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The Preparation and Properties of the Twelve-Membered Ring Hexametaphosphate Anion

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A true hexametaphosphate anion was prepared and some of its physical properties were measured. The hydrolysis rates for the ring opening to sodium hexapolyphosphate were determined at 30 and 60° at pH values of 4, 7, and 11. X-Ray powder patterns were obtained for the following salts: $Na_6P_6O_{18}$, $Na_6P_6O_{18} \cdot 6H_2O$, $Li_6P_6O_{18}$, and $Li_6P_6O_{18} \cdot 6H_2O$.

Introduction

Sodium phosphate glasses have been referred to as sodium hexametaphosphates for over 100 years.[1] The phosphate glasses are not pure compounds but mixtures with a wide distribution of molecular weights, and most of the molecules in the glass belong to the polyphosphate system rather than the metaphosphate system.[2] To refer to sodium phosphate glasses as sodium hexametaphosphate is a double misnomer, since the phosphate glasses are neither metaphosphates nor pure hexamers. The name has persisted because no method has been known for the preparation of useful quantities of a true hexametaphosphate. Sodium hexametaphosphate is, however, a minor constituent of sodium polyphosphate glasses.[3] It has been very recently reported that a crystalline sodium hexametaphosphate can be extracted from the sodium phosphate glasses.[4] The work reported here not only confirms the fact that a true crystalline hexametaphosphate does exist, but moreover discusses yet another source of the salt.

The hexametaphosphate reported here was discovered in the lithium phosphate system as a submerged phase. The salt is a minor constituent (5 to 20%) of lithium phosphate systems with a Li_2O/P_2O_5 ratio near 7:5 when the systems are prepared at temperatures below 300°. Since most of the confusion about the hexametaphosphate anion has resulted from work on the erroneous "sodium hexametaphosphate," the true crystalline sodium hexametaphosphate was prepared and the sodium salt will receive as much attention as the parent compound, lithium hexametaphosphate.

The lithium phosphates have been the subject of several recent investigations, but the existence of the hexametaphosphate has not been reported.[5] This has probably resulted from the fact that the salt can be most easily prepared and extracted as a pure phase from the mid-range of the $LiPO_3$–$Li_4P_2O_7$ phase system and would not appear as a defined phase in the phase diagram. Most of the other work on the lithium system has centered about the $LiPO_3$ composition.

Experimental

The Preparation of Sodium Hexametaphosphate Hexahydrate.—Lithium hexametaphosphate was prepared by first mixing 115.3 g. of 85% H_3PO_4 and 51.7 g. of Li_2CO_3. When the reaction subsided, the slurry was transferred to a platinum dish and heated in a muffle furnace at 200° for 1 hr. The temperature of the furnace was increased to 275° and the sample was heated at this temperature for 5 hr.

The phosphate was removed from the furnace and a 0.2-g. sample was taken for analysis by paper chromatography. If pyro- and hexametaphosphate were the only two spots on the chromatograph, the reaction was complete. If, however, longer chain phosphates were evident, the phosphate was heated for 2 hr. more at 275°. When the reaction was complete the phosphate was ground to a powder and added to 800 ml. of water. The slurry was stirred for 15 min. and then the solids were filtered from the solution. The solution contained only pyro- and hexametaphosphate.

The solution was passed through a column containing at least 500 ml. of a strong acid ion-exchange resin in the hydrogen form. The solution was neutralized with sodium carbonate until the pH was between 5 and 6. Sodium hydroxide was not used in the neutralization because it generates excessive heat during the reaction. Methyl alcohol (300 ml.) was slowly added (acetone does not yield a good crystal) to the solution, allowing the system to nucleate. The first substance to crystallize was sodium hexametaphosphate hexahydrate. More methyl alcohol was added if it was judged that the sodium hexametaphosphate precipitation was incomplete. Care was taken not to add an excessive quantity of methyl alcohol, however, because the sodium pyrophosphate will precipitate also. The advent of sodium pyrophosphate precipitation was easily checked by observing the crystals of the slurry with a microscope. The sodium hexametaphosphate appeared as parallelograms while the pyrophosphate precipitated as the characteristic monoclinic needles.

