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New Sodium Phosphates[1,2]

BY EDWARD J. GRIFFITH

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Orthophosphoric acid reacts with monosodium orthophosphate at elevated temperatures to form melts of acid metaphosphates. When properly seeded, these melts yield a new variety of crystalline phosphates which have the general formula $M_xH_y(PO_3)_{x+y}$, where M is one equivalent of metal ion. The following new compounds were prepared: $Na_2H_2(PO_3)_4$, $Na_2H(PO_3)_3$, $[Na_3H(PO_3)_4]_n$, $Na_2(NH_4)_2(PO_3)_4$, $CaNa_2(PO_3)_4$ and $K_2Na_2(PO_3)_4$, and some of their properties were studied. The $Na_2H(PO_3)_3$ exists in two crystalline modifications. One form is soluble in water, and the other is not. A phase study was made of the $Na_2O-H_2O-P_2O_5$ system, showing the various phase transformations which occur.

Introduction

When orthophosphoric acid is heated between 200 and 300°, it undergoes a condensation polymerization to form condensed phosphoric acids and water vapor. Prolonged heating at 300° yields a phosphoric acid containing approximately 88.7% phosphoric oxide. As the reaction temperature is raised above 300°, more water is liberated; at temperatures above 800°, a product is obtained that contains as much as 92% phosphoric oxide.[3]

In the latter composition, there is less than one hydrogen atom per phosphorus atom in the melt, whereas the product formed near 300° contained at least one hydrogen atom per phosphorus atom. More energy is, therefore, required to polymerize a metaphosphoric acid to a branched or cross-linked polymer than is required to condense an orthophosphate to the metaphosphate composition. The thermal dehydration of phosphoric acid to the anhydride, P_4O_{10}, has never been reported in the literature.

One can take advantage of the above facts to prepare crystalline acid metaphosphate salts. They are prepared by heating mixtures of acidic phosphates, in which the M_2O/P_2O_5 ratio is less than unity, until the M_2O-H_2O/P_2O_5 ratio equals unity. [For simplicity, M will refer to one equivalent of cation exclusive of hydrogen cations throughout this article. Throughout this article H_2O will refer to water of composition rather than water of crystallization unless otherwise stated.] The temperature of the reaction must be high enough to cause the phosphate to polymerize but must not be so high as to drive out enough water to cause branching in the phosphate if the desired product is an acid metaphosphate. Figure 1 is the base plane of the three-dimensional phase diagram of the $Na_2O-H_2O-P_2O_5$ system. It is a composition diagram. It will be noted that the acid metaphosphates lie on the line separating the ultraphosphate region from the polyphosphate region. The ultraphosphates are cross-linked[4] and branched structure while the polyphosphates are linear chain molecules. The metaphosphates are ring compounds.[5]

Experimental

The Preparation of $Na_2H_2(PO_3)_4$.—Mix 138.0 g. of $NaH_2PO_4 \cdot H_2O$ with 115 g. of 85% orthophosphoric acid contained in a platinum dish. Place the dish in a cool muffle furnace, and raise the temperature of the furnace to 500° during a period of about one hour and hold the temperature at 500° for one hour. Lower the temperature of the furnace to 300°, and the clear melt crystallizes within *ca.* 12 hours. It has been found that the crystallization process is hastened if the melt is chilled to a glass and the glass tempered at 250°. If the melt does not crystallize, it may be seeded by passing the current from a three-volt, dry-cell battery through a slightly supercooled melt for about five minutes. Platinum electrodes are used in passing the current through the melt. After crystallizing, remove the sample from the furnace, grind it to a powder, and wash the powder with *ca.* 100 ml. of water for each 100 g. of product. Filter the sample in a Buchner funnel and wash it with 100 ml. of acetone for each 50 g. of product. The sample may be dried at 100°.

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(1) E. J. Griffith, THIS JOURNAL, **76**, 5892 (1954).

(2) Presented before the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, April, 1955.

(3) E. H. Brown and C. D. Whitt, *Ind. Eng. Chem.*, **44**, 615 (1952); G. Tarbutton and M. E. Deming, THIS JOURNAL, **72**, 2086 (1950).

