N(CH_3)_4Cl$ was titrated with a solution containing 0.02044 *M* $H_6P_4O_{13}$, 0.2013 *M* HCl, and 1.60 *M* $N(CH_3)_4Cl$. The fact that these curves coincide is strong evidence that the compound titrated was essentially pure linear tetraphosphate since the presence of lower phosphate should have displaced the two curves.

Curve 3, Fig. 1, was obtained for the titration of 0.02 *M* $(N(CH_3)_4)_6P_4O_{13}$ in the presence of 1 *M* $N(CH_3)_4Cl$ but with 0.12 *M* guanidinium ion also present with a solution containing 0.0814 *M* HNO_3 and 1 *M* $N(CH_3)_4Cl$. Curves 4 and 5 were obtained for similar titrations except that 1 *M* KNO_3 and 1 *M* $NaNO_3$ replaced 1 *M* $N(CH_3)_4Cl$ as the supporting electrolyte. All of these solutions were 0.12 *M* in guanidinium ion which was added as the cation of the 0.02 *M* $(N(CH_3)_4)_6P_4O_{13}$. The lowering of the pH values in curves 3, 4, and 5 from the corresponding values in curve 2 probably is due to complex formation of $P_4O_{13}^{6-}$ with guanidinium, potassium, and sodium ions. Complexes with potassium and sodium ions might be anticipated since corresponding complexes[19] had been obtained with $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$, but the complexes with guanidinium ions have never been reported. Research on these complexes will be reported in later papers.

Due to the overlap of equilibria involving the tetraphosphate species associated with various numbers of hydrogen ions, the stepwise acidity constants at unit ionic strength were solved by Bjerrum's method discussed in a previous paper.[19] Briefly $\bar{n}$, the mean number of hydrogen ions associated with tetraphosphate, was solved by the expression

$$\bar{n} = ([H^+]_t - [H^+] + [OH^-])/[P_4O_{13}^{6-}]_t$$

where $[H^+]_t$ and $[P_4O_{13}^{6-}]_t$ are the total added concentrations of tetraphosphate and hydrogen ions and $[H^+]$ and $[OH^-]$ are the equilibrium concentration of hydrogen and hydroxide ions. The total added concentrations were obtained from the titration data.

TABLE I

TITRATION DATA

Titration of 25 ml. of alkaline solution containing 0.02044 *M* tetramethylammonium tetraphosphate and 0.571 *M* tetramethylammonium chloride with increasing volumes of an acidic solution containing 0.02044 *M* tetramethylammonium tetraphosphate, 0.2013 *M* HCl, and 1.478 *M* tetramethylammonium chloride; ionic strength = 1.00 + 0.03; $T = 25°$.

H^+ added, ml.	pH	a	$\bar{n}_{\text{exp}}$	$\bar{n}_{\text{theory}}$
0.00	9.78	0	...	...
1.30	8.39	0.487	0.487	0.484
1.34	8.36	0.501	0.501	0.502
2.80	7.50	0.992	0.992	0.992
3.00	7.39	1.055	1.055	1.048
4.40	6.68	1.474	1.474	1.454
4.50	6.62	1.502	1.502	1.492
6.36	4.41	1.997	1.997	2.000
6.38	4.29	2.002	2.002	2.013
7.00	3.13	2.154	2.108	2.115
9.00	2.48	2.607	2.404	2.404
10.00	2.31	2.814	2.513	2.529
16.00	1.83	3.843	2.937	2.966
18.00	1.75	4.123	3.032	3.044
22.00	1.63	4.610	3.176	3.160

$[H^+]$ and $[OH^-]$ were calculated from the pH by assuming the activity coefficient of hydrogen and hydroxide ions in 1 *M* $(CH_3)_4NNO_3$ to be 0.80. Throughout this paper brackets indicate concentrations and parentheses indicate activities. For convenience the equilibria were expressed as over-all complexity constants thus

$$\beta_n = [H_nP_4O_{13}{}^{(6-n)-}]/(H^+)^n[P_4O_{13}{}^{6-}] = \prod_{n=1}^{n=N} K_n{}^{-1}$$

Bjerrum's formation function was written in the following form and solved by determinants. In the region where $a < 2$ only the terms containing β_1 and β_2 need to be considered.

$$\bar{n} = (1-\bar{n})\beta_1(H^+) + (2-\bar{n})\beta_2(H^+)^2 + (3-\bar{n})\beta_3(H^+)^3 + (4-\bar{n})\beta_4(H^+)^4 + (5-\bar{n})\beta_5(H^+)^5 + (6-\bar{n})\beta_6(H^+)_6$$