After the sodium hexametaphosphate was precipitated it was filtered from the solution and air dried. The percentage pyrophosphate in the sample was determined by an end group titration. The hexametaphosphate contains no weakly acidic groups and titrates as the salt of a strong acid. If the phosphate contained an excessive quantity of pyrophosphate, the purity was improved by redissolving and reprecipitating the hexametaphosphate with methyl alcohol. The yield was usually about 10 g. of sodium hexametaphosphate hexahydrate, but yields as large as 15 to 20 g. have been obtained.

The identity of the phosphate was confirmed with a two-dimensional chromatograph[6] as well as by X-ray powder patterns. The percentage phosphorus in the compound was determined by titration after hydrolysis[7] and the water of crystallization was

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(1) T. Fleitmann, *Ann. Physik*, **78**, 233, 338 (1849).
(2) J. R. Van Wazer, *J. Am. Chem. Soc.*, **72**, 647 (1950).
(3) J. R. Van Wazer and E. Karl-Kroupa, *ibid.*, **78**, 1772 (1956).
(4) E. Thilo and U. Schulke, *Angew. Chem.*, **75**, 1175 (1963).
(5) M. M. Markowitz, H. Stewart, and D. A. Boryta, *Inorg. Chem.*, **2**, 768 (1963); M. M. Markowitz, R. F. Harris, and W. N. Hawley, *J. Inorg. Nucl. Chem.*, **22**, 293 (1961); F. Kasparek, *Montash. Chem.*, **92**, 1023 (1961); E. Thilo and H. Grunze, *Z. anorg. allgem. Chem.*, **281**, 262, 284 (1955).
(6) E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956).
(7) E. J. Griffith, *ibid.*, **28**, 525 (1956).

analyzed by fusion with zinc oxide.[8] The percentage of metal oxides associated with the phosphates were analyzed by the following methods. The sodium was precipitated as sodium magnesium uranyl acetate and determined gravimetrically. The potassium was precipitated as potassium tetraphenylboron and determined gravimetrically. The lithium was determined by flame photometry and the ammonium analysis was done by the Kjeldahl method.

The most convenient method of preparing salts other than sodium is to neutralize the acidic solution of hexametaphosphate with the desired metal carbonate after the solution is removed from the ion-exchange resin. For the high purity samples used for the standard X-ray patterns, a high purity sodium salt was first obtained and the sodium salt was then re-ion-exchanged to the acid, and this acid solution was neutralized with the desired metal carbonate.

Discussion and Results

The sodium hexametaphosphate molecule is a twelve-membered ring of alternate phosphorus and oxygen atoms, and when subjected to conditions under which it hydrolyzes, the ring opens to yield the hexapolyphosphate anion. The hexametaphosphate anion is not to be confused with the apparent hexametaphosphate anions which are in reality two trimetaphosphate anions bridged through a metal oxide linkage.[9]

The proof of the hexametaphosphate structure is based upon two separate analyses—two-dimensional paper chromatography after hydrolysis and n.m.r. spectra on the unhydrolyzed salt. High-resolution P^{31} n.m.r. spectra were obtained at 24.3 Mc./sec. on concentrated aqueous solutions of the lithium and sodium salts. In both cases the spectra showed a single sharp peak with a chemical shift of $+22.5 \pm 0.2$ p.p.m. with respect to 85% H_3PO_4 as an external reference. When saturated solutions of $Na_3P_3O_9$ and $Na_4P_4O_{12}$ were added to the sample, the peak for the hexametaphosphate anion remained completely resolved and was found to lie between the peaks for $P_3O_9^{-3}$ and $P_4O_{12}^{-4}$, which appeared at +21.2 and 23.4 p.p.m., respectively. The chemical shift of the hexametaphosphate anion was independent of pH over the range pH 6 to 11 as 10% tetramethylammonium hydroxide was added to the solution.

From these n.m.r. data, the following conclusions can be drawn concerning the structure of the hexametaphosphate anion: (1) The phosphorus nuclei are all located in identical environments. (2) Both the chemical shift and the pH independence of this shift[10] are consistent with a ring phosphate of the general formula $(PO_3)_n^{-n}$, where n is other than 3 or 4.

