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Structure and Properties of the Condensed Phosphates. XVII. The Preparation and Thermal Decomposition of Sodium Acid Tripolyphosphate Salts

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The preparation of $Na_4HP_3O_{10}\cdot H_2O$ is described. The thermal decompositions of $Na_4HP_3O_{10}\cdot H_2O$ and $Na_3H_2P_3O_{10}\cdot 1.5H_2O$ have been investigated by thermogravimetric, X-ray diffraction, and ion-exchange chromatographic analyses. The salts do not undergo simple dehydration on heating, but disproportionate to form intermediate pyrophosphates, losing water in several steps. The final products from $Na_4HP_3O_{10}\cdot H_2O$ on heating to constant weight above 400° are anhydrous $Na_5P_3O_{10}$ and Maddrell's salt, $NaPO_3$, form II. The latter also is obtained by similar treatment of $Na_3H_2P_3O_{10}\cdot 1.5H_2O$.

The sodium acid salts of tripolyphosphoric acid have received little attention compared with the commercially important salt $Na_5P_3O_{10}$. Huber[1] reported the preparation of $Na_3H_2P_3O_{10}\cdot Na_5P_3O_{10}\cdot 3H_2O$ by precipitation with alcohol from an acetic acid solution of $Na_5P_3O_{10}$, but his product identification rests entirely on wet chemical analyses. The pure trisodium salt,[2] $Na_3H_2P_3O_{10}\cdot 1.5H_2O$, has been characterized by its X-ray diffraction pattern.[3]

Preliminary attempts in this Laboratory to prepare a pure tetrasodium salt, $Na_4HP_3O_{10}$, yielded a product with a unique but previously unreported diffraction pattern. The X-ray data also indicated the presence of a large amount of $Na_5P_3O_{10}\cdot 6H_2O$ as an impurity.

The purpose of this study was to isolate this unknown salt from the contaminating $Na_5P_3O_{10}\cdot 6H_2O$ and determine its composition. During the work a preparative method for high purity $Na_4HP_3O_{10}\cdot H_2O$ was developed, and the stepwise reactions involved in the thermal decomposition of the sodium acid tripolyphosphate hydrates were investigated.

Experimental Details

$Na_4HPO_3O_{10}\cdot H_2O$.—A procedure was developed for the preparation of $Na_4HP_3O_{10}\cdot H_2O$ in high purity. Monsanto technical grade $Na_5P_3O_{10}$ was recrystallized[4] four times from ethanol–water to obtain pure $Na_5P_3O_{10}\cdot 6H_2O$ as a starting material. To a slurry of 499 g. of the hexahydrate in 750 ml. of water, 208 g. of 60% $HClO_4$ (Merck) was added with vigorous stirring. This amounts to 1.2 equivalents of acid per gram-ion of tripolyphosphate. The slurry was stirred until solution was essentially complete and then filtered through a fine sintered glass funnel to remove potential seed crystals of $Na_5P_3O_{10}\cdot 6H_2O$. One hundred ml. additional water was added, and the solution was heated to 40–45°. Methyl alcohol was added slowly with stirring until faint cloudiness was apparent. At this point 0.5 g. of finely ground $Na_4HP_3O_{10}\cdot H_2O$ (previously prepared by a fractional crystallization procedure) was added as seed crystals, along with sufficient additional methanol to make a total of 900 ml. of added alcohol. Vigorous mechanical stirring induced rapid crystallization of the desired solid phase, which was filtered on a coarse sintered glass funnel and washed twice with 250-ml. portions of 50% water–methanol. The air dried product was free flowing. Total yield was 317 g. of $Na_4HP_3O_{10}\cdot H_2O$, or 82% based on the original hexahydrate.

