of supporting electrolyte; (3) less nickel is recovered from nickel amalgams formed out of solutions containing a large excess of supporting electrolyte—when bromate is added much less is obtained.

For Ni(I) to exist in a concentration less than 0.1% that of Ni(II) in the presence of metallic Ni, the potential for the reaction Ni(I) = Ni(II) + e^- must be greater than about 0.46 v. *vs.* NHE. From the observed electrode reduction potential of Ni(II) the reversible potential for the reaction Ni(I) = Ni(II) + e^- could be no more than 0.75 v. *vs.* the NHE. Thus the potential of the couple Ni(S) = Ni(I) + e^- must be between the limits of 0.04 and −0.25 v. *vs.* NHE. In order to observe Ni(I) it is therefore necessary that it be "stabilized" kinetically with respect to direct electroreduction and with respect to disproportionation.

We have no satisfactory explanation of the role of the various salts described in this paper in stabilizing Ni(I). It would seem that one feature they have in common is the possibility of altering the activity of water to the extent that the hydration structure of Ni(I) is changed. A second possibility is that the positive ions become so concentrated in the double layer that further reduction of Ni(I) is inhibited.

BERKELEY, CALIFORNIA

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

The Acidity of Triphosphoric Acid[1]

BY JAMES I. WATTERS, E. DAN LOUGHRAN AND SHELDON M. LAMBERT

RECEIVED MAY 31, 1956

Triphosphoric acid $H_5P_3O_{10}$, and tetramethylammonium triphosphate $((CH_3)_4N)_5P_3O_{10}$, were prepared by passing solutions of the sodium salt through cation-exchange resin columns charged with hydrogen ions and tetramethylammonium ions, respectively. The column was kept near 0° and the acid or salt was titrated with tetramethylammonium hydroxide or hydrochloric acid using a glass electrode immediately after warming the solution to 25°. One hydrogen ion was found to be largely dissociated in 0.01 *M* acid. The values obtained for the successive dissociation constants of the four remaining hydrogen ions at an ionic strength of 1.0 were $K_2 = 10^{-1.06}$, $K_3 = 10^{-2.11}$ $K_4 = 10^{-5.83}$ and $K_5 = 10^{-8.81}$. At an ionic strength of 0.1 the values of the last three constants were $K_3 = 10^{-2.15}$, $K_4 = 10^{-6.00}$ and $K_5 = 10^{-8.73}$. Extrapolated to infinite dilution the values became $K_3 = 10^{-2.30}$, $K_4 = 10^{-6.26}$ and $K_5 = 10^{-8.90}$.

Introduction

Although sodium triphosphate is available in commercial quantities there have been few published studies on the strength of the acid. This is in part due to the tendency of the triphosphate ion to form complexes with all metal ions including the alkali group and also to its rather rapid rate of hydrolysis, forming pyrophosphoric and orthophosphoric acids.

According to Monk[2] the first formation constant for the sodium complex is $10^{2.5}$. Van Wazer and Campanella[3] obtained a somewhat smaller complexity constant for sodium with several condensed polyphosphate glasses. They also investigated the complexes of other metal ions. Friess[4] found that triphosphoric acid hydrolyzes about six times faster than pyrophosphoric acid. The reaction is catalyzed by hydrogen ion. Rudy and Schloesser[5] published titration curves for triphosphoric acid in the presence of sodium ion but did not attempt to calculate the acidity constants since they were aware of the complex formation. Incidental to an anion-exchange study of condensed phosphates Buekenkamp, Rieman and Lindenbaum[6] calculated the thermodynamic acidity constants by the application of the Debye–Hückel equation to data obtained in the titration of the acid with potassium hydroxide. They mention several limitations on the accuracy of their constants which were satisfactory for their purpose. Their values were $pK_3 = 2.79$, $pK_4 = 6.47$ and $pK_5 = 9.24$.