(4) J. R. Van Wazer and E. J. Griffith, *ibid.*, **77**, 7140 (1955).

(5) J. R. Van Wazer and K. A. Holst, *ibid.*, **72**, 639 (1950).

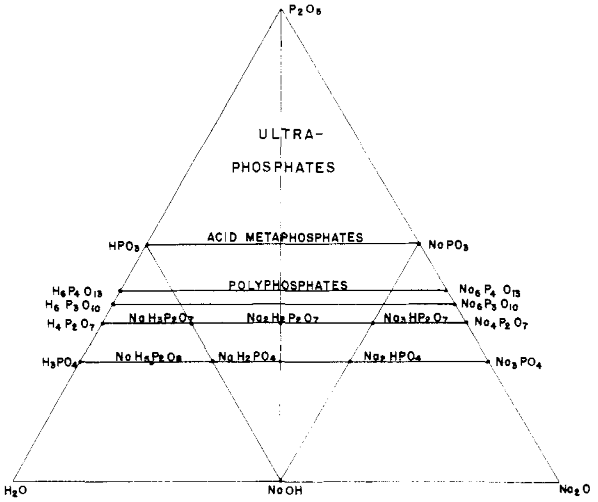

Fig. 1.—A composition diagram of the Na_2O–H_2O–P_2O_5 system.

The entire sodium acid metaphosphate system is highly susceptible to preferential crystallization if seeds of another phase are present. The platinum ware must be boiled in an acidic aqueous solution between each preparation if pure compounds are to be obtained.

ANALYSIS OF $Na_2H_2(PO_3)_4$

	Calcd. as $Na_2H_2(PO_3)_4$	Found by anal.
% P_2O_5	78.0	78.1
% H_2O	4.9	4.9
% Na_2O (by difference)	17.1	17.0

Preparation of $Na_2H(PO_3)_3$.—Disodium monohydrogen metaphosphate may be made by a procedure similar to the procedure outlined above, but it has been found that a more trustworthy method involves the reaction of $Na_2H_2(PO_3)_4$ and $Na_3P_3O_9$ (sodium trimetaphosphate).

Mix 182 g. of $Na_2H_2(PO_3)_4$ and 102 g. of $Na_3P_3O_9$ in a platinum dish. Heat the mixture for 1 hour at 600° and then reduce the temperature of the furnace to 350° and allow the sample to crystallize at this temperature for 24 hours.

It is not practical to wash the disodium monohydrogen trimetaphosphate free of glass because of the rapid solubility of $Na_2H(PO_3)_3$-I. (Hereafter, "I" will refer to the soluble form of $Na_2H(PO_3)_3$.) Sometimes a second insoluble form, $Na_2H(PO_3)_3$-II, of this salt is obtained when crystallization is allowed to take place near 200°. The second form is difficult to prepare in a pure condition, however. The most reliable method of obtaining it is by quenching a melt obtained during the preparation of form I and tempering the glass thus obtained at 200° for several days. The crystalline product thus obtained is then ground to a powder and washed with 100 ml. of water per 20 g. of salt. This is best done by stirring the salt and water together for 24 hours, filtering off the liquid phase and air-drying the resulting salt. The yield from this reaction seldom exceeds 10% of theory.

ANALYSIS OF $[Na_2H(PO_3)_3]_n$

	Calcd. as $Na_2H(PO_3)_3$	Found by anal. Soluble form I	Found by anal. Insoluble form II
% P_2O_5	75.0	75.4	75.2
% H_2O	3.8	3.6	3.5
% Na_2O	21.2	21.0	21.3

Preparation of $[Na_3H(PO_3)_4]_n$.—Mix 138.0 g. of $NaH_2PO_4 \cdot H_2O$ with 38.4 g. of 85% H_3PO_4 in a platinum dish. Heat the mixture to 600° for one hour, and reduce the temperature to 350°. The clear liquid melt will crystallize in about 12 hours at this temperature. The compound is insoluble in water and may be freed of any glassy material by washing it with distilled water. A single crystal X-ray analysis of this compound suggests that the formula should be $[Na_4H(PO_3)_5]$; but since the chemical analysis consistently agreed with the formula $[Na_3H(PO_3)_4]_n$, it was retained despite the fact that this formula could be in error. The differences in the percentages of P_2O_5, Na_2O and H_2O in the two formulas are not much greater than the errors in the analyses, however.

