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The Condensation of Orthophosphates with Acid Anhydrides

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Thilo *et al.* prepared potassium trimetaphosphate and sodium trimetaphosphate by treating monopotassium and monosodium orthophosphate respectively in a mixed solution of acetic acid and acetic anhydride.[1,2] Kasparek reported on the dehydration of various dihydrogen orthophosphates and pyrophosphates using the mixed solution mentioned above.[3,4] In a previous paper,[5] the present authors reported on the dehydration of mono-, di-, and trisodium orthophosphates in the same solution at 100 °C. In every case, the main product was the sodium trimetaphosphate. In the present work, the condensation reactions of mono- di-, and trisodium orthophosphates were carried out in mixed solutions of acetic acid and propionic, *n*-butyric, isobutyric, succinic, or maleic anhydride.

Experimental

Materials and Procedure. All the materials used were of a commercial grade. The water of the crystallization of orthophosphate was removed by heating it in an air bath at 120 °C. When propionic, *n*-butyric, or isobutyric anhydride was used as the dehydrating agent, 50 g of the anhydride was taken in a four-necked, round-bottomed, 200 ml flask; then 50 ml of acetic acid and 5 g of orthophosphate were added. The three samples of the mixture were heated, stirred, and refluxed at 100 °C for 10, 20, and 30 hr respectively. In the cases of succinic and maleic anhydrides, 25 g of the anhydride was placed in a four-necked, round-bottomed, 200 ml flask; then 100 ml of acetic acid and 5 g of orthophosphate were added, and the mixture was treated in the way described above. Each mixture was cooled after reaction periods of 10, 20, and 30 hr. The resulting precipitate was filtered off and washed with acetone. The composition of the phosphates con-

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

[2] I. Grunze, E. Thilo, and H. Grunze, *Chem. Ber.*, **93**, 2631 (1960).

[3] F. Kasparek, *Monatsh. Chem.*, **92**, 1023 (1961).

[4] F. Kasparek, *ibid.*, **93**, 822 (1962).

[5] M. Watanabe and T. Senda, This Bulletin, **45**, 2111 (1972).

tained in the precipitate was determined 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 sieve, and their X-ray diffraction pattern was taken with a Toshiba Model ADG-102 X-ray diffractometer.

Paper Chromatography. The separation and determination of condensed phosphates were performed with the method described in the present authors' previous paper.[5]

Results and Discussion

Mono-, di-, and trisodium orthophosphates were dissolved completely in a mixed solution of acid anhydride and acetic acid at 100 °C. A white product was freshly precipitated; appeared as a condensed phosphate. The quantity of the precipitate increased with increasing in the reaction time in every case. As Tables 1, 2, 3, and 4 show, except for the NaH_2PO_4–$(CHCO)_2O$–CH_3COOH system, the main product is trimetaphosphate. When propionic, *n*-butyric, or isobutyric anhydride is used as dehydrating agent, the content of trimetaphosphate in the precipitate increases with an increase in the reaction time, while the orthophosphate content decreases. In the condensation of mono- or disodium orthophosphate, a small amount of condensed phosphates, which have a longer chain than that of tripolyphosphate, exists after a reaction period of 10 hr. Tripolyphosphate also exists after reaction periods of 10, 20, and 30 hr. On the other hand, in the reaction of trisodium orthophosphate, the longer-chain phosphates and tripolyphosphate do not exist after any reaction period except in the case of the Na_3PO_4–$(CH_3CH_2CO)_2O$–CH_3COOH system. In the condensation of monosodium orthophosphate with succinic or maleic anhydride, the content of trimetaphosphate is smaller than that of di- or trisodium orthophosphate. In the reactions of di- and trisodium orthophosphates with succinic and maleic anhydrides, the content of trimetaphosphate at a reaction time of 40 hr is more than 90% in all cases.

Table 1. Distribution of phosphates in the products of the orthophosphate–propionic anhydride–acetic acid system (P%) (RT: reaction time)

RT (hr)	System	Ortho	Pyro	Tri	Tri-meta	Higher
10	Na 1	20.4	42.1	16.5	19.5	1.5
	Na 2	7.7	10.5	7.3	73.1	1.4
	Na 3	18.3	35.5	0.5	45.7	—
20	Na 1	5.9	9.5	7.3	77.3	—
	Na 2	6.6	8.9	10.4	74.1	—
	Na 3	12.3	32.6	—	55.1	—
30	Na 1	1.4	5.3	4.7	88.6	—
	Na 2	2.8	4.0	6.8	86.4	—
	Na 3	6.7	12.0	—	81.3	—

Na1: monosodium orthophosphate–propionic anhydride-acetic acid system.
Na2: disodium orthophosphate–propionic anhydride–acetic acid system.
Na3: trisodium orthophosphate–propionic anhydride–acetic acid system.

