[CONTRIBUTION FROM THE RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL COMPANY]

The Mechanism of Formation of Sodium Triphosphate from Orthophosphate Mixtures[1]

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The condensation reactions which take place when mixtures of sodium orthophosphates, having a mole ratio Na_2O/P_2O_5 of 5/3, are heated to higher temperatures have been investigated by means of thermal analysis, X-ray diffraction, chromatographic analysis and wet-chemical analysis coupled with dehydration studies. Intimate equimolar mixtures of $NaH_2PO_4 \cdot Na_2HPO_4$ and $Na_2HPO_4 \cdot 2H_2O$, obtained as polycrystalline granules by drying of aqueous solutions, lose 3/2 moles of constitutional water when heated to 210° and change to a mixture of crystalline $Na_4P_2O_7$, and an amorphous phase. The amorphous phase is shown by combined X-ray and chromatographic analysis to be a mixture of ortho-, pyro-, tri-, ring meta-, and longer chain polyphosphates. Further heating at somewhat higher temperatures results in evolution of more water and consumption of equivalent amounts of $Na_4P_2O_7$ and the amorphous phase to give $Na_5P_3O_{10}$ (I), the high temperature form, which then changes to the low temperature form II. A mechanism is proposed which involves diffusion of only small cations and water through the amorphous phase to support the reaction. Mobile equilibrium between water and condensed phosphate ions maintains a level of orthophosphate to support the reaction $HPO_4^{2-} + HP_2O_7^{3-} \rightarrow P_3O_{10}^{5-} + H_2O$, which occurs at the growing crystal face of $Na_5P_3O_{10}$.

Introduction

Sodium triphosphate, $Na_5P_3O_{10}$, can be prepared[2] by thermal dehydration and/or fusion of various mixtures of any variety of phosphates having an over-all mole ratio, Na_2O/P_2O_5, of 5/3; however, the most efficacious method employs intimate mixtures of orthophosphates prepared *in situ* by drying appropriate solutions. Thermal dehydration of such an *in situ* mixture at temperatures between *ca.* 300 and *ca.* 600° then gives good yields of $Na_5P_3O_{10}$ without fusion of the entire mass.

$Na_5P_3O_{10}$ is bimorphic; it has low and high temperature modifications, II and I, respectively, that have, according to thermal analysis, high temperature microscopy and quench studies, a transition temperature of *ca.* 500°. This is an erratic transformation and the existence of $Na_5P_3O_{10}$-I in preparations which were never heated higher than *ca.* 400° were interpreted to mean that the transition point was considerably below 500°.

Heating of ortho mixtures to constant weight at successively higher temperatures[3] points to a mechanism involving initial condensation of pyrophosphate salts with subsequent condensation and/or reorganization to give form II. This is shown by the following equations which describe preliminary studies[3] on the thermal decomposition of some crystalline phosphates

$$2Na_2HPO_4 \cdot 2H_2O \xrightarrow{200°} Na_4P_2O_7 + 5H_2O \quad (1)$$

$$2(NaH_2PO_4 \cdot Na_2HPO_4) \xrightarrow{200°} Na_2H_2P_2O_7 + Na_4P_2O_7 + 2H_2O \quad (2)$$

$$2Na_4P_2O_7 + Na_2H_2P_2O_7 \xrightarrow{250°} 2Na_5P_3O_{10} + H_2O \quad (3)$$

In eq. 3, it should be noted that three dimeric molecules, in crystalline state as derived from reactions 1 and 2, react to give two trimeric molecules. Obviously many complex intermediate steps must be involved. It has been observed[3] that the pyrophosphates obtained *via* the reaction given in eq. 2 give much poorer yields at, say 350°, than the direct, uninterrupted heating of the ortho mixture at the same temperature.

$$NaH_2PO_4 \cdot Na_2HPO_4 + Na_2HPO_4 \cdot 2H_2O \longrightarrow Na_5P_3O_{10} + 4H_2O \quad (4)$$

It appeared then that the two-step conversion might have a different mechanism from that of the direct conversion, hence a new approach was made in which techniques of thermal-, X-ray diffraction, chromatographic- and chemical-analyses of quenched, partly reacted mixtures were combined with dehydration studies.