Experimental

The sodium tripolyphosphate was prepared from anhydrous sodium tripolyphosphate, Monsanto technical grade, by recrystallizing four times to yield a 99.5% pure product according to a procedure developed by P. G. Arvon[7] in the Monsanto Laboratory. Eight hundred and forty g. of the salt was dissolved in 3.8 l. of water. The solution was filtered and treated with 1.4 l. of methanol with vigorous stirring. The crystalline $Na_5P_3O_{10}{\cdot}6H_2O$ was collected on a filter, air-dried by suction and then allowed to air dry overnight. The precipitate was dissolved to produce a 13% solution by weight, and again crystallized by the addition of methanol in the same ratio. The crystals were filtered and dried as before. Four hundred and forty g. of crystalline product was leached by being thoroughly stirred with 200 ml. of water, filtered, and the filtrate discarded. Another crystallization, a leaching and a final crystallization were made using the same procedure and the same proportions as in the last steps. According to Quimby[8] the commercial 85 to 94% anhydrous salt can be made 99% pure by 3 to 5 recrystallizations from water with ethanol added to the extent of 25% by volume. Redistilled, carbonate-free water was used for all of the dilutions.

The tetramethylammonium chloride, used for the adjustment of ionic strength and for charging the column, was prepared from the Matheson Coleman and Bell 99+% product which was further purified by recrystallization from a solution containing methanol and acetone.[9]

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[1] Based in part on a thesis by E. Dan Loughran submitted in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1955. Presented before the Division of Physical and Inorganic Chemistry, 129th Meeting of the American Chemical Society, Dallas, Texas, 1956.

[2] C. B. Monk, *J. Chem. Soc.*, 427 (1949).

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

[4] S. L. Friess, *ibid.*, **74**, 4027 (1952).

[5] H. Rudy and H. Schloesser, *Ber.*, **73**, 484 (1940).

[6] J. Buekenkamp, Wm. Rieman and S. Lindenbaum, *Anal. Chem.*, **26**, 505 (1954).

[7] R. A. Ruerwein, private communication, Monsanto Chemical Co., Dayton, Ohio.

[8] O. Quimby, *J. Phys. Chem.*, **58**, 603 (1954).

[9] P. L. Pickard and W. E. Neptune, *Anal. Chem.*, **27**, 1358 (1955).

The stock solution of the carbonate-free tetramethylammonium hydroxide was prepared by passing the chloride salt through an anion-exchange resin, Dowex 2-X7.5, 20–50 mesh, medium porosity, charged with hydroxide ions. The column was 6 cm. in diameter, 125 cm. in height and had a stopcock on the lower end. It was coated throughout the interior with paraffin and filled to a height of 75 cm. with resin supported on a Pyrex glass wool plug. The system was completely closed and nitrogen was constantly swept through the top of the column. The supernatant base was stored under nitrogen in a polyethylene bottle. The stock solution was finally diluted to the desired concentration, standardized against 0.1 *N* HCl, and transferred from a polyethylene bottle to a microburet by the classical closed system protected from CO_2 of the air by ascarite bulbs.

The triphosphoric acid solution was prepared by passing a solution of the sodium salt having a concentration twice that finally desired 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 column was fitted with a Pyrex water jacket, 4 cm. in diameter, through which ice-water was constantly circulated. 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 acid was warmed to 25 ± 0.1°, diluted to the desired concentration and immediately titrated with standardized, carbonate-free tetramethylammonium hydroxide 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. The titration was performed in a stoppered Berzelius beaker with a stream of nitrogen flowing over the solution. The solution was stirred after each addition of base. *p*H measurements were made with the Beckman model G *p*H meter with the Beckman All Purpose Glass electrode and the Beckman reference electrode inserted directly in the acid solution.

The tetramethylammonium triphosphate was prepared in a manner similar to that for the acid. It was found necessary to use Dowex 50-X2, 100–200 mesh, high porosity cation-exchange resin due to the larger ion size. The diameter of the column was increased to 3 cm. due to the slower flow rate through the high porosity resin. The eluted salt was warmed to 25 ± 0.1°, diluted to the desired concentration and immediately titrated with standardized hydrochloric acid in the manner described above.