The complexity constants were converted to the hybrid stepwise acidity constants having the form

$$K_n = (H^+)[H_{n-1}P_4O_{13}{}^{(5-n)-}]/[H_nP_4O_{13}{}^{(6-n)-}]$$

In solutions containing approximately 0.01 to 0.022 *M* tetraphosphate with the ionic strength adjusted to unity with $N(CH_3)_4NO_3$ the first two hydrogen ions were found to be essentially quantitatively dissociated. The remaining successive p*K* values were $pK_3 = 1.36$, $pK_4 = 2.23$, $pK_5 = 6.63$, and $pK_6 = 8.34$ in the presence of $N(CH_3)_4Cl$ at $\mu = 1.00 \pm 0.03$ at 25°. The pH values at $\bar{n} = 0.5$ and 1.5 were 8.36 ± 0.02 and 6.61 ± 0.02, corresponding to a pK_6 of 8.34 ± 0.02 and a pK_5 of 6.63. Thus, within the experimental error of 0.02, pK_6 and pK_5 are equal to the corresponding pH values at $a = 0.5$ and 1.5 as would be predicted since their magnitudes differ by 1.71 log units. This permits the calculation of the thermodynamic equilibrium constants, K_5 and K_6, at infinite dilution by measuring the pH after successive dilutions of solutions at $a = 0.5$ and 1.5. The data obtained in these dilution experiments are given in Table II. Plotting the pH *vs.* the square root of the tetraphosphate concentration yielded a nearly straight line for the three lowest concentrations. Extrapolating to infinite dilution yielded pH values of 9.13 and 7.36 for $a = 0.5$ and 1.5, respectively. The solution of Bjerrum's function for these points yielded $pK_6 = 9.11$ and $pK_5 = 7.38$ at infinite dilution and 25°. Concentration was used instead of the ionic strength in the graphs since the latter is not readily applicable when the ionic charge is distributed over a polymer molecule. The use of an excess of a uni-univalent supporting electrolyte to maintain the ionic strength has yielded unsatisfactory results in this[19] and other laboratories.[20-22]

TABLE II

$[P_4O_{13}{}^{6-}]_t$	pH at $a = 0.5$	pH at $a = 1.5$
0.01560	8.60	6.79
.00780	8.69	6.84
.00390	8.80	6.98
.00195	8.91	7.08

For comparison the last three p*K* values of linear pyro-, tri-, and tetraphosphoric acids at unit and zero ionic strengths are summarized in Table III.

TABLE III

	$H_4P_2O_7$	$H_5P_3O_{10}$	$H_6P_4O_{13}$
	A. At $\mu = 0$		
pK_N	9.42	9.24	9.11
pK_{N-1}	6.76	6.50	7.38
pK_{N-2}	2.64	2.30	
	B. At $\mu = 1$ (1 *M* $(CH_3)_4NNO_3$)		
pK_N	8.93	8.81	8.34
pK_{N-1}	6.13	5.83	6.63
pK_{N-2}	1.81	2.11	2.23
pK_{N-3}	0.82	1.06	1.36

As would be predicted the pK_N values decrease and the pK_{N-1} values increase with increase in chain length with the exception of K_{N-1} of $H_5P_3O_{10}$. The limiting difference should be 0.60, corresponding to the statistical factor of 4 since there are only half as many available sites but twice as many hydrogen ions to dissociate in the K_{N-1} equilibria. The anomalously low value of pK_4 of $H_5P_3O_{10}$ probably is due to the coiling of the triphosphate ion around the first hydrogen ion so both terminal tetrahedra are involved in its bonding to produce a particularly stable configuration. The opening of this structure when the second hydrogen ion is associated is reflected in the relatively low value of K_4 for triphosphoric acid. Consequently, at $\mu = 1$, pK_5 of $H_5P_3O_{10}$ is nearly as large as pK_4 of $H_4P_2O_7$ and pK_4 of $H_6P_3O_{10}$ is even smaller than pK_3 of $H_4P_2O_7$.

It is interesting that since this paper was first submitted, Irani and Callis[23] independently have reported an anomalous behavior of triphosphoric acid in nuclear magnetic resonance studies and have interpreted their observation by a similar model.

---

(20) J. R. Partington and H. J. Stonehill, *Phil. Mag.*, [7] **22**, 857 (1936).

(21) W. J. Argersinger, Jr., and D. M. Mohilner, *J. Phys. Chem.*, **61**, 99 (1957).

(22) H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Co., New York, N. Y., 1960, p. 18.

(23) R. R. Irani and C. F. Callis, *Inorg. Chem.*, **1**, 813 (1962).