Experimental

Starting Materials.—In most of the experiments below the ortho mixture used was prepared by drum-drying an aqueous sodium orthophosphate solution which had a mole ratio Na_2O/P_2O_5 = 1.686 as determined by *p*H titration analysis, total P_2O_5 content of 51.98% and an ignition loss of 14%. X-Ray diffraction analysis of this mixture showed it to consist of $NaH_2PO_4 \cdot Na_2HPO_4$, $Na_2HPO_4 \cdot 2H_2O$ and anhydrous Na_2HPO_4.[4] The drum-dried mixture had the form of coarse polycrystalline aggregates ranging from less than 1 mm. to about 8 mm. Some particles were thin and flake-like while others were dense and roughly spherical.

Thermogravimetric Analysis.—A thermogravimetric apparatus was constructed in which both sample weight and temperature could be observed simultaneously and continuously during the reaction. Three or four gram samples of the orthophosphate mixture, contained in a small porcelain crucible, were suspended by a three mil tungsten wire from one arm of a chainomatic analytical balance. The suspension wire passed through the floor of the balance and through the top of a high table. A pot furnace, 3 in. in diameter by 5 in. deep, was mounted beneath the table so that it could be raised into position around the sample. The furnace could then be closed with a split cover containing a small hole through which the suspension and thermocouple wires could pass without contact. This thermocouple, made of 3 mil Pt and Pt + 10% Rh wire, was placed with its hot junction in the middle of the sample and the extension leads brought out along the suspension wire and over to a fixed support at right angles to the suspension wire. The sensitivity of the balance was about 0.3 mg. with these wires in place. The temperature was recorded continuously on a 2.5 millivolt recording potentiometer. The sample weight was obtained manually by one observer at intervals of about 5 mg. weight change, with the corresponding time in seconds being recorded by another observer. The zero of time was taken when the pre-heated furnace was raised into position around the

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[1] Presented at the 130th meeting of the American Chemical Society, Atlantic City, Sept., 1956.

[2] (a) B. Topley, *Quart. Rev.*, **3**, 345 (1948); (b) E. P. Partridge, V. Hicks and G. W. Smith, THIS JOURNAL, **63**, 454 (1941).

[3] Unpublished results, Monsanto Chemical Co.

[4] R. P. Langguth and J. W. Edwards, Monsanto Chemical Co., unpublished results. *In situ* mixtures of sodium orthophosphates, having Na_2O/P_2O_5 ratios of 5/3, made by rapid drying on steam heated flaking rolls, have been shown to consist of $NaH_2PO_4 \cdot Na_2HPO_4$ and Na_2HPO_4 (dihydrate and anhydrous) in substantial agreement with the phase diagram published by Wendrow and Kobe, *Ind. & Chem.*, **44**, 1439 (1952).

TABLE I

X-RAY ANALYSIS OF REACTION MIXTURES

$Na_2HPO_4 + NaH_2PO_4 \cdot Na_2HPO_4 \xrightarrow{250°}$

Time in furnace, min.	Composition, wt. % Na_2HPO_4	$NaH_2PO_4 \cdot Na_2HPO_4$	$Na_4P_2O_7$	$Na_5P_3O_{10}$ (I)	$Na_5P_3O_{10}$ (II)
0	34	66	..	..	..
15	8	13	49	..	..
20	..	..	66	..	..
30	..	..	51	25	..
45	..	..	26	48	2
60	..	..	19	54	26
120	..	..	8	15	63

TABLE II

COMPOSITION OF MIXTURE AT VARIOUS STAGES OF REACTION; FURNACE AT 250°

Sample	Water loss, moles	X-Ray anal., % of total P_2O_5 as: Ortho	Pyro	Tri	Chromatographic anal., % of total P_2O_5 as: Ortho	Pyro	Tri	Long chain[b]	Mol ratio ortho to amor. pyro
A	0.75	46	39	..	49.9	50.0	0.0	0.0	..
B[a]	1.50	0	63	0	9.3	86.4	3.1	1.0	0.80
C	1.55	0	62	8	6.7	86.3	6.6	0.4	.56
D	1.70	0	49	33	5.7	63.9	27.9	2.5	.72
E	1.95	0	11	83	0.4	18.6	81.0	0.1	..
F[c]	2.00	0	6	94	0.4	6.9	92.6	0.1	..

[a] According to the chromatographic analysis sample B contained 0.15% P as trimeta, an amount barely above the detection limit. [b] "Long chain" is principally tetrapoly-, containing some pentapolyphosphate. [c] F heated to constant weight at 400°.

sample. This furnace contained a large heavy-walled stainless steel crucible which surrounded the sample and thus reduced thermal gradients. The furnace was temperature controlled and kept at a fixed temperature throughout each experiment.

