[CONTRIBUTION FROM CALGON, INC.]

The Sodium Metaphosphate System. Two New Crystalline Phases of Sodium Metaphosphate Produced by Thermal Means[1]

BY ROBERT W. LIDDELL

The present contribution is primarily a study of two new forms of crystalline sodium metaphosphate obtained by a controlled crystallization from the melt. Previous investigators, with the exception of Huber and Klumpner,[2] have confined their work almost entirely to studying the more stable crystalline materials produced by molecular dehydration of monosodium orthophosphate or disodium pyrophosphate at various temperatures, ignoring the possibility of any intermediate forms.

In the study by Partridge, Hicks and Smith,[3] the following diagram showing the relationship between the various forms of sodium metaphosphate was presented.

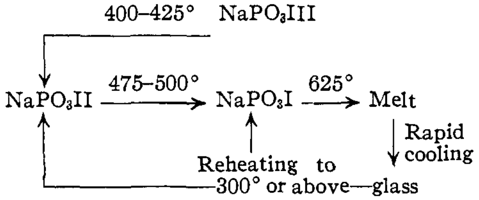

Fig. 1.—The sodium metaphosphate system according to Partridge, Hicks and Smith.

Since then the high-temperature fibrous sodium Kurrol salt has again been prepared and recharacterized by Huber and Klumpner,[2] and their results have been verified in this laboratory. Also a $NaPO_3$ (III) has been reported which has different X-ray spacings[4] than given by the above authors. The author has prepared two additional crystalline forms of sodium metaphosphate which in aqueous solutions exhibit the same properties as those of $NaPO_3$ (I), commonly referred to as trimetaphosphate. On crystallization from aqueous solution, each of these forms yields the hexahydrate of trimetaphosphate, $(NaPO_3)_3.6H_2O$, at 20°, or the monohydrate $(NaPO_3)_3.H_2O$, at approximately 40°, with mixtures of these two forms and perhaps others at intermediate temperatures.

Experimental

First New Form.—Sufficient reagent grade monosodium orthophosphate monohydrate in a platinum dish was melted in an electric muffle furnace to produce a clear melt at 750–800° about 3 mm. deep. The dish was then transferred quickly into another furnace at 500° and the furnace set on automatic control at 525°. After about ten minutes, crystallization to characteristic brilliant plates took place. After a few more minutes incipient recrystallization into the ordinary $NaPO_3$ (I) was observed. When this was noted, the dish was removed from the furnace and cooled quickly by placing it on a heavy steel plate.

TABLE I

First new phase		Second new phase		$NaPO_3I$	
I[a]	*d* in Å.	I[a]	*d* in Å.	I[a]	*d* in Å.
4	7.5	4	8.6	9	6.8
4	6.7	4	6.2	8	5.1
10	5.7	10	5.2	3	3.98
6	5.1	4	4.29	8	3.87
6	5.0	4	3.97	10	3.41
4	4.77	4	3.35	5	3.34
2	4.38	3	3.32	1	3.11
2	4.29	4	3.22	7	3.05
1	4.06	8	3.08	2	2.85
2	3.83	7	3.03	6	2.78
7	3.45	6	2.91	3	2.73
4	3.37	8	2.86	1	2.66
3	3.30	3	2.70	2	2.60
10	3.25	3	2.64	6	2.54
1	3.14	6	2.59	2	2.47
8	3.07	4	2.53	3	2.41
8	3.02	4	2.41	1	2.27
8	2.98	3	2.29	1	2.21
2	2.80	4	2.25	3	2.18
3	2.75	2	2.18	3	2.14
3	2.62	2	2.16	4	2.03
4	2.51	2	2.09	3	1.988
4	2.47	5	2.04	2	1.956
1	2.38	3	1.97	1	1.931
4	2.23	5	1.94	3	1.913
4	2.17	2	1.87	4	1.874
2	2.15	2	1.83	3	1.851
2	1.95	6	1.81	1	1.807
4	1.90	6	1.78	1	1.765
6	1.88	5	1.674	1	1.725
3	1.78	4	1.651	2	1.699
3	1.75	3	1.600	3	1.674
3	1.71	3	1.533	1	1.632
3	1.695	4	1.452	2	1.613
3	1.620	3	1.430	1	1.585
3	1.607	3	1.387	3	1.556
2	1.477	2	1.360	2	1.513
4	1.451	4	1.335	2	1.504
		3	1.285	2	1.465
		3	1.262	2	1.452
				5	1.430
				1	1.411
				1	1.390
				2	1.379
				1	1.365
				2	1.344
				1	1.332
				2	1.323
				2	1.313