Results and Discussion

Curve 1, Fig. 1, 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. Curve 2, Fig. 1, was obtained for the titration of 0.00943 *M* $H_5P_3O_{10}$ with a solution containing 0.0528 *M* $(CH_3)_4NOH$ and exactly the same concentration of $((CH_3)_4N)_5P_3O_{10}$ as the solution titrated. All solutions contained sufficient $(CH_3)_4NCl$ to produce an ionic strength of 1.0. The ordinate, *a*, is the number of equivalents of base or acid added per mole of triphosphate ion.

Spectroscopic observations and spot tests with magnesium uranyl acetate[10] indicated that all of the sodium was removed in the column. Any remaining sodium ion would decrease the number of equivalents required to reach the first end-point in titrating the acid. Any unavoidable hydrolysis in the column or during the early portion of titration should not affect the first end-point appreciably in the acid titration since ortho-, pyro- and triphosphoric acids all contain one moderately highly ionized hydrogen ion per phosphorus atom with an acidity constant of the order of 10^{-2} or larger. The number of equivalents in the $H_2P_3O_{10}{}^{3-}$ to $HP_3O_{10}{}^{4-}$ range would increase by one in both the acid and salt titrations if hydrolysis were complete since both ortho- and pyro-acids contain hydrogen ions with acidity constants to replace the one of triphosphoric acid in this range. The number of equivalents in the $HP_3O_{10}{}^{4-}$ to $P_3O_{10}{}^{5-}$ range should not increase much in the acid titration since essentially only the last hydrogen ion of pyrophosphoric acid and not that of orthophosphoric acid would be titrated in this range.

One cannot apply previously calculated hydrolysis rate constants since these were made in the presence of alkalies. Furthermore the extent of hydrolysis on the exchange resin is not known. However, it was observed from ratio of the amounts of base required to reach the three end-points in the acid titration that appreciable hydrolysis did occur if the acid solution was left at room temperature for a few hours or even if it was stored at 0° for several days. The determination of various phosphates in mixtures on the basis of the several end-points is discussed by Gerber and Miles[11] as well as by Bell.[12]

Since the *p*H in the range of "*a*" values between zero and three for the acid titration and between two and five for the salt titration is close to that for concentrated hydrochloric acid having a concentration three times that of the triphosphate, the first three ionization constants must have values in the order of 10^{-2} or larger. Due to the high degree of dissociation and the possibility of the constants having similar values, Bjerrum's method was applied in a manner described by Hindman and Sullivan.[13] The constants may be expressed as stepwise complexity constants, thus

$$\beta_n = \frac{(H_nP_3O_{10}{}^{(5-n)})^-}{[H^+]^n(P_3O_{10}{}^{5-})}$$

where parentheses indicate concentrations and brackets indicate activities. In this case the latter were obtained from *p*H readings. To calculate $\bar{n}$, the average number of bound hydrogen ions per triphosphate, the total number of millimoles of triphosphate and hydrogen ion (bound as well as dissociated) were obtained from the titration data. The concentrations of dissociated hydrogen ions were assumed to be equal to the known concentrations of hydrochloric acid having the same *p*H in the presence of the same concentration of indifferent electrolyte. It was found that the *p*H values were 0.10 ± 0.02 unit smaller than the measured *p*H values. The corresponding activity coefficient, 0.80, is consistent with the results of Harned and Ehlers.[14] Their values were found valid for known solutions of hydrochloric acid in which the ionic strength was adjusted with $(CH_3)_4NCl$ instead of the acid itself. The titration data for $((CH_3)_4N)_5P_3O_{10}$ with HCl are given in Table I.

Bjerrum's formation function may be written in the form

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

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[10] Earle R. Caley and C. W. Foulk, THIS JOURNAL, **51**, 1664 (1929).

[11] A. B. Gerber and F. T. Miles, *Ind. Eng. Chem., Anal. Ed.*, **10**, 519 (1938).