Prior to the construction of the thermogravimetric apparatus, thermal analysis curves on the orthophosphate mixtures were made using the same furnace but without suspending the sample from a balance.

X-Ray Diffraction Analysis.—All of the X-ray diffraction work was done using a Geiger-counter recording X-ray diffractometer (G. E. XRD-3). The X-ray analyses were made using the diffraction maxima recommended by Mabis and Quimby[5]; however, their detailed procedure was not used and therefore the results are considered semi-quantitative in nature. The accuracy is estimated to be within ±10% of the absolute value. Cu Kα radiation was used.

Chromatographic Analyses.—The products from some of the dehydration experiments were also analyzed by paper chromatography[6] using both the one- and two-dimensional techniques. The comparison of these analyses with the X-ray diffraction results helps to characterize the non-crystalline components in the samples. These chromatographic analyses are believed to be accurate to 0.5%, with a sensitivity of detection of 0.1%.

Results and Discussion

The steps involved in the thermal conversion of an orthophosphate mixture ($Na_2O/P_2O_5 = 1.686$) to sodium tripolyphosphate were first determined by analysis of quenched two-gram portions that had been heated for various periods of time at several different temperatures. Typical X-ray diffraction data, showing the variation of composition with time in the temperature range 225 to 300°, are illustrated by the results at 250° given in Table I. These data clearly indicate that $Na_4P_2O_7$ and $Na_5P_3O_{10}$ (I), both crystalline, rise in concentration successively and then diminish as they are consumed by subsequent reactions. In other similar experiments both of these compounds have been observed in even higher amounts, the highest for $Na_4P_2O_7$ approaching the theoretical for completion of the reactions of eq. 1 and 2, but with no crystalline $Na_2H_2P_2O_7$ except in mixtures heated for long periods near 200°.

Thermal analysis curves made in an attempt to determine the beginning of the reaction of eq. 3 on the assumption that 1 and 2 were completed before formation of the triphosphate failed to shed light on this particular part of the problem because no breaks due to triphosphate formation were detectable, as can be seen by examination of the upper curve in Fig. 1.

In a further effort to find the reaction temperature, the thermal analysis experiments were expanded to thermogravimetric analysis, thus obtaining a simultaneous record of the temperature and weight of the sample with respect to heating time. Several runs were made with typical data as shown in Fig. 1. Breaks in the thermal curve show incongruent melting of $Na_2HPO_4 \cdot 2H_2O$ at 82° and boiling of the saturated solution at 109°. The strong break at 210° indicates the first loss of constitutional water. No other breaks could be discerned at higher temperatures. The weight *vs.* time curve reflects the corresponding losses of water without any particular effect being evident in the neighborhood of point B, a point calculated to represent the weight loss corresponding to completion of reactions in eq. 1 and 2.

In order to identify the actual chemical species in the mixture at points A, B, C, D, E and F in Fig. 1, identical thermogravimetric runs were made which were then stopped short at these points of weight and the samples quickly removed and cooled by immediately grinding them in a large mortar. The results of these experiments are recorded in Table II. The X-ray diffraction analysis gives the crystalline components only, with Na_2HPO_4 and $NaH_2PO_4 \cdot Na_2HPO_4$ accounting for the ortho-, $Na_4P_2O_7$ being the only pyro- compound, while both forms I and II triphosphate were observed. Note that the crystalline orthophosphates fell rapidly below the detection limit (*ca.* 1%) even though appreciable amounts of ortho- remained in the mixture for samples B, C, and D as shown in the chromatographic analyses. This leaves most of the ortho- in the amorphous phase. Similar comparison shows the amorphous phase to contain a large amount of pyrophosphate. It is believed that the triphosphate in B is in the amorphous phase since strong diffraction maxima of form I, which subsequently appears first, would be detectable if present in excess of about 1%. The data

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

(6) Editha Karl-Kroupa, *ibid.*, **28**, 1091 (1956).