[a] Relative intensities are estimated on a scale of 10, the higher figures denoting the stronger lines.

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Chicago, Ill., April, 1948.

[2] Huber and Klumpner, *Z. anorg. allgem. Chem.*, **251**, 213 (1943).

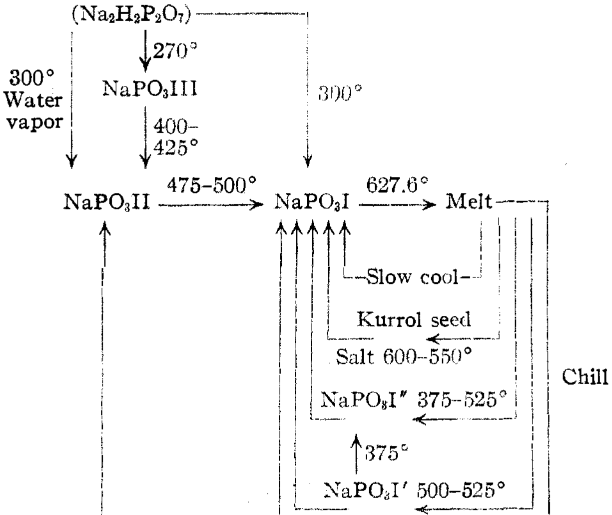
[3] Partridge, Hicks and Smith, THIS JOURNAL, **63**, 454 (1941).

[4] A. S. T. M. Card Index of X-Ray Diffraction Data, First Supplementary Set, II-1725 (1945).

It was necessary to keep the melt shallow in order to prevent excessive temperature lag with resultant inversion into $NaPO_3$ (I). The products consisted mainly of a crystalline material having maximum and minimum refractive indices of 1.500 and 1.495, together with a small amount of $NaPO_3$ (I) at the surface with indices of 1.480 and 1.474 and a little residual glass. Table I shows the X-ray spacings determined by the Debye-Scherrer powder method with a General Electric Model XRD Type I unit using a camera of 143.2 mm. diameter and copper $K\alpha$ radiation filtered through a nickel foil.

This same new crystal form was also produced from an $NaPO_3$ melt dried by heating for two hours at 1000°, which had a water content of 0.03% as determined by mixing with three parts by weight of freshly ignited anhydrous tetrasodium pyrophosphate and igniting at 1000° to constant weight. By the use of a commercial glass with an $Na_2O:P_2O_5$ ratio of 1.15, the inversion to ordinary $NaPO_3$ (I) could be inhibited for a longer time although in this case $Na_5P_3O_{10}$ (II) was formed as an impurity.

Second New Form.—The second new crystal form was obtained by placing a clear sodium metaphosphate melt at about 650° in a furnace controlled at 375°. Secondary crystallization to trimetaphosphate was not as rapid as with the first form, perhaps due to the lower temperature, but a small amount of glass in parts of the material was frequently obtained. This second new form was also produced, with $Na_5P_3O_{10}$ (II) as an impurity, from a commercial glass with an $Na_2O:P_2O_5$ ratio of 1.15 by the same controlled crystallization from the melt, or by annealing at 375° for three hours the mixture of the first new form and $Na_5P_3O_{10}$ (II), prepared as described previously. The maximum and minimum refractive indices of this second new crystal form were found to be 1.520 and 1.475. The X-ray spacings are listed in Table I. Occasionally refractive indices of 1.501 and 1.515 were obtained, but this was thought due merely to a different orientation of the crystals and not to another crystal form, since the X-ray patterns were always identical.



