September, 1980] © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***53***, *2663—2665 (1980)* 2663

The Synthesis and Decomposition of Calcium Tetraphosphate

Makoto Watanabe,* Hiroyasu Suzumori, Mioko Maeda, and Tamotsu Yamada
Department of Industrial Chemistry, Chubu Institute of Technology,
Matsumoto-cho, Kasugai, Aichi 487

(Received January 24, 1980)

Calcium tetraphosphate was made by hydrolyzing cyclotetraphosphate in a 5-mol dm^{-3}-solution of sodium hydroxide, neutralizing the phosphate solution with 1 mol dm^{-3} hydrochloric acid, and then adding calcium chloride to the solution. The P/Ca molar ratio of the product was 1.4—1.5. The tetraphosphate was an amorphous substance containing 20—30% of water and was decomposed to phosphates with a shorter chain length with bound water at room temperature or at a higher temperature. Upon decomposition at 300 °C, the main product at the early stage was pyrophosphate. The hydrolysis of the tetraphosphate obeyed the first-order kinetics with respect to the concentration of the phosphate, and the activation energy of the hydrolysis was 105 kJ mol^{-1} at pH 3.5.

Studies of calcium orthophosphates have been made by many workers, but calcium polyphosphates have not been studied well, and even the synthetic methods for most of them have not yet been published. Among chain polyphosphates, the phosphates having shorter chain lengths than that of triphosphate have been investigated well because of the ease of the synthesis of these phosphates. Polyphosphates with longer chains than that of tetraphosphate are, however, very difficult to prepare. Tetraphosphate ions are made by the hydrolysis of cyclotetraphosphate in an aqueous sodium hydroxide solution, but they have not been isolated and have not yet been studied well. In this paper, we will discuss the synthesis of calcium tetraphosphate by means of the hydrolysis of cyclotetraphosphate and some properties of the phosphate.

Experimental

Materials and Procedure. All the materials used, other than the sodium cyclotetraphosphate, were of a commercial grade. The sodium cyclotetraphosphate tetrahydrate was made by the method described in the literature.[1] About 20 g of sodium cyclotetraphosphate tetrahydrate was added to 50 cm^3 of a 5-mol dm^{-3}-aqueous solution of sodium hydroxide, and the mixture was stirred at about 20 °C for 4 d. Most of the sodium cyclotetraphosphate tetrahydrate was not dissolved in the sodium hydroxide solution, while the tetraphosphate produced by the hydrolysis of the cyclophosphate was well dissolved in the alkaline solution. Therefore, the progress of the hydrolysis of the cyclophosphate to tetraphosphate was observed visually by the defecation of the solution. The solution was filtered and neutralized with 1-mol dm^{-3} hydrochloric acid at a temperature below 3 °C, and then an aqueous solution of calcium chloride, which has been made by dissolving 30 g of calcium chloride in 30 cm^3 of water, was added to the tetraphosphate solution. A white precipitate was filtered off, washed with cold water and ethanol, and then dried in an air bath at 50 °C.

Paper Chromatography. One-dimensional paper-chromatographic separation was carried out by using acidic (for the separation of chain phosphates) and basic (for the separation of ring phosphates) solvents.[2] About 0.5 g of the product was dissolved in 25 cm^3 of a 2—8% aqueous disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA) solution. About 8 mm^3 of the solution was spotted on Toyo No. 51A filter paper (2 by 50 cm). The development was run at 5 °C for 2 d.

Colorimetric Measurement of Phosphates. Every individual spot on the chromatogram was cut at the demarcation line and placed in a 100-cm^3 beaker containing 10 cm^3 of a 0.1 mol dm^{-3}-ammonium hydroxide solution. After 1 h, the solution was transferred to a 25-cm^3 volumetric flask, together with 10 cm^3 of wash water, and a 1-cm^3 portion of Lucena-Conde and Prat's reagent[3] was added to the flask. The flask was heated in a boiling-water bath for 1 h, subsequently cooled by placing it in a bath of cold water, and diluted to the mark with water. The absorbance of the blue solution was measured by means of a Shimadzu Spectronic 88 spectrophotometer at 830 nm. The phosphate content (P%) was calculated by means of the absorbance data.