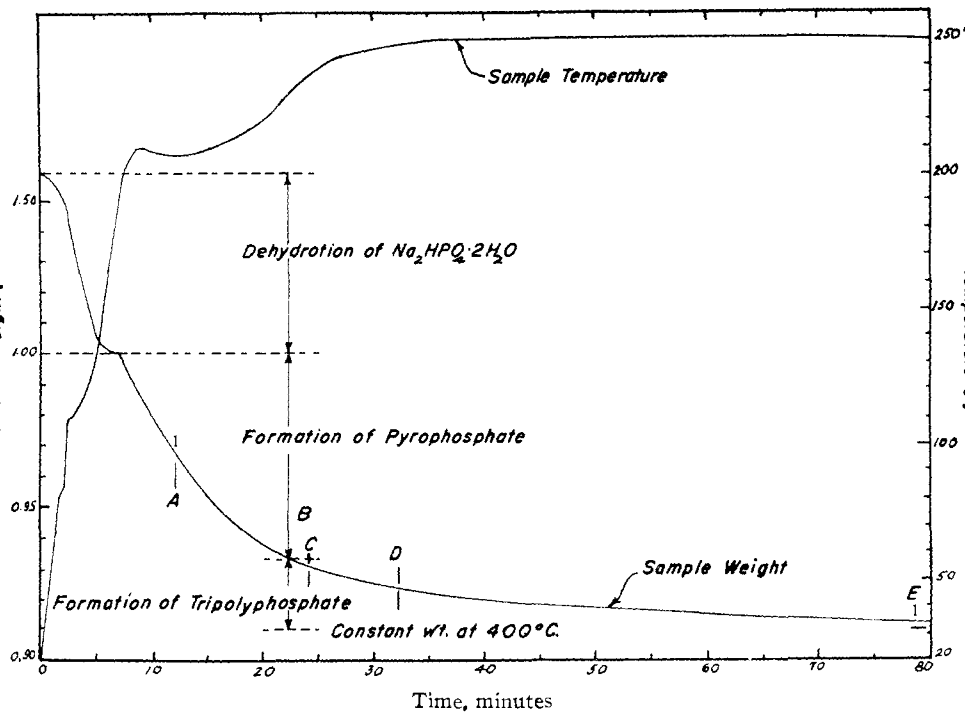

Fig. 1.—Thermogravimetric curves for dehydration of an orthophosphate mixture to sodium triphosphate.

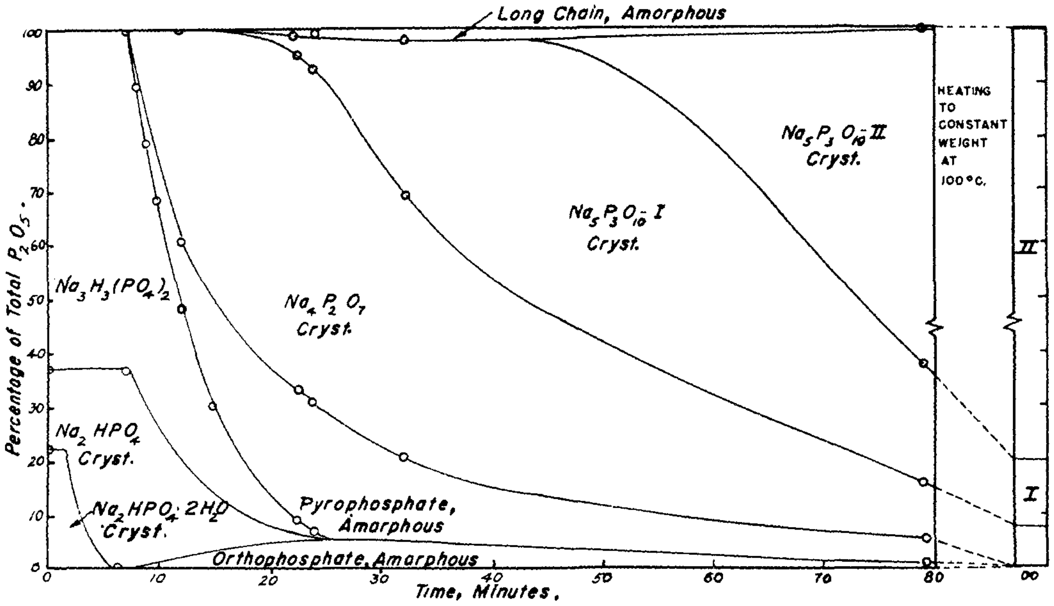

Fig. 2.—Change of composition with time during thermal dehydration of an orthophosphate mixture to sodium triphosphate.

do not permit firm conclusions about amorphous triphosphate in subsequent samples although the preponderance of high X-ray results suggest that the amorphous phase contains at most only a low concentration of triphosphate. Analytical results for long chains are erratic for unknown reasons; however, the trend in the data suggests that long chains build up to a maximum concentration and then decline. The long chain polyphosphates were mostly tetrapolyphosphate.