The entire preparation was carried out as rapidly as possible to minimize hydrolysis of the tripolyphosphate ion in the acid solution at the elevated temperature. Precipitations with alcohol from stoichiometric aqueous solutions containing only one equivalent of acid per gram ion of tripolyphosphate resulted in appreciable contamination of the product with $Na_5P_3O_{10}\cdot 6H_2O$, as did attempted recrystallizations without readjustment of the *p*H to a more acid region. Addition of the methanol at room temperature rather than at 40–45° resulted in the separation of a heavy liquid phase which crystallized only with difficulty and always contained a large amount of $Na_5P_3O_{10}\cdot 6H_2O$. The purity of the $Na_4HP_3O_{10}\cdot H_2O$ was determined by standard wet chemical, ion-exchange chromatographic,[5] X-ray diffraction, and thermogravimetric analyses.

$Na_3H_2P_3O_{10}\cdot 1.5H_5O$.—Trisodium acid tripolyphosphate was prepared according to the method of Corbridge and Tromans,[3] and its X-ray diffraction pattern matched the reported one.

Thermal Decomposition.—Thermogravimetric analyses were performed on a Chevenard thermobalance manufactured by the Société Adamel, Paris, France. The bal-

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[1] H. Huber, *Z. anorg. u. allgem. Chem.*, **230**, 123 (1936).

[2] A. Boulle and C. Morin, *Compt. rend.*, **245**, 1928 (1957).

[3] D. E. C. Corbridge and F. R. Tromans, *Anal. Chem.*, **30**, 1101 (1958).

[4] J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, New York, N. Y., 1958, p. 648.

[5] R. H. Kolloff, ASTM Bulletin No. 237, 74–80 (TP94–TP100), April, 1959.

ance was connected by mechanical linkage to a strip chart recorder. The heating rate was programmed for an approximately linear temperature increase of 150° hr.$^{-1}$. The samples were uniformly ground and packed in a platinum crucible. The heating curves were reproducible for similar size samples. Separate runs were interrupted at each weight plateau on the heating curve and the sample quickly cooled by removing it from the oven. X-ray diffraction patterns were taken at room temperature on the material present at each plateau, and confirming ion-exchange analyses also were run in some cases.

Results and Discussion

Preparation and Identification.—Tetrasodium acid tripolyphosphate was prepared and identified as the monohydrate, $Na_4HP_3O_{10}\cdot H_2O$. The P^{31} nuclear magnetic resonance spectrum of a freshly prepared aqueous solution exhibited only the customary doublet and triplet peaks due to the end and middle phosphorus atoms in the tripolyphosphate anion, with no peak attributable to orthophosphate. Ion-exchange chromatographic analyses confirmed that 98% of the phosphorus was present as tripolyphosphate. The analytical data are summarized in Table I. Ignition loss always gave high water analyses, due to the tendency of the sample to sputter violently at 235–255°. The smallest ignition loss observed when sputtering was minimized was still 0.9% higher than the H_2O content by difference. The validity of the latter is reflected in the total percentage composition which is high by exactly the amount attributed to loss of solid. The higher water content of the previously reported[1] "double salt" may be due to similar difficulties or to the presence of some $Na_5P_3O_{10}\cdot 6H_2O$, which we found to form by disproportionation when $Na_4HP_3O_{10}\cdot H_2O$ is recrystallized from water. The chemical analysis plus the absence of any peaks due to either $Na_5P_3O_{10}\cdot 6H_2O$ or $Na_3H_2P_3O_{10}\cdot 1.5H_2O$ in the X-ray diffraction pattern suggests that such contamination was minimized in our preparation. The X-ray data for $Na_4HP_3O_{10}\cdot H_2O$ are reported in Table II.

TABLE I

ANALYSIS OF $Na_4HP_3O_{10}\cdot H_2O$

Analysis	Theory, %	Experiment, %
P_2O_5	58.51	58.89
Alkaline Na_2O	8.53[a]	8.02[a]
Total Na_2O	34.07	33.74
H_2O (by diff.)	7.42[a]	7.37[a]
H_2O (by ignition)	7.42	8.28
Total	100.00	100.91
Tripolyphosphate (% P)	100.0	98.0
Pyrophosphate	0.0	0.7
Orthophosphate	.0	.9
Trimetaphosphate	.0	.5
Total	100.0	100.1

[a] Not included in total.