Paper chromatographic analyses are required to determine whether the salt is a pentamer, hexamer, or higher metaphosphate. A two-dimensional chromatograph confirmed the fact that the phosphate is a metaphosphate of higher molecular weight than tetrametaphosphate, and the location of the developed spot narrowed the possibilities to either pentametaphosphate or hexametaphosphate, but since only two metaphosphates (trimeta and tetrameta) are known, R_f values are not reliable enough to distinguish between pentameta- and hexametaphosphate. A 1% solution of the phosphate was prepared and twice the quantity of sodium hydroxide necessary to neutralize the acid formed during the hydrolytic ring opening of the metaphosphate was added to the solution. The phosphate was allowed to hydrolyze at room temperature, and the course of the reaction was followed with two-dimensional paper chromatography. The hydrolysis products are polyphosphates and these can be easily identified because reliable R_f values and internal standards are available. The first chromatographs showed only a metaphosphate spot. After an elapsed time of 3 weeks the chromatographs showed the metaphosphate spot and six polyphosphate spots corresponding exactly to ortho-, pyro-, tri-, tetra-, penta-, and hexapolyphosphates. The chromatographs were clean between the hexapolyphosphate spot and the origin. Each time the analysis was repeated the results were the same. The phosphate is a hexametaphosphate.

Properties of the Hexametaphosphate.—The lithium and sodium hexametaphosphates are well-defined crystalline salts. When precipitated from aqueous solutions with methyl alcohol the hexahydrates of both salts are obtained, $Li_6P_6O_{18}\cdot 6H_2O$ and $Na_6P_6O_{18}\cdot 6H_2O$. When either of these hydrates is heated above 120°, the corresponding anhydrous hexametaphosphates, $Li_6P_6O_{18}$ and $Na_6P_6O_{18}$, are obtained without decomposing the phosphate rings.

Anal. Calcd. for $Na_6P_6O_{18}\cdot 6H_2O$: Na_2O, 25.83; P_2O_5, 59.15; H_2O, 15.02. Found: Na_2O, 25.12; P_2O_5, 59.23; H_2O, 15.54. Calcd. for $Li_6P_6O_{18}\cdot 6H_2O$: Li_2O, 13.78; P_2O_5, 68.29; H_2O, 17.23. Found: Li_2O, 14.37; P_2O_5, 68.40; H_2O, 17.71.

Crystalline ammonium hexametaphosphate and crystalline potassium hexametaphosphate have also been prepared from the lithium hexametaphosphate. The identity of the phosphate anion was established to be the hexametaphosphate by paper chromatography, but the exact compositions of the ammonium salts have not yet been completely established because of difficulties in obtaining reproducible analyses of the ammonium salts. The potassium hexametaphosphate has been isolated only as the anhydrous crystalline salt, $K_6P_6O_{18}$. Both the ammonium and potassium salts lack the thermal stability of the sodium and lithium hexametaphosphates.

Anal. Calcd. for $K_6P_6O_{18}$: K_2O, 39.89; P_2O_5, 60.11. Found: K_2O, 38.99; P_2O_5, 60.95.

The anhydrous lithium hexametaphosphate exhibits a remarkable thermal stability for a twelve-membered ring. It may be heated to 550° without destroying the structure. A differential thermal analysis of the lithium hexametaphosphate showed no thermal activity until the phosphate reached a temperature of 550°, where a weak endotherm was recorded. This was followed by an exotherm which peaked near 630°. To check the validity of the analysis, a sample of $Li_6P_6O_{18}$ was heated to 500° and then analyzed by paper chromatography.

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[8] E. J. Griffith and C. F. Callis, *J. Am. Chem. Soc.*, **81**, 833 (1959).

[9] G. W. Morey, *ibid.*, **74**, 5783 (1951); E. J. Griffith, *Inorg. Chem.*, **1**, 962 (1962).

[10] M. M. Crutchfield, C. F. Callis, R. R. Irani, and G. C. Roth, *ibid.*, **1**, 813 (1962).

The chromatograph showed that the hexametaphosphate had not been degraded at 500°.

Despite the fact that lithium hexametaphosphate is stable, all attempts to seed a melt having a $LiPO_3$ composition with crystalline lithium hexametaphosphate failed to yield lithium hexametaphosphate in large quantity. When a lithium phosphate glass with a metaphosphate composition is tempered at 400°, it crystallizes to $Li_4P_4O_{12}$, lithium tetrametaphosphate.