Determination of Phosphorus, Calcium, and Sodium in the Product. About 0.2 g of the product and 0.7445 g of EDTA were dissolved in water by using a 100-cm^3 volumetric flask. The amounts of phosphorus and calcium in the solution were determined by means of the molybdenum-blue method with Lucena-Conde and Prat's reagent and by means of the EDTA back-titration method with an NN indicator respectively. In the case of the back titration of a calcium ion in this system, the pH of the solution should be larger than 13, because the change in color of the solution is not clear in the pH regions smaller than 13. Atomic-absorption analysis was used for the determination of a sodium ion by using a Jarrell-Ash atomic-absorption spectrophotometer, AA80, while the analysis was performed by dissolving the product in a dilute hydrochloric acid solution.

X-Ray Diffractometry. The X-ray diffraction diagrams of the samples were taken with nickel-filtered Cu $K\alpha$ radiation by using a Toshiba X-ray diffractometer, ADG-102.

DTA and TG. The samples were heated at the heating rate of 5 °C min^{-1} in an ordinary atmosphere by using a Cho Balance TRDA$_1$-H-type apparatus.

Decomposition of the Tetraphosphate. The decomposition of the tetraphosphate at room temperature and at 300 °C in the atmosphere was measured by the paper-chromatographic and colorimetric methods described above.

Hydrolysis of the Tetraphosphate. EDTA 4.0 g was dissolved in 100 cm^3 of water, and then 3.0 g of the tetraphosphate was dissolved in the EDTA solution. The hydrolysis of the tetraphosphate was measured by using the phosphate solution at pH 3.5 and at 50, 60, or 70±0.05 °C. The separation and the determination of the tetraphosphate and its hydrolysis products were carried out by means of the method described above.

Results and Discussion

Composition of the Product. The yield of the product depended upon the pH of the phosphate solution;

it was about 27 g for pH 10—7, about 22 g for pH 8—5, and about 16 g for pH 6—3. Paper-chromatographic identification showed that the product was tetraphosphate. As will be discussed below, the tetraphosphate was decomposed to phosphates with shorter chain lengths in the atmosphere at room temperature, so it was difficult to hold pure tetraphosphate. The product thus obtained contained 20—30% of water and was X-ray-diffractometrically amorphous. An effective amount of a sodium ion was not detected in the product. The P/Ca molar ratio of the product was 1.4—1.5. The P/Ca ratio of tricalcium tetraphosphate, $Ca_3P_4O_{13}$, is 1.33, while that of the product is a little larger. The defect of calcium may be supplemented by hydrogen.

Decomposition of the Tetraphosphate at Room Temperature. As is shown in Table 1, the tetraphosphate is gradually decomposed to phosphates with shorter chain lengths in the ordinary atmosphere at room temperature. No weight change was observed in the sample. Therefore, the decomposition may be caused by the water contained in the product. Since the content (P%) of triphosphate is about three times that of orthophosphate at each decomposition time, the decomposition of triphosphate and pyrophosphate once produced to orthophosphate may not occur, and the following decomposition process can be concluded:

$$\begin{tikzcd}[row sep=small] & \text{Triphosphate + Orthophosphate} \\ \text{Tetraphosphate} \arrow[ur] \arrow[dr] & \\ & \text{2(Pyrophosphate)} \end{tikzcd}$$

DTA and TG. DTA and TG curves of the product are given in Fig. 1. A rapid weight loss of the product and a corresponding big endothermic peak are observed below 150 °C. This reaction may be caused by removing the bound water. The succeeding gradual weight loss of the product from 150—380 °C is considered to be the condensation reaction of phosphates. An exothermic and an endothermic reaction are observed at around 560 and 740 °C respectively. The sample heated at a temperature below that of the exothermic reaction was amorphous and gave no X-ray diffraction peaks, while the sample heated at a higher temperature than that of the exothermic reaction gave some X-ray diffraction peaks. As Fig. 2 shows, these peaks are assigned to those of β-type calcium pyrophosphate (ASTM card, No. 9—346). Accordingly, the exothermic reaction is caused by the crystallization of amorphous calcium pyrophosphate to the β-form. As will be discussed below, the tetraphosphate was decomposed to phosphates with shorter chain lengths by heating it at 300 °C, and the main decomposition product was pyrophosphate in the initial stage of heating. The endothermic reaction at about 740 °C may be due to the melt of a part of the phosphate species, because the sample which was taken out and cooled after the endothermic reaction was sintered. All the X-ray diffraction peaks of the sample after the endothermic reaction were assigned to those of the β-form of calcium pyrophosphate, and an increase in the intensity of the peaks was observed in comparison with that of the peaks of the sample after the exothermic reaction described above.