TABLE II

X-RAY DATA FOR $Na_4HP_3O_{10}\cdot H_2O$

d, Å.	I/I_1	*d*, Å.	I/I_1	*d*, Å.	I/I_1
6.04	5	2.690	75	1.938	5
5.40	60	2.670	45	1.897	5
4.54	40	2.616	5	1.877	5
4.260	55	2.552	20	1.812	10
3.620	30	2.396	10	1.805	10
3.475	15	2.273	10	1.789	5
3.328	20	2.220	20	1.749	5
3.000	100	2.125	10	1.737	5
2.915	20	2.008	10	1.723	5
2.740	20	1.973	10	1.718	5

Radiation: Cu, Kα Filter: Ni

$\lambda = 1.542$ Å. I/I_1: By diffractometer

All the experiments which led to the preparative procedure outlined in the Experimental section suggest that obtaining a pure product of $Na_4HP_3O_{10}\cdot H_2O$ from an aqueous solution can be achieved by control of competing crystallization rates. The solution always contains in dynamic equilibrium the three anions—$P_3O_{10}^{-5}$, $HP_3O_{10}^{-4}$, and $H_2P_3O_{10}^{-3}$—each of which predominates in a different *p*H range. The solubilities of the various salts are such that if precipitation with alcohol is carried out after the addition of only one equivalent of acid per gram-ion of tripolyphosphate, where $HP_3O_{10}^{-4}$ predominates, $Na_5P_3O_{10}\cdot 6H_2O$ also will precipitate. By adjusting conditions to the acid side of $HP_3O_{10}^{-4}$, with the addition of 1.2 equivalents of acid per gram-ion of tripolyphosphate, the concentration of the least soluble species, $P_3O_{10}^{-5}$, is reduced to a point where it is less than or barely exceeds its solubility product. Then, proper seeding techniques can be used to preferentially increase the rate of crystallization of $Na_4HP_3O_{10}\cdot H_2O$ over the competing $Na_5P_3O_{10}\cdot 6H_2O$ and $Na_3H_2P_3O_{10}\cdot 1.5H_2O$. Since the rapid protonic equilibria instantly readjust the relative ionic populations of the solution as the $HP_3O_{10}^{-4}$ ion is depleted by the comparatively slow crystallization process, the rates of crystallization of the competing salts can be kept small enough to prevent significant contamination of the product.

Decomposition Studies.—Figure 1 shows thermogravimetric curves for (a) $Na_4HP_3O_{10}\cdot H_2O$, (b) $Na_3H_2P_3O_{10}\cdot 1.5H_2O$, and (c) $Na_5P_3O_{10}\cdot 6H_2O$.

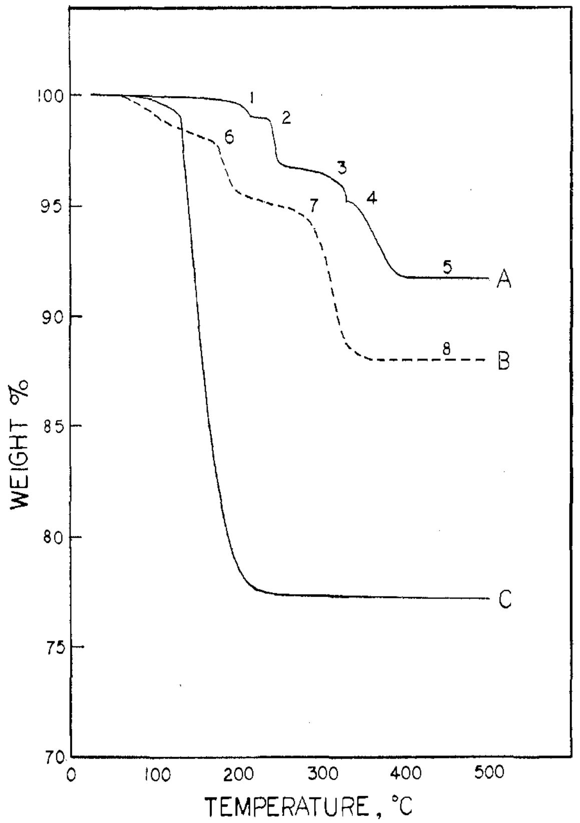

Fig. 1.—Thermogravimetric curves for (A) $Na_4HP_3O_{10}\cdot H_2O$, (B) $Na_3H_2P_3O_{10}\cdot 1.5\,H_2O$, and (C) $Na_5P_3O_{10}\cdot 6H_2O$.