ANALYSIS OF $[Na_3H(PO_3)_4]_n$

	Calcd. as $Na_3H(PO_3)_4$	Found by anal.
% P_2O_5	73.6	73.6
% H_2O	2.3	2.3
% Na_2O	24.1	24.1

X-Ray and Crystal Data.—The X-ray analyses of the samples were obtained with a General Electric XRD-3 X-ray unit using a nickel filter and copper $K\alpha$ radiation. The data were taken from samples which had been ground and then screened through a 400-mesh screen. Figure 2 is a photograph of the powder patterns of the salts of the sodium acid metaphosphate system. Table I is a compilation of the crystal properties of the compounds. In no instance were the crystals suitable for obtaining interference patterns, and it is for this reason that this information was not included.

Other Sodium Acid Metaphosphate Compositions.—Compositions in which the atomic ratio of hydrogen to sodium is greater than unity could not be completely crystallized, and the crystals that were obtained from these melts always had the same composition as $Na_2H_2(PO_3)_4$ and exhibit X-ray patterns characteristic of this compound. Attempts to obtain the crystalline metaphosphoric acid reported by Rechid[6] failed. She reported a crystalline metaphosphoric acid with a melting point greater than 800°.

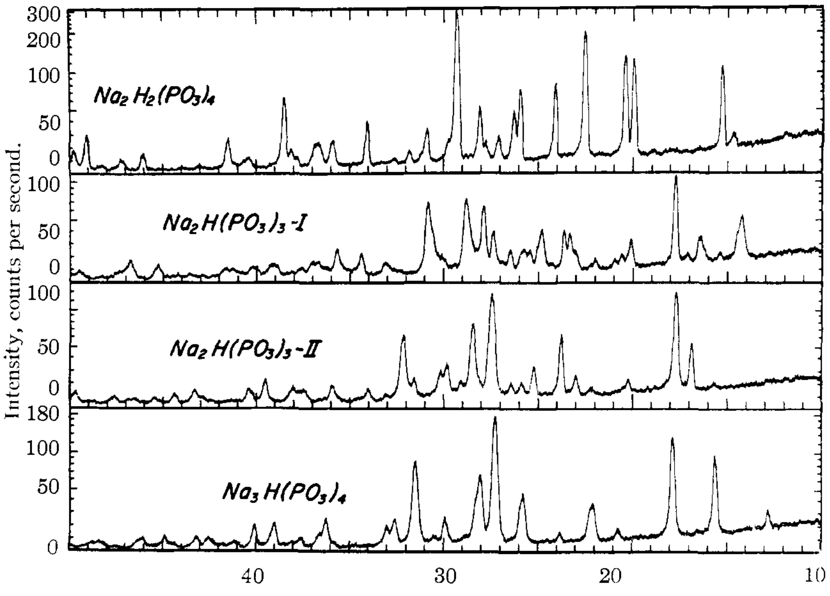

Fig. 2.—The X-ray diffraction patterns of the sodium acid metaphosphates.

A thermal analysis of the acid metaphosphate system indicates that the eutectic between $Na_2H_2(PO_3)_4$ and Na_2H-

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(6) Mme. Rechid, *Compt. rend.*, **196**, 860 (1933).