The sodium metaphosphate system according to the data of the present study.

There was considerable overlapping in the temperature range of formation of these two forms. The first form has been produced at temperatures of from 375° to 525°; its proportion to the second form varied with the temperature. At temperatures much above 525° it was either not produced or was too transient to be retained readily; in the lower temperature ranges it may also have been formed during the cooling process and not after the material in the platinum dish had reached the recorded temperature. The second form has been found at temperatures as high as 525°, accompanying the first form, and at temperatures as low as 350°, along with considerable residual glass, but the conditions for producing the maximum amount of the relatively pure materials are given above. More than a dozen preparations of each form were made by the preferred method and practically all of these were of the composition described.

In aqueous solution the chemical properties of both of these new crystal forms were similar to those of ordinary $NaPO_3$ (I). They did not repress calcium ion against soap, and when free from glass gave no precipitate with dilute silver nitrate or barium chloride solution. The solubility in the water was approximately that of the trimetaphosphate. These facts together with the formation of hydrates identical with those of $NaPO_3$ (I) indicate that both the first and the second new form are merely different crystal forms of $NaPO_3$ (I), which may therefore be called $NaPO_3$ (I′) and $NaPO_3$ (I″), respectively.

Sodium Kurrol Salt.—On treating a sodium metaphosphate melt at 600–550° with seed crystals as described by Huber and Klumpner,[2] long fibrous crystals of Kurrol salt having essentially the properties given by these authors were obtained. The author was unable to obtain seed crystals from an acid melt in the 650–550° range given by Huber and Klumpner and a temperature slightly below 500° gave the best results. Several attempts to prepare the Kurrol salt from a sodium metaphosphate melt without seeding were unsuccessful.

Discussion

In the present state of confusion in the nomenclature of inorganic chemistry and mineralogy and the still obscure relationships among all of the possible forms of metaphosphate, it seems unwise to attempt to change the accepted nomenclature of the known members of this series. Therefore, for this reason, the general scheme of nomenclature of Partridge, Hicks and Smith[3] will be used so far as possible, particularly since this system has been followed by Morey and Ingerson,[5] and Quimby.[6]

It has been found impossible to duplicate the $NaPO_3$ III of Partridge, Hicks and Smith,[3] and further study of their X-ray films and data by R. K. Scott of our Laboratories has led to the conclusion that their material was a mixture of $NaPO_3$ (I) and $NaPO_3$ (II). It should, therefore, be noted that the $NaPO_3$ (III) in the second diagram is not the $NaPO_3$ (III) of Partridge, Hicks and Smith.[3] The $NaPO_3$ (III) having the X-ray spacings given in the reference[4] was prepared by heating monosodium orthophosphate monohydrate to a temperature of 270 ± 5° for sixteen hours and then washing out the residual soluble material. Heating for the same period at 225 ± 5° and 245 ± 5° gave a product which was completely soluble in water. On heating, the insoluble $NaPO_3$ (III) was transformed wholly into the insoluble $NaPO_3$ (II) at a temperature of 425° and into $NaPO_3$ (I) at temperatures of 500° and above.

It is interesting to note that under apparently identical conditions of heating, varying amounts of $NaPO_3$ (I) and $NaPO_3$ (II) have been obtained from both monosodium orthophosphate and

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(5) Morey and Ingerson, *Am. J. Sci.*, **242**, 1 (1944).