The composition of the crystalline mixture at each numbered plateau was determined by X-ray diffraction of cooled samples. Ion-exchange chromatographic analyses provided an additional check on sample composition for $Na_4HP_3O_{10}\cdot H_2O$. The results are summarized in Table III.

The first two weight loss steps correspond to a total loss of approximately one-half mole of water per mole of $Na_4HP_3O_{10}\cdot H_2O$. The intermediate plateau results from melting of the salt with a resultant decrease in the rate of water loss due to reduced surface area. Vigorous boiling of the melt between 235 and 255° causes very rapid weight loss, after which the melt again solidifies. Further changes are less dramatic, with the last two breaks corresponding more or less closely to the loss of one-fourth and three-fourths of a mole of water, respectively (see Table IV). After all hydrate and bound water has been lost, above 400°, there remains a mixture of anhydrous $Na_5P_3O_{10}$ (form II) and Maddrell's salt, $NaPO_3$ (form II).[6]

The reactions are summarized as

$$\begin{array}{c}
Na_4HP_3O_{10}\cdot H_2O \xrightarrow[100-260^\circ]{-{}^1/_2H_2O} {}^1/_2Na_4P_2O_7 + Na_2H_2P_2O_7 \\[1em]
{}^1/_2Na_4P_2O_7 + {}^1/_4Na_2H_2P_2O_7 \xrightarrow[260-335^\circ]{-{}^1/_4H_2O} {}^1/_2Na_5P_3O_{10} \\[1em]
{}^3/_4Na_2H_2P_2O_7 \xrightarrow[335-390^\circ]{-{}^3/_4H_2O} {}^3/_{2x}(NaPO_3)_x \\[0.5em]
\hline \\
Na_4HP_3O_{10}\cdot H_2O \xrightarrow{-1{}^1/_2H_2O} {}^3/_{2x}(NaPO_3)_x + {}^1/_2Na_5P_3O_{10}
\end{array}$$

Ion-exchange analyses revealed small amounts of ortho- and metaphosphates which are not accounted for in this simplified mechanism. Possible reorganization in the melt, as well as the quenching rate, can affect the level of amorphous products. The major reactions, however, must be those outlined above.

Interpretation of the heating curve for $Na_3H_2P_3O_{10}\cdot 1.5H_2O$ is less straightforward than for the tetrasodium salt. X-ray analysis showed poorly crystalline products at the intermediate steps. The only crystalline product after the first break was some unchanged starting material. The second plateau showed largely amorphous products with some crystalline $Na_2H_2P_2O_7$. The final product was Maddrell's salt (form II). The total weight loss corresponds to slightly less than 2.5

TABLE III

SUMMARY OF PRODUCT IDENTIFICATION FOR THERMOGRAMS

		Composition				
			% P by ion exchange			
Curve	Step	X-ray	Ortho	Pyro	Tripoly	Meta
A	1	$Na_4HP_3O_{10}\cdot H_2O$	0.9	0.7	98.0	0.5
A	2	$Na_4P_2O_7$ + glass	3.0	92.7	4.3	0
A	3	$Na_4P_2O_7 + Na_2H_2P_2O_7$	2.0	94.7	3.3	0
A	4	$Na_5P_3O_{10} + Na_2H_2P_2O_7$	1.3	80.7	15.9	2.1
A	5	$Na_5P_3O_{10} + (NaPO_3)_x$	...	...	...	...
B	1	$Na_3H_2P_3O_{10}\cdot 1.5H_2O$	...	...	...	...
B	6	$Na_3H_2P_3O_{10}\cdot 1.5H_2O$ + amorphous	...	...	...	...
B	7	$Na_2H_2P_2O_7$ + amorphous	...	...	...	...
B	8	$(NaPO_3)_x$	...	...	...	...
C	1	$Na_5P_3O_{10}\cdot 6H_2O$	...	...	...	...