TABLE I

THE CRYSTAL PROPERTIES OF SODIUM ACID METAPHOSPHATE

	$Na_2H_2(PO_3)_4$	$Na_2H(PO_3)_2$-I	$Na_2H(PO_3)_3$-II	$Na_3H(PO_3)_4$
Color	Colorless	Colorless	Colorless	Colorless
Shape	Blade-like	Needle	Needle	Fibrous
Interference color	Highly colored	Highly colored	White	Highly colored
Extinction	Parallel	....	Parallel	Parallel to long axis when horizontal; not parallel when inclined
Extreme refractive indices	1.485–1.555	1.478–1.530	1.490–1.564	1.485–1.529
System	....	....	....	Monoclinic

$(PO_3)_2$ has the approximate composition, $P_2O_5 = 77\%$, $H_2O = 4\%$ and $Na_2O = 19\%$; while the eutectic between $Na_2H(PO_3)_3$ and $[Na_3H(PO_3)_4]_n$ has the approximate composition, $P_2O_5 = 75.7\%$, $H_2O = 3.6\%$ and $Na_2O = 20.7\%$. The samples prepared with ratios of hydrogen to sodium atoms less than $^1/_5$ resulted in either insoluble sodium metaphosphate or sodium trimetaphosphate or both, as the principal crystalline components, when determined by X-ray analyses.

Preparation of $Na_2(NH_4)_2(PO_3)_4$.—Dissolve 20 g. of $Na_2H_2(PO_3)_4$ in about 100 ml. of water containing 10% excess of the stoichiometrical quantity of ammonium hydroxide required to neutralize the acidic phosphate. Then slowly add methanol to this solution until no more precipitate forms upon the addition of 5 ml. of methanol to the solution. The product is a white, crystalline, water-soluble solid. Two other compounds were made by a similar procedure. $CaNa_2(PO_3)_4$ and $K_2Na_2(PO_3)_4$ were prepared by adding either CaO or KOH to a solution of $Na_2H_2(PO_3)_4$ and precipitating the salts with methanol. Each of the three salts has a unique X-ray pattern. It should be possible to prepare the mixed-cation salt of any metal, provided the mixed-cation salt is less soluble in methanol-water mixtures than is either of the normal salts [*e.g.*, $Na_4(PO_3)_4$ or $M_4(PO_3)_4$].

Analyses of Phosphates.—The percentage of phosphoric oxide contained in the samples was obtained by first boiling a weighed sample of the respective phosphate in 1 *N* hydrochloric acid for 12 hours in a flask equipped with a reflux condenser.[7] (The more rapid method of hydrolysis reported by the author was also employed.) Then the sample was titrated as orthophosphate with sodium hydroxide. The Precision-Dow Automatic Titrometer was used throughout the work.

The water content was determined by first firing a porcelain crucible containing 2 g. of C.P. zinc oxide at 600° until a constant weight was obtained. Then a 1-gram sample of powdered phosphate was weighed into the crucible and mixed with zinc oxide. The sample was fired at 550° until a constant weight was obtained. The loss of weight was calculated as water.

The sodium oxide content was obtained by difference or, in a few instances, by magnesium uranyl acetate precipitation.[8]

Phase Studies.—An approximate phase diagram was prepared for the $NaPO_3$–HPO_3 system (see Fig. 3) from thermal analyses data, X-ray data and chemical analyses. The direct thermal analyses were obtained exclusively from heating curves because the acid metaphosphates crystallize too slowly to obtain cooling curves from their melts. A microscope furnace of the type described by Partridge, Hicks and Smith[9] was also used to supplement the thermal curves.

The heating curves were obtained with a Minneapolis Honeywell Instrument Company two-point automatic temperature recorder. The recorder was wired to a pair of thermocouples in such manner that one point recorded the temperature of the phosphate being heated, while the second point recorded the differential temperature between the phosphate sample and the wall of an alundum crucible[9] which contained the platinum crucible, which in turn contained a 10-g. sample of powdered phosphate. A pot-type muffle furnace was used to heat the samples. The furnace was equipped with a variable transformer to regulate the rate of heating.

The microscope furnace was used only in a qualitative manner because the temperatures of fusion found by the microscope furnace technique were not very reproducible. Errors as large as 20° for a melting point were not uncommon.

