The Reaction of Mono-, Di-, and Trisodium Orthophosphate in a Mixed Solution of Acetic Acid and Acetic Anhydride

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Mono-, di-, or trisodium orthophosphate was heated at 100°C in an equivolume mixture of acetic acid and its anhydride. By X-ray diffractometry and paper chromatography, the products from these three sodium salts of orthophosphate were found to be sodium trimetaphosphate. At the end of the 30-hr reaction period, the purity of the trimetaphosphate was higher than 90%. The ease of formation of the trimetaphosphate ring under various conditions was shown, and the stability of the ring was discussed on the basis of the strain of the bonding angle.

Some condensed phosphates are synthesized by the dehydration of orthophosphate at a high temperature. Thilo and his co-workers made potassium trimetaphosphate by treating monopotassium dihydrogen orthophosphate with a mixture (1: 1) of acetic acid and its anhydride at 90°C.[1] Kasparek reported the dehydration of alkalimetal salts of dihydrogen orthophosphates with acetic anhydride.[2] In the present work, we succeeded in synthesizing trimetaphosphate not only from monosodium orthophosphate, but also from di- and trisodium orthophosphate, which had been treated in an equivolume mixture of acetic acid and its anhydride at 100°C. The reactivity of these three sodium salts of orthophosphate in the mixed solution was examined.

Experimental

Materials and Instruments. All the materials used were of a commercial grade. The water of crystallization of the orthophosphates was removed by heating them at 120°C in an air bath. The instruments used for the analysis of phosphates were a Toshiba X-ray diffractometer, ADG-102, and a Shimadzu photoelectric photometer, Spectronic-20.

Reaction of the Orthophosphates in a Mixture (1: 1) of Acetic Acid and Its Anhydride. After 50-m*l* portions of acetic acid and of acetic anhydride had been taken in a 300-m*l*, four-necked, round-bottom flask, 5 g of the orthophosphate was added to the solution and then the mixture was heated at 100°C with a mantle-heater, while being stirred and refluxed at the same time, for 5, 10, 15, 20, 25, or 30 hr. At first, these sodium salts of orthophosphates were completely dissolved in the mixed solution at 100°C, the solution gradually became turbid, with a white deposit. The quantity of the white deposit increased with the increase in the reaction time. The reaction mixture at each reaction time was cooled; the deposit was filtered off and then washed with ethyl alcohol. The compositions of the deposit and of the filtrate were estimated from the data obtained by X-ray diffractometry and paper chromatography.

X-ray Diffractometry. The samples were ground with an agate mortar until they could pass through a 150-mesh screen. Their X-ray diffraction patterns were taken by means of the powder method.

Paper Chromatography. About 1 g of the white deposit was dissolved in 50 m*l* of water, and then 3 μ*l* of the solution or the filtrate obtained by the filtration of the reaction mixture were placed on a filter paper (Toyo No. 51A of 2 by 40 cm) and developed at room temperature for 20 hr by using an acidic and a basic solvent. The acidic solvent was prepared by mixing 73.5 m*l* of isopropyl alcohol, 5.0 g of trichloroacetic acid, 0.25 m*l* of concentrated aqueous ammonia, and 26.5 m*l* of water; it was used for the separation of ortho-, pyro-, tripoly-, and long-chain phosphates. The basic solvent was prepared by mixing 38.7 m*l* of isopropyl alcohol, 20.0 m*l* of isobutyl alcohol, 0.5 m*l* of concentrated aqueous ammonia, and 40.8 m*l* of water and was used for the separation of trimeta- and tetrametaphosphates. After the solutions of phosphate had been developed for 20 hr, the filter paper was dried at 75°C for more than 30 minutes in an air bath. The paper was sprayed with a perchloric acid-molybdate solution. After it had dried again, the paper was exposed to ultraviolet rays in order to reduce the molybdophosphates to blue complexes. Each band of the phosphates on the filter paper was identified by the same treatment as in the case of a reference solution of a known mixture of phosphates.

Colorimetric Determination of Phosphorus. The separated phosphates on the paper chromatograms were determined as follows. Filter paper containing each separated phosphates was cut at the demarcation line, and each part was immersed in 10 m*l* of a 0.1N aqueous solution of ammonia in a 50-m*l* Erlenmeyer flask for 1 hr. The resulting solution was transferred to a 25-m*l* volumetric flask, and then 10 m*l* of water and 2 m*l* of Lucena-Conde and Prat's reagent[3] were added. The flask was placed in boiling water for 1 hr, then cooled in a bath of cold water, and diluted to the mark with water. The absorbance of the solution was measured at 800 mμ. The compositions of the phosphates were calculated from the absorbance data.