Table IV

Thermal Decomposition of $Na_4HP_3O_{10}\cdot H_2O$

Step of heating curve	% total H_2O loss			
	Theory	Experiment		
1 → 3	33	36	39	40
3 → 4	17	17	18	15
4 → 5	50	47	43	45
1 → 5	100	100	100	100

water molecules per mole, indicating that the original 1.5-hydrate is somewhat unstable to air drying. The weight loss in the initial step was smaller when samples were air dried for long periods before ignition.

The thermogravimetric curve for $Na_5P_3O_{10}\cdot 6H_2O$, shown in Fig. 1 for comparison, is not characterized by stable intermediate compositions such as those found for the corresponding acid salts.

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Phosphorus Complexes of Group III Acids. I. Boron Acids and 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

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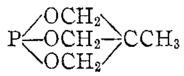
One to one complexes of the bicyclic phosphite, $CH_3C(CH_2O)_3P$, have been prepared with the acids BH_3, B_3H_7, $B(CH_3)_3$, and BF_3. The compound $CH_3C(CH_2O)_3PBH_3$ has a melting point of 199° and a measured dipole moment of 8.60 ± 0.05 D. This is in good agreement with a value estimated using additive bond moments. Trimethylamine will remove BH_3 groups from the complex to give $CH_3C(CH_2O)_3P$ and $(CH_3)_3NBH_3$. ΔH for the process: $CH_3C(CH_2O)_3P_{(s)} + B(CH_3)_{3(g)} = CH_3C(CH_2O)_3PBH_{3(s)}$ is estimated to be -14.4 ± 0.5 kcal./mole on the basis of pressure–temperature data. Comparable data for the complex $(CH_3)_3NB(CH_3)_3$ give an approximate value of -25 kcal./mole. The foregoing values suggest that $CH_3C(CH_2O)_3P$ is a weaker base toward both BH_3 and $B(CH_3)_3$ than is trimethylamine.

Introduction

The synthesis of the bicyclic phosphite ester



4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane first was reported by Verkade and Reynolds.[1] The caged structure of this molecule should lead to rather unusual behavior as a ligand and some of its rather striking transition metal chemistry has been reported by Verkade and Piper.[2] It was felt that complexes of this phosphite ester with reference acids such as BH_3, BF_3, $B(CH_3)_3$, and B_3H_7 would be of interest for two reasons. First, the consistent coördination pattern of these electron acceptors should lead to simple one to one adducts, uncomplicated by any variations in coördination number. Secondly, much already has been published in this area and comparisons with earlier work are readily available.[3-7]

Experimental

Preparation of $CH_3C(CH_2O)_3P$.—The phosphite, $CH_3C(CH_2O)_3P$, was prepared by a reaction first reported by Wadsworth and Emmons[8] but described in detail by Newman.[9] One mole of 2-hydroxymethyl-2-methyl-1,3-pro-

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(1) J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

(2) J. G. Verkade and T. S. Piper in "Advances in the Chemistry of the Coordination Compounds," S. Kirshner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 634.

(3) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *J. Am. Chem. Soc.*, **66**, 435 (1944).

(4) R. W. Parry and T. C. Bissot, *ibid.*, **78**, 1524 (1956).

(5) R. W. Parry, G. Kodama, and C. E. Nordman, WADD Tech. Rept. 60-262, Univ. of Michigan, April, 1960.

(6) T. Reetz, *J. Am. Chem. Soc.*, **82**, 5039 (1960).

(7) F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1958).

(8) W. S. Wadsworth and W. D. Emmons, Abstracts, 138th National Meeting, American Chemical Society, New York, N. Y., p. 97-P.

(9) M. S. Newman, private communication.