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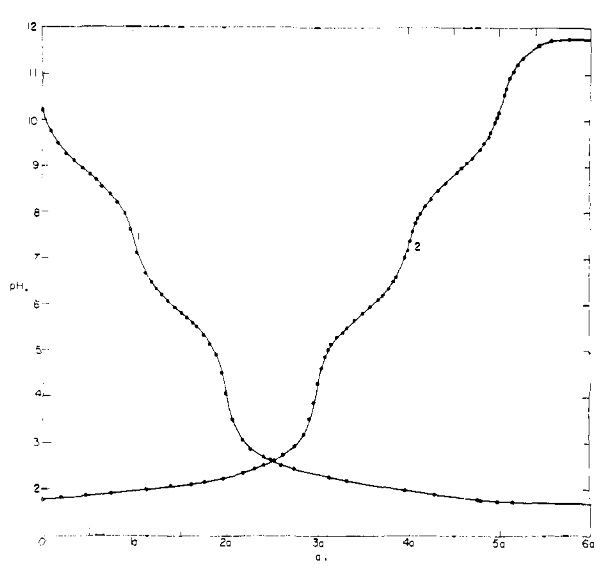

Fig. 1.—Curve 1, 0.00919 M $((CH_3)_4N)_5P_3O_{10}$ titrated with a solution 0.0543 M in HCl and 0.00919 M in $H_5P_3O_{10}$. Both solutions contained sufficient $(CH_3)_4NCl$ to produce $\mu = 1.0$. Curve 2, 0.00943 M $H_5P_3O_{10}$ titrated with a solution 0.0528 M in $(CH_3)_4NOH$ and 0.00943 M in $((CH_3)_4N_5P_3O_{10}$. Both solutions contained sufficient $(CH_3)_4NCl$ to produce $\mu = 1.0$.

Because two hydrogen ions were associated throughout the range the equation was modified in the actual calculations by defining n^* as the average number of hydrogen ions combined with $H_2P_3O_{10}^{3-}$ and β_{n^*} as the corresponding complexity constants.

Thus $\beta_{n^*} = \beta_n/\beta_2$ and $n^* = \bar{n} - 2$

$$n^* = (1 - n^*)\beta_3^*[H^+] + (2 - n^*)\beta_4^*[H^+]^2 + (3 - n^*)\beta_5^*[H^+]^3$$

The simultaneous solution of equations in groups of three established that only two constants, having magnitudes in the order of log $\beta_3^* = 2$ and log $\beta_4^* = 3$ were required to account for all the data.

TABLE I

The titration of 25 ml. of a solution of 0.0388 M $((CH_3)_4N)_5P_3O_{10}$ with a solution 0.4043 M in HCl and 0.0388 M in $((CH_3)_4N)_5P_3O_{10}$ at 25°. All solutions contained sufficient $(CH_3)_4NCl$ to produce an ionic strength of 1.0.

a	pH	$\bar{n}_{\text{theory}}$	$\bar{n}_{\text{experiment}}$
2.20	2.80	2.23	2.23
2.49	2.35	2.39	2.35
2.75	2.10	2.56	2.50
3.05	1.91	2.71	2.65
4.02	1.50	3.07	3.02
4.83	1.30	3.24	3.21
5.40	1.20	3.33	3.36
6.03	1.10	3.41	3.46
6.40	1.05	3.45	3.52
7.56	0.92	3.60	3.66

By successive substitutions of these constants into the formation function, the values finally obtained were log $\beta_3^* = 2.11 \pm 0.05$, and log $\beta_4^* = 3.17 \pm 0.10$. Converting to the usual stepwise acidity constants the p values are $pK_3 = 2.11 \pm 0.05$, $pK_2 = 1.06 \pm 0.10$ and $pK_1 = \alpha$ at an ionic strength adjusted to unity with tetramethylammonium chloride. The satisfactory agreement between $\bar{n}_{\text{experimental}}$ and $\bar{n}_{\text{theoretical}}$ is shown in Table I. It is observed that $\bar{n}$ varied from 2 to 3.5, thus the predominant equilibrium might be anticipated to involve K_3, as is evident from the relative values of the constants. The value of pK_3 is therefore believed to be very reliable. The value of pK_2 is somewhat less reliable since the equilibrium becomes significant only at the low pH range approaching unity where the error in hydrogen ion concentration becomes large relative to the total triphosphate concentration. The thermodynamic value of K_3 was obtained by extrapolation to infinite dilution for $a = 2.5$. The constant was calculated as before, using hydrogen ion activity coefficients given by Harned and Ehlers[14] for similar ionic strengths. The results are shown in Fig. 2. In calculating K_3, the most dilute solutions were too dilute for accuracy. At an ionic strength of 0.1 the value of pK_3 was 2.15, while the graphic extrapolation to infinite dilution yielded $pK_3 = 2.30$.