Results and Discussion

The chemical compositions of the phosphates contained in the white deposit are shown in Tables 1, 2, and 3. The data indicate that the main product from these three sodium salts of orthophosphate is trimetaphosphate and that its purity increases with an increase in the reaction time and is higher than 90% at a reaction time of 30 hr. The compositions of the filtrate at the reaction time of 30 hr were as follows: for monosodium orthophosphate, 45.8% of orthophosphate, 16.7% of pyrophosphate, and 37.5% of an unknown substance; for disodium orthophosphate, 53.7% of orthophosphate, 19.2% of pyrophosphate, and 27.1% of an unknown substance; for trisodium orthophosphate,

1) I. Grunze, K. Dostal, and E. Thilo, *Z. Anorg. Allg. Chem.*, **302**, 221 (1959).

2) F. Kasparek, *Monatsch.*, **92**, 1023 (1961).

3) F. Lucena-Conde and L. Prat, *Anal. Chim. Acta*, **16**, 473 (1957).

TABLE 1. DISTRIBUTION OF PHOSPHATES OF THE PRODUCTS FROM THE NaH_2PO_4–$(CH_3CO)_2O$–CH_3COOH SYSTEM (P%) (R. T.: reaction time)

R. T. (hr)	Ortho	Pyro	Tri	Tri-meta	Tetra-meta	Higher
5	2.3	2.9	9.4	70.2	—	15.2
10	2.2	2.5	8.6	73.0	—	13.7
15	2.0	2.2	6.3	86.4	—	3.1
20	1.7	2.0	5.2	89.2	—	1.9
25	1.3	1.8	5.4	89.7	—	1.8
30	1.0	1.0	5.0	91.5	—	1.5

TABLE 2. DISTRIBUTION OF PHOSPHATES OF THE PRODUCTS FROM THE Na_2HPO_4–$(CH_3CO)_2O$–CH_3COOH SYSTEM (P%) (R. T.: reaction time)

R. T. (hr)	Ortho	Pyro	Tri	Tri-meta	Tetra-meta	Higher
5	3.2	5.4	7.7	69.0	—	14.7
10	2.2	3.0	9.3	75.4	—	10.1
15	2.7	3.4	9.4	76.7	—	7.8
20	2.7	2.8	5.5	86.0	—	3.0
25	1.4	1.5	4.8	88.9	—	3.4
30	1.4	1.0	4.2	91.0	—	2.4

TABLE 3. DISTRIBUTION OF PHOSPHATES OF THE PRODUCTS FROM THE Na_3PO_4–$(CH_3CO)_2O$–CH_3COOH SYSTEM (P%) (R. T.: reaction time)

R. T. (hr)	Ortho	Pyro	Tri	Tri-meta	Tetra-meta	Higher
5	1.9	2.1	8.6	76.0	—	11.4
10	1.4	1.9	3.1	82.0	—	11.0
15	1.8	1.5	4.0	89.3	—	3.4
20	1.0	1.0	4.2	91.3	—	2.5
25	1.3	1.5	2.8	92.4	—	2.0
30	0.5	1.4	2.7	93.7	—	1.7

86.8% of orthophosphate, and 13.2% of pyrophosphate, while the quantity of the unknown substance was so small that it could not be determined. The unknown substances contained in these filtrate, are all the same substance, which has an R_f value of 0.60 for the acidic solvent employed in this chromatography. The unknown substance may be an orthophosphate the hydrogen atoms of which are replaced by acetyl groups.

The X-ray diffraction patterns of the white deposits are given in Fig. 1. From the results, it is clear that the white deposits are sodium trimetaphosphate. The sodium trimetaphosphate was identified by comparing the X-ray patterns of the white deposits with those of the "A.S.T.M. Diffraction Data File." According to the above results, the following reactions were considered for the formation of trimetaphosphate:

$$3NaH_2PO_4 + 3(CH_3CO)_2O = (NaPO_3)_3 + 6CH_3COOH$$

$$\begin{pmatrix} 3Na_2HPO_4 + 3CH_3COOH = 3NaH_2PO_4 + 3CH_3COONa \\ 3NaH_2PO_4 + 3(CH_3CO)_2O = (NaPO_3)_3 + 6CH_3COOH \end{pmatrix}$$

$$\begin{pmatrix} 3Na_3PO_4 + 6CH_3COOH = 3NaH_2PO_4 + 6CH_3COONa \\ 3NaH_2PO_4 + 3(CH_3CO)_2O = (NaPO_3)_3 + 6CH_3COOH \end{pmatrix}$$

By using the above equations, the theoretical amounts of sodium trimetaphosphate to be obtained per 100 g of each orthophosphate were calculated. The theoretical values, the experimental values, and the yields of sodium trimetaphosphate are given in Table 4.