(6) Quimby, *Chem. Revs.*, **40**, 141 (1947).

disodium pyrophosphate. Thus Tammann,[7] and Karbe and Jander[8] reported that the results obtained at approximately 300° were inconsistent, but could offer no explanation. Boulle[9] found that when this heating was carried out in a stream of water vapor, his form B ($NaPO_3$ (II) was produced in a pure state. Such a condition may also be approximated by rapidly heating the monohydrate of monosodium orthophosphate in a fairly thick layer to 300°. The author has found that when the reverse is true, namely, when the vapor pressure of water was low, as when anhydrous disodium pyrophosphate was sprinkled in a very thin layer in a platinum dish and introduced into a furnace at 330°, $NaPO_3$ (III) was the principal product. Intermediate conditions, as for example slow heating to 300° using a moderately thick layer of material gave $NaPO_3$ (I) as the major product.

Quite a number of chemical compounds exhibit different polymorphic forms which, however, have the same chemical properties; the metaphosphate system appears to be unique in the fact that it comprises a number of crystalline phases, some of which in aqueous solution exhibit different chemical properties, while others behave identically when dissolved.

The diagram presents the current state of information concerning the sodium metaphosphate system.

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Summary

1. Two new crystalline sodium metaphosphates have been produced which in aqueous solution behave like $NaPO_3$ I.

2. The sodium metaphosphate diagram of Partridge, Hicks and Smith has been revised to show more recent developments including those of the present study.

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[7] Tammann, *J. prakt. Chem.*, **45**, 463 (1892).

[8] Karbe and Jander, *Kolloid-Beihefte*, **54**, 9 (1944).

[9] Boulle, *Compt. rend.*, **206**, 915 (1938).

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Cuprammonium–Glycoside Complexes. I. Conductometric Measurements

BY RICHARD E. REEVES AND JULIUS R. JUNG, JR.

In the continued investigation of cuprammonium–glycoside complexes, a means other than one dependent upon optical activity was required for the recognition of these complexes. Such a method was necessary for the study of complex formation between cuprammonium and inactive glycols, as well as for those substances which, though optically active, form complexes without exhibiting large rotatory changes.

Our earlier work,[2,3] dealing exclusively with the optical method of measurements, had shown that highly active complexes form between cuprammonium and properly oriented glycol groups. It was found that such complex formation was associated with a decrease in conductivity in the cuprammonium solution; hence it was decided to follow this phenomenon by the conductometric method of measurement.

By this method many degrees of affinity for cuprammonium could be detected in the various substances tested. It was possible to distinguish the D- and L-forms of 2,3-butanediol from the *meso* variety. Various methyl α-hexopyranosides could be sharply distinguished from each other, and a difference was encountered between the complex-forming tendency of a number of α- and β-glycoside pairs. Furthermore, it was shown that the substance D-glucosan$<1,5>\beta<1,6>$ (levoglucosan) does react with cuprammonium, although on the basis of optical rotation measurements it was previously reported not to react.[4]

Experimental Part

The physical properties of all the substances employed in this investigation were in excellent agreement with the properties listed in the literature.

A stock solution containing between 5 and 8 g. of copper per liter was prepared by passing a current of air through a concentrated A. C. S. standard ammonium hydroxide solution in the presence of copper turnings. The ammonia and turnings were contained in a tall glass cylinder which was cooled in an ice-bath during the reaction. This stock solution may be preserved in the refrigerator without added stabilizer for a long time. After analysis for copper and ammonia, portions of the stock solution were diluted to contain 0.01 mole of copper (0.635 g.), 3 moles of ammonia, and 10 ml. of ethanol per liter. This standard solution, "cupra A," was employed in most of the conductivity experiments; whenever a different solution was used a notation will be made regarding its composition.

To permit the use of small amounts of glycosides very dilute cuprammonium solutions were required. The specific conductance of various ammonium hydroxide solutions with and without 0.01 molar copper are shown in Fig. 1. Inspection of this figure shows that conductance is least sensitive to ammonia concentration in the region

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] R. E. Reeves, *Sci.*, **99**, 148 (1944).

[3] R. E. Reeves, *J. Biol. Chem.*, **154**, 49 (1944).

[4] K. Hess, W. Weltzien and E. Messmer, *Ann.*, **435**, 1-144 (1924).