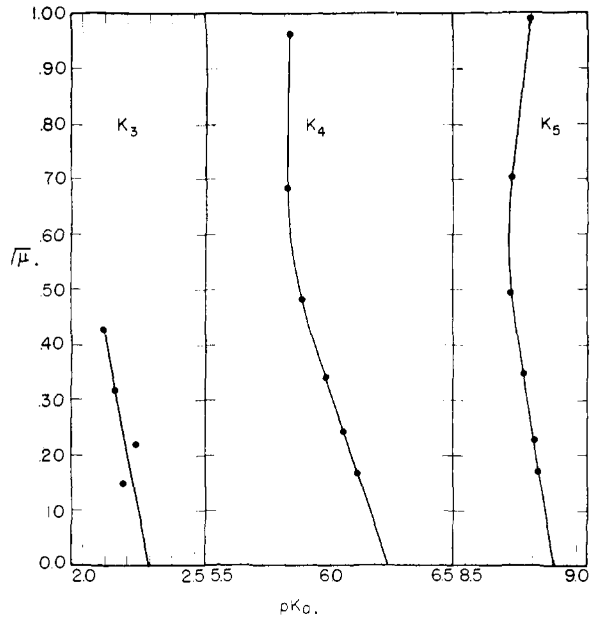

Fig. 2.—Curve K_3, 10.00 ml. of 0.0396 M $H_5P_3O_{10}$ + 11.02 ml. of 0.0898 M $(CH_3)_4NOH$. (a = 2.50); curve K_4, 25.00 ml. of 0.00991 M $((CH_3)_4N)_5P_3O_{10}$ + 4.36 ml. of a solution 0.0507 M in HCl and 0.00991 M in $H_5P_3O_{10}$. Both solutions contained sufficient $(CH_3)_4NCl$ to produce $\mu = 1.0$ (a = 1.50); curve K_5, 24.00 ml. of 0.00883 M $((CH_3)_4N)_5P_3O_{10}$ + 1.15 ml. of a solution 0.0561 M in HCl and 0.00883 M in $H_5P_3O_{10}$. Both solutions contained sufficient $(CH_3)_4NCl$ to produce $\mu = 1.0$ (a = 0.50).

If the first hydrogen ion dissociated from a terminal P atom there would be two structures having the formula $H_3P_3O_{10}^{2-}$ and K_2 would be an apparent dissociation constant. However, the experimental values of K_1, K_2 and K_3 differ by tenfold or better indicating significantly different acidic strengths for the various H^+ ions. A comparison of the first ionization constants of phosphoric acid and pyrophosphoric acid indicates that the replacement of an $-OH$ group in phosphoric by the $-OPO_3H_2$ of pyrophosphoric acid enhances the acidity by considerably more than the increase in statistical probability of 4 to 3. By analogy one would expect that the single hydrogen ion held by the central P atom of triphosphoric acid to be even more acidic. These arguments indicate that the H^+ ion held by the central P atom is the most highly dissociated. The second ion can then ionize from either terminal P atom to yield identical structures. If this is the case K_2 is a real equilibrium constant.

The calculations of K_4 and K_5 were simple since the constants were sufficiently different in magnitude so that the addition of hydrogen ion was stepwise and the degree of dissociation was negligible compared to the concentrations of the triphosphate species involved. Furthermore the effect of hydrolysis was negligible except in the most dilute solutions near a *p*H of 9. The hydrolysis correction consists of the addition or subtraction of $K_w/f[H^+]$ due to the following type of reaction

$$P_3O_{10}^{5-} + HOH \rightleftarrows HP_3O_{10}^{4-} + OH^-$$

The values of K_4 and K_5 were accordingly calculated by the following general equation for the acid titration.