The *d* spacings obtained from X-ray diffraction powder patterns are compiled in Table I. The *d* spacings are arranged in descending order of their relative intensities. These values were taken from the best patterns obtained in this work, but the relative intensities are considered to be only approximately in the correct order and are surely subject to improvement. All of the hexametaphosphates (including the lithium salt) used in the X-ray work were obtained from the sodium hexametaphosphates by the ion-exchange technique. This was done because the best criterion of purity had been established for the sodium salt and the conversions of the sodium salt to the other systems were straightforward and trouble-free.

TABLE I

X-RAY POWDER PATTERN DATA for HEXAMETAPHOSPHATE,[a] Cu $K\alpha_1$ RADIATION

Substance	*d*, Å.
$Li_6P_6O_{18} \cdot 6H_2O$	4.392
	6.910
	5.534
	3.398
	2.957
$Li_6P_6O_{18}$ (anhydrous)	4.766
	3.690
	4.643
$Na_6P_6O_{18} \cdot 6H_2O$	3.587
	4.924
	5.092
	3.299
	7.190
$Na_6P_6O_{18}$ (anhydrous)	4.595
	2.688
	5.639
	4.350

[a] Arranged in descending order of approximate relative intensities.

Hydrolysis Rates.—The sodium hexametaphosphate was allowed to hydrolyze at pH values of 4, 7, and 11 and at temperatures of 30.0 and 60.0°. The solutions were prepared by dissolving 2.5 g. of $Na_6P_6O_{18} \cdot 6H_2O$ in 50 ml. of distilled water. No swamping electrolyte was added to the system as in previous work.[11] The pH of the solutions was adjusted with sodium hydroxide or hydrochloric acid as required. Analyses of the phosphate solutions were made by paper chromatographic methods.[12]

The hexametaphosphate anion is very resistant to hydrolysis in the pH range from 4 to 11 at both 30 and 60°. The first-order specific rate constants for the hydrolytic degradation of the hexametaphosphate anion are shown in Table II. The hydrolysis process is characterized by a very low energy of activation when compared to the values for other condensed phosphates. An activation energy near 20 kcal. has been considered normal for the scission of a P–O–P linkage. This decreased influence of temperature may perhaps be attributed to the flexible nature of large rings and their ability to distribute and transfer energy without rupturing the ring.

TABLE II

THE FIRST-ORDER RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE HYDROLYTIC DEGRADATION OF SODIUM HEXAMETAPHOSPHATES

	Values of 10^9k, sec.$^{-1}$		
Temp., °C.	pH 4	pH 7	pH 11
30	5.8 ± 2.7	6.0 ± 2.0	5.3 ± 1.2
60	21 ± 2	15 ± 5	16 ± 4
Δ*E*, kcal.	9	6	6

The rate constants were calculated by the least-squares method using an average of ten analytically determined points per curve and the estimated errors in the rate constants were calculated at the 95% confidence limit. The logarithm of the concentrations of the hexametaphosphate ion was graphed *vs.* time and a straight line was obtained from the data taken over a 1-year period. Therefore, the reaction was followed for less than one half-life in each case.

The indifference to changes in pH was also unexpected. The rate constants at 30 or 60° and pH values of 4, 7, and 11 are all the same value at 30 or 60° within the reliability of the analytical methods used in this work. In an effort to obtain differences in the values that were meaningful, the course of the hydrolysis was followed by analyses for almost 1 year, but the differences were less than the errors in the analyses.

Under the conditions chosen for the hydrolysis study the polyphosphates hexa-, penta-, tetra-, tri-, and pyrophosphate remain at low concentrations throughout the course of the hydrolysis. In no case did the concentration of a single degradation product exceed more than 1.0% of the total phosphorus in the system, except for a continual buildup of orthophosphate, of course.

As noted earlier, high yields of hexa- and penta-polyphosphates can be obtained from solutions of sodium hexametaphosphate to which an excess of NaOH has been added. Since the concentration of the degradation products remained low during the reaction, no attempt was made to follow their formation and degradation during this work. The hydrolysis of the pure polyphosphate in the range from penta- to deca-polyphosphate will be dealt with under more suitable conditions in a forthcoming article.

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