TABLE 1. DECOMPOSITION OF THE PRODUCT IN THE ATMOSPHERE AT ROOM TEMPERATURE

Reaction time/d	Phosphate/P% Ortho	Pyro	Tri	Tetra
0	—	—	—	100
2	2.7	3.2	8.7	85.4
4	3.9	4.5	12.0	79.6
9	4.8	6.2	14.1	74.9
15	5.5	8.3	15.9	70.3
19	6.2	12.1	17.7	64.0

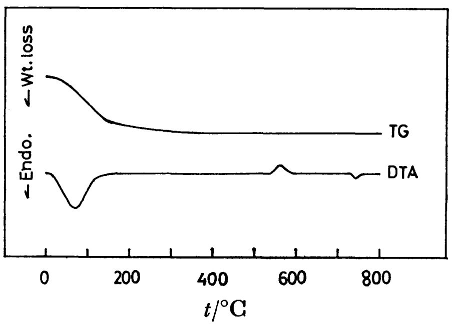

Fig. 1. DTA and TG curves of the product.

Decomposition of the Product at 300 °C. As Table 2 shows, the tetraphosphate thus obtained is readily decomposed to tri-, pyro-, and orthophosphates by heating at 300 °C. Among the decomposition products, the value of the pyrophosphate content is the largest at a short heating time. Therefore, the scission of the middle P–O–P linkage of the tetraphosphate may take place in preference to that of the end P–O–P linkage. This phenomenon was not observed in the decomposition of room temperature. The decomposition products, once produced, are condensed to phos-

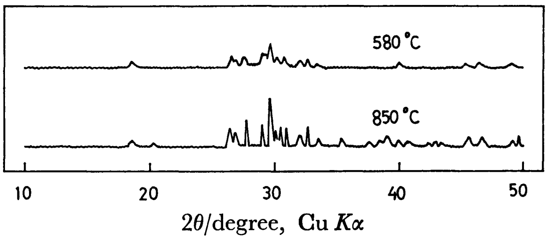

Fig. 2. X-Ray diffraction patterns of the product heated at 580 or 850 °C for 1 h.

TABLE 2. DECOMPOSITION OF THE PRODUCT IN THE ATMOSPHERE AT 300 °C

Heating time/min	Phosphate/P% Ortho	Pyro	Tri	Tetra	Higher
0	1.9	4.4	8.9	84.8	—
10	29.9	48.1	15.6	6.1	0.3
20	17.5	49.5	22.1	8.2	2.7
30	12.0	45.7	24.2	11.6	6.5
40	9.3	41.2	25.4	12.5	11.6
50	5.6	33.2	25.1	14.3	21.8

Table 3. Hydrolysis of the product at pH 3.5 and 70 °C

Reaction time/min	Phosphate/P%				Rate const $\times 10^3$/min^{-1}
	Ortho	Pyro	Tri	Tetra	
0	2.7	3.2	8.2	85.9	
15	3.8	3.7	12.0	80.5	4.3
30	5.5	4.2	14.5	75.8	4.2
45	6.4	4.5	18.0	71.1	4.2
60	6.9	5.1	20.5	67.5	4.0
90	10.6	5.9	26.2	57.3	4.5
120	13.3	7.4	28.0	51.4	4.3
					mean, 4.3

phates with longer chain lengths.

Hydrolysis of the Product. According to the results listed in Table 3, the hydrolysis of tetraphosphate obeyed first-order kinetics with respect to the concentration of tetraphosphate at pH 3.5 and 70 °C. The increase in the pyrophosphate content with the reaction time is so much slower than that of tri- and orthophosphates that the