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

where f is the activity coefficient of a univalent ion.

At an ionic strength adjusted to unity with $(CH_3)_4NCl$, the values of pK_4 and pK_5 were found to be 5.83 and 8.81. At an ionic strength of 0.1 the values of pK_4 and pK_5 were found to be 6.00 and 8.73, respectively. Extrapolated to zero ionic strength the values were $pK_4 = 6.26$ and $pK_5 = 8.90$.

Although the experiments were performed using cells with liquid junctions the error due to this cause is believed to be very small since the effect is in part cancelled through the use of standard buffers and hydrochloric acid solutions of known concentrations to standardize the *p*H meter. Experiments are in progress to determine the thermodynamic functions using cells without liquid junction at various temperatures.

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COLUMBUS, OHIO

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORIES OF HARVARD UNIVERSITY]

Barium Ethylene Phosphate

BY JUNJI KUMAMOTO, JAMES R. COX, JR., AND F. H. WESTHEIMER

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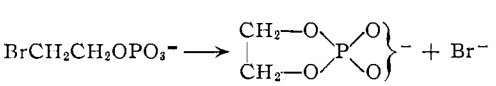
The barium salt of ethylene phosphate has been prepared from barium bromoethyl phosphate. Salts of ethylene phosphate undergo hydrolysis in alkaline solution to salts of hydroxyethyl phosphate; the rate of the reaction is almost ten million times that for the corresponding hydrolysis of salts of dimethyl phosphate.

A series of recent investigations[1] have shown that five-membered cyclic phosphate esters are intermediates in the hydrolysis of ribonucleic acids. These cyclic phosphates rapidly hydrolyze to open-chain monoesters of phosphoric acid.[1,2] However, qualitative data[3] suggest that most diesters of phosphoric acid are relatively resistant to alkaline hydrolysis. The cyclic phosphate esters previously[1,2] examined contained at least one additional hydroxyl group. In order to investigate further the peculiarities of five-membered cyclic phosphate esters, the simplest member of the series, ethylene phosphate (I) has been synthesized according to equation 1, and the rate of its hydrolysis has been compared to that for dimethyl phosphate.


(1)

I

Experimental

Barium bromoethyl phosphate was synthesized by Flexser's modification[4] of Outhouse's procedure.[5] Eleven g. of water was slowly introduced into 110 g. of phosphorus oxychloride. After the initial reaction subsided, the mixture was cooled to 0°, and 100 g. of ethylene bromohydrin was slowly added. The reaction mixture was warmed under vacuum for a half an hour to remove hydrogen chloride. The product (about 100 cc.) was again cooled to 0°, and added in small portions to 100 cc. of cold water in a large porcelain mortar. Between each addition of the phosphate ester mixture, solid $Ba(OH)_2 \cdot 8H_2O$ was added, and ground in the mortar until it reacted; the *p*H was maintained around 8–9 (external indicator). The mixture was filtered, and the filtrate discarded. Barium bromoethyl phosphate was leached from the wet filter cake with successive 100-cc. portions of water. An equal volume of ethanol was added to the aqueous extracts; the desired salt precipitated from the aqueous alcohol. After six extractions, the yield was 30 g., or about 12%. The compound could be recrystallized from water by the addition of alcohol.

Anal. Calcd. for $C_2H_4BrPO_4Ba \cdot H_2O$: C, 6.70; H, 1.68; Br, 22.31. Found: C, 7.14; H, 1.70; Br, 22.66.

This salt (the monohydrate) had previously been obtained by another method.[6]

Barium Ethylene Phosphate.—Barium bromoethyl phosphate (6.5 g.) was dissolved in 100 cc. of water, and warmed to 75° for 15 minutes. During this interval, the *p*H was maintained at 7.0 with barium hydroxide added by means of

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