The results given in Fig. 1 and Table II have been combined to construct Fig. 2, a cumulative plot of the change of composition with time for the reaction mixture heated at 250°. The boundaries have been drawn in on the basis of the various analyses while the weight loss data were used for interpolation of several curves. For example, the boundary between $Na_4P_2O_7$ and $Na_5P_3O_{10}$ is established by analytical data at the points shown by circles while the curve from 32 to 79 min. was interpolated on the assumption that for this region triphosphate formation is directly proportional to the amount of water evolved. The curve between the two forms of $Na_5P_3O_{10}$ was sketched in on the basis of data from Table I and other similar experiments not reported in detail herein.

Mechanism.—The above results show that the *in situ* mixture of $Na_3H_3(PO_4)_2$ and Na_2HPO_4-$(0-2)H_2O$, obtained by rapid drying of appropriate orthophosphate solutions loses constitutional water when heated to 210° leaving a mixture of crystalline $Na_4P_2O_7$ and an amorphous phase. The elemental composition of the amorphous phase is approximately that of $Na_2H_2P_2O_7$ (into which it transforms and crystallizes on prolonged heating at 200°).[3] Other species in this phase include ortho-, tri-, tetra-, and ring meta- and longer chain polyphosphates. Further heating of this reaction mixture at somewhat higher temperatures, 225–400°, results in evolution of more water and consumption of proportional amounts of $Na_4P_2O_7$ and the amorphous phase to form $Na_5P_3O_{10}$ (I) and/or (II). Which of the two forms of sodium triphosphate predominates depends on uncertain factors which are associated in some cases with the size of the polycrystalline granules of ortho mixture, rate of heating, etc.[3]

The simplest mechanism consistent with the various experiments above has

$$HPO_4^{2-} + HP_2O_7^{3-} \longrightarrow P_3O_{10}^{5-} + H_2O \quad (5)$$

as the primary reaction for formation of triphosphate, with this reaction taking place at the crystal-amorphous phase interface. The reaction thus conceived can proceed by dissolution of $Na_4P_2O_7$ in the amorphous phase, countercurrent migration of Na^+ and H^+, sustenance of equilibrium between ortho- and condensed phosphates in the amorphous phase by the presence of water evolved in the reaction (eq. 5), and without the need of diffusion of any type of ion in the crystalline phases nor appreciable diffusion of phosphate ions of any degree of condensation. Although the molar concentration of orthophosphate in the amorphous phase approaches that of pyrophosphate until the reaction nears completion, this is not essential to the proposed mechanism and probably does not occur at higher temperatures. The water liberated at the growing $Na_5P_3O_{10}$ crystal face is ideally situated to hydrolyze polyphosphates contained in the amorphous phase and thereby maintain an adequate concentration of orthophosphate where it is needed, that is, near the interface between product and amorphous phase, where postulated formation of triphosphate occurs.

This mechanism explains the beneficial effect of water, an effect which has been investigated in some detail by McGilvery and Scott[7] who suggested that water participates in hydrolytic equilibria of polyphosphates. These authors further suggested that these equilibria in the reaction mass maintain an adequate concentration of *pyrophosphate* for support of a reaction series leading to triphosphate through tetraphosphate by hydrolytically cleaving a terminal PO_4 tetrahedron from the chain.

Crystallization of triphosphate, if formed randomly in the reaction mixture by hydrolytic cleavage of tetraphosphate, would seem to be an extremely slow, diffusion-controlled process which would lead to high concentrations of triphosphate in the amorphous phase. The results presented herein indicate that triphosphate either crystallizes as fast as formed or is formed in a crystalline state, so that random formation by cleavage is not a likely mechanism.

Rather than a random cleavage, let us consider formation by cleavage at the growing crystal face. This hydrolytic cleavage mechanism, if diffusion of large anions is excluded, would require synthesis and subsequent cleavage of tetraphosphate ions near the growing crystal of product. The synthesis of tetraphosphate requires pyrophosphate while the cleavage yields orthophosphate. Thus the cleavage mechanism leads to the presence of ionic species in the reaction zone which can react in a single step to give the triphosphate ion and water as in equation 5. It would be expected, then, that the reaction of ortho- and pyrophosphate as postulated in this paper would be dominant.

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[7] J. D. McGilvery and A. E. Scott, *Can. J. Chem.*, **32**, 1100 (1954).