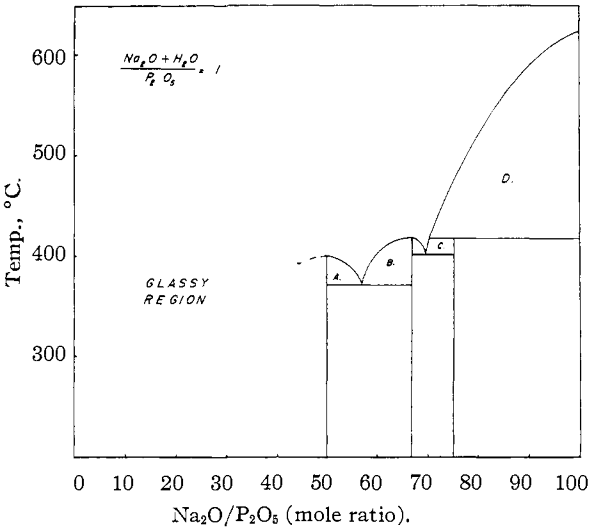

Fig. 3.—A phase diagram of the sodium acid metaphosphate system: area A contains $Na_2H_2(PO_3)_4$ plus liquid; area B contains $Na_2H(PO_3)_3$ plus liquid; area C contains $Na_3H(PO_3)_4$ plus liquid; and area D contains $[NaPO_3]$ plus liquid.

The sodium acid metaphosphates are not very stable near the temperature of fusion. Any of the compounds in the system will convert to insoluble sodium metaphosphate and an ultraphosphate glass when heated at temperatures just below their melting points for several weeks. A Chevenard thermobalance was used to determine the loss of weight of the pure compounds during heating. If a sample is heated at a heating rate of 50°/hr. until a temperature of 500° is reached, the loss of weight is less than 5% of the total weight of water of constitution of the sample. But when the sample is held at 500° for several hours, considerably more of the weight is lost. This means that in order for the phase diagram, Fig. 3, to be strictly correct, the vapor phase should have been considered.

Properties of the Soluble Acid Metaphosphate Salts.—$Na_2H_2(PO_3)_4$ is a white crystalline compound. It is slowly soluble in water, yielding an acidic solution. A 1% solution of $Na_2H_2(PO_3)_4$ has a *p*H of 1.3. When an aqueous solution is neutralized with sodium carbonate and methanol is added to the solution, a nearly quantitative yield of the well-known $Na_4P_4O_{12}\cdot4H_2O$ is obtained. Laboratory quantities of tetrametaphosphate have been prepared in this way, and it is an easy way to prepare pure tetrametaphosphate. The sodium tetrametaphosphate tetrahydrate was identified by X-ray analyses. This is accepted as proof of the structure and molecular weight of $Na_2H_2(PO_3)_4$. It is disodium dihydrogen tetrametaphosphate.

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[7] J. R. Van Wazer, E. J. Griffith and J. R. McCullough, *Anal. Chem.*, **26**, 1755 (1954); E. J. Griffith, *ibid.*, **28**, 525 (1956).

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

[9] E. P. Partridge, V. Hicks and G. W. Smith, *ibid.*, **63**, 454 (1941).

Disodium dihydrogen tetrametaphosphate has an X-ray pattern unlike any sodium phosphate previously reported in the literature. It melts near 400°; if the melt is quenched between cold copper plants, a transparent glass is obtained. The glass is much more hygroscopic than the crystalline compound.

$Na_2H(PO_3)_3$-I has properties similar to $Na_2H_2(PO_3)_4$. When methanol is rapidly added to an aqueous solution of the soluble form of $Na_2H(PO_3)_3$, a thick filterable gel-like material is obtained. All of the compositions in the range $0.67 \leq Na_2O/P_2O_5 < 0.75$ exhibit this gel-like formation when methanol is added to an aqueous solution of the salt. The filtered gels are flammable, owing to the very large quantity of methanol contained in them. A fresh precipitate may contain more than 50 weight per cent. methanol even though the sample was precipitated from aqueous solution. If a solution of $Na_2H(PO_3)_3$ is neutralized with NaOH and very slowly precipitated from solution, a white crystalline precipitate is obtained which has an unidentifiable X-ray pattern, but a paper chromatographic analysis of the sample indicates it is sodium trimetaphosphate. This is tentatively accepted as proof that the formula of the salt is $Na_2H(PO_3)_3$. This is in line with the very low intrinsic viscosity of a solution of $Na_2H(PO_3)_3$. The intrinsic viscosity of the solution was too low to be measured accurately.