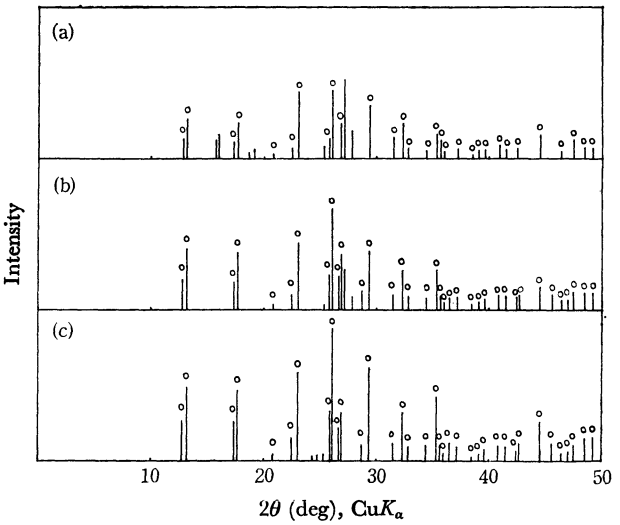

Fig. 1. X-Ray diffraction patterns of white deposites.
(a): NaH_2PO_4–$(CH_3CO)_2O$–CH_3COOH system
(b): Na_2HPO_4–$(CH_3CO)_2O$–CH_3COOH system
(c): Na_3PO_4–$(CH_3CO)_2O$–CH_3COOH system
○: Lines due to sodium trimetaphosphate

TABLE 4. THE YIELDS OF SODIUM TRIMETAPHOSPHATE

	NaH_2PO_4	Na_2HPO_4	Na_3PO_4
EV	80.6	67.1	57.5
CV	85.0	71.8	62.2
Yield	94.8	93.4	92.4

EV: Gram quantities of sodium trimetaphosphate obtained by the experiment per 100 g of each orthosphate.
CV: Gram quantities of sodium trimetaphosphate obtained by calculation per 100 g of each orthophosphate.
Yield: The yields (%) of sodium trimetaphosphate.

It is well known that sodium trimetaphosphate is usually made by heating monosodium orthophosphate to temperatures between 500 and 600°C. The sodium trimetaphosphate is formed very readily as a well-crystallized salt. It can also be prepared by cooling a sodium metaphosphate melt to the right temperature or by heating various mixtures of sodium phosphates exhibiting an over-all composition corresponding to the metaphosphate. It is very difficult, on the other hand, to prepare tetrametaphosphates by heating monomer phosphates; they are prepared by slowly adding phosphorus pentoxide to ice water. Anhydrous sodium tetrametaphosphate is irreversibly transormed to sodium trimetaphosphate at temperatures around 400°C; it cannot be restored by any known subsequent treatment of the sodium trimetaphosphate. Sodium salts of pyro- and tripolyphosphate are made by heating sodium phosphates which have a composition corresponding to these phosphates. It is difficult to prepare tetrapolyphosphates by heating phosphates, however, they are made by the alkaline hydrolysis of tetrametaphosphate. Usually, it is very difficult to prepare condensed phosphates, which are larger than tetra. Condensed phosphates hydrolyze to the uncondensed form in an aqueous solution. It is also well known that small

rings (mainly trimeta and a little tetrameta) are formed as the long chains are hydrolyzed. In view of the above facts, sodium trimetaphosphate may have a very stable structure and the trimetaring may be made readily. Phosphorus exhibits sp^3-bonding in the phosphates. The usual hybridization of the oxygen atom lies between p^2 and sp, so the bond angle of P–O–P lies between 90° and 180°. If the P–O–P angle is near the average value of 135° and if the O–P–O angle is 109°28′, the total bond angle of the trimetaring is very close to that of the six membered-ring, which is planar. The trimetaphosphate ion is considered to have a D_{3h} symmetry in an aqueous solution.[4]

4) W. P. Griffith and K. J. Rutt, *J. Chem. Soc. A*, 2331 (1968).