Table 2. Distribution of phosphates in the products of the orthophosphate–*n*-butyric anhydride-acetic acid system (P%) (RT: reaction time)

RT (hr)	System	Ortho	Pyro	Tri	Tri-meta	Higher
10	Na 1	19.6	39.6	15.8	23.1	1.9
	Na 2	5.9	9.5	8.8	73.5	2.3
	Na 3	19.5	33.5	—	47.0	—
20	Na 1	6.6	10.0	5.9	77.5	—
	Na 2	3.8	3.4	5.3	87.5	—
	Na 3	12.5	35.3	—	52.2	—
30	Na 1	1.8	4.2	4.3	89.7	—
	Na 2	1.2	2.3	1.0	95.5	—
	Na 3	3.0	3.4	—	93.6	—

Na1: monosodium orthophosphate–*n*-butyric anhyde–acetic acid system.
Na2: disodium orthophosphate–*n*-butyric anhydride–acetic acid system.
Na3: trisodium orthophosphate–*n*-butyric anhydride–acetic acid system.

Table 3. Distribution of phosphates in the products of the orthophosphate–isobutyric anhydride–acetic acid system (P%) (RT: reaction time)

RT (hr)	System	Ortho	Pyro	Tri	Tri-meta	Higher
10	Na 1	15.8	48.1	11.8	22.9	1.4
	Na 2	6.0	8.9	7.5	76.4	1.2
	Na 3	18.7	39.9	—	41.4	—
20	Na 1	5.1	10.3	7.6	77.0	—
	Na 2	4.9	8.5	9.3	77.3	—
	Na 3	13.9	27.6	—	58.5	—
30	Na 1	2.0	2.1	2.2	93.7	—
	Na 2	2.2	4.8	9.5	83.5	—
	Na 3	7.4	12.5	—	80.1	—

Na1: monosodium orthophosphate–isobutyric anhydride–acetic acid system.
Na2: disodium orthophosphate–isobutyric anhydride–acetic acid system.
Na3: trisodium orthophosphate–isobutyric anhydride–acetic acid system.

Table 4. Distribution of phosphates in the products of the orthophosphate–succinic anhydride–acetic acid and –maleic anhydride–acetic acid system (P%) (RT: reaction time)

RT (hr)	System	Ortho	Pyro	Tri	Tri-meta	Higher
20	SNa 1	35.2	15.2	8.5	41.1	—
	SNa 2	8.7	8.9	8.7	73.7	—
	SNa 3	7.3	5.5	8.6	78.6	—
	MNa 1	91.8	3.1	0.6	4.5	—
	MNa 2	15.9	11.3	6.7	66.1	—
	MNa 3	3.0	8.3	6.6	82.1	—
40	SNa 1	11.5	10.2	7.5	70.8	—
	SNa 2	2.5	3.0	1.2	93.3	—
	SNa 3	1.2	3.2	0.7	94.9	—
	MNa 1	57.9	22.8	1.1	18.2	—
	MNa 2	2.4	2.5	2.7	92.4	—
	MNa 3	2.0	1.8	2.1	94.1	—

(S, M, Na1, Na2, and Na3 represent succinic anhydride, maleic anhydride, mono-, di-, and trisodium orthophosphate respectively.)

Griffith and Buxton[6] reported that, when sodium polyphosphate (with a longer chain than in tetra) was hydrolyzed, trimetaphosphate was formed, while in the hydrolysis of polyphosphate with cations other than the sodium ion, scarcely no trimetaphosphate was formed. They concluded from these facts that the sodium ion is related to the formation of the trimetaphosphate ring. The fact that, in the present work, the main product is trimetaphosphate, seems related to the above conclusion. The yield of the precipitate and the theoretical value of $(NaPO_3)_3$ to be obtained per 5.00 g of each of the orthophosphates are shown in Table 5. The theoretical values are calculated assuming that the orthophosphates are completely converted into $(NaPO_3)_3$ by means of the equations described in the previous paper.[5] The formation process of sodium trimetaphosphate has already been discussed by Kasparek,[3] the same process has also been considered for these condensation reactions.

TABLE 5. THE YIELDS OF THE DEPOSITS AND THE THEORETICAL AMOUNTS OF $(NaPO_3)_3$ PER 5 g OF ORTHOPHOSPHATES

		Acid anhydride				
	TV	PP	NBT	IBT	SC	MC
Na 1	4.25	4.20	4.15	4.10	3.45	3.04
Na 2	3.59	3.48	3.45	3.55	3.24	2.47
Na 3	3.11	2.85	2.92	3.10	2.93	2.25

Na1: monosodium orthophosphate, Na2: disodium orthophosphate, Na3: trisodium orthophosphate, TV: theoretical value, PP: propionic anhydride, NBT: *n*-butyric anhydride, IBT: isobutyric anhydride, SC: succinic anhydride, MC: maleic anhydride.

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[6] E. J. Griffith and R. L. Buxton, *J. Amer. Chem. Soc.*, **89**, 2884 (1967).