The crystals formed throughout the entire sodium acid metaphosphate system are of a more or less fibrous nature. This seems to be contradictory to the conclusion that two of the anions of the acid metaphosphate system are of relatively low molecular weight. There is a possibility that the structure reorganizes upon dissolving in water, but this is not believed to be the case. At any rate, the aqueous solutions of the two soluble sodium acid metaphosphates behave as though they were derived from salts of simple anions.

Acknowledgment.—The author wishes to express his gratitude to Dr. J. W. Edwards and Mr. Ralph Ferguson for the extensive X-ray work they did to make this work possible. They not only aided in proving that the acid metaphosphates were new inorganic compounds, but their analyses were the basis for determining the number of compounds contained in the system.

DAYTON, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LEHIGH UNIVERSITY]

The Hydration of Sodium Triphosphate

BY A. C. ZETTLEMOYER AND C. H. SCHNEIDER

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The anhydrous–hydrate transformation of the two crystalline forms of sodium triphosphate was studied by means of "hydration" vapor pressure and rate of hydration measurements at 25 and 50°. For phase I the "hydration pressures" are 10 and 41 mm. at 25 and 50°, and for phase II, 12 and 64 mm. Phase I hydrates much more rapidly than phase II under similar conditions.

It is well known that anhydrous sodium triphosphate exists in two crystalline forms. Morey and Ingerson[1] in 1944 presented crystallographic data for both phases and designated the high temperature phase as phase I and the low temperature phase as phase II. The transition temperature is said to be approximately 450°. More recently Raistrick[2] discussed an X-ray diffraction method for analyzing the two phases in a mixture. This method has been greatly improved by Mabis and Quimby.[3]

Very little work has been reported concerning differences between these two crystalline forms, except for the crystallographic data mentioned above and the work reported by Dymon and King.[4] However, recently, McGilvery[5] discussed a method for determining the relative amounts of phase I and phase II by means of the difference in their heats of hydration. Hydration of either phase at room temperature produces the hexahydrate, $Na_5P_3O_{10} \cdot 6H_2O$. Although the existence of an octahydrate has been reported,[6,7] it is now generally believed that only the hexahydrate exists.

It must be emphasized that the anhydrous-hydrate transformation is not an equilibrium process. It has not been possible to dehydrate the hexahydrate to the anhydrous salt by any simple method.[8-10] Because of the non-equilibrium conditions, the usual methods of vapor pressure determinations were not feasible. Throughout this paper the data will be designated as "hydration pressures" rather than vapor pressures in order to emphasize this fact.

Materials and Procedure

The anhydrous sodium triphosphate phases I and II were prepared by heating the purified hexahydrate to 600° for phase I and below 450° for phase II. The hexahydrate was purified by repeated crystallization from an aqueous solution of commercial triphosphate (57.5% P_2O_5, 90% tripoly-, 9.5% pyro- and 0.5% ortho-) by the slow addition of ethanol. 90% of the particles of both phases were in the

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(1) G. W. Morey and E. Ingerson, *Am. J. Sci.*, **242**, 1 (1944).

(2) B. Raistrick, *Roy. Coll. Sci. J.*, **19**, 9 (1949).

(3) A. J. Mabis and O. T. Quimby, *Anal. Chem.*, **25**, 1814 (1953).

(4) J. J. Dymon and A. J. King, *Acta Cryst.*, **4**, 378 (1951).

(5) J. R. McGilvery, ASTM Bulletin (TP89), 45, July, 1953.

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

(7) P. Bonneman-Bemia, *Ann. Chim.*, **16**, 395 (1941).

(8) O. T. Quimby, *Chem. Revs.*, **40**, 141 (1947).

(9) E. Thilo and H. Seeman, *Z. anorg. allgem. Chem.*, **267**, 65 (1951).

(10) O. T. Quimby, *J. Phys. Chem.*, **58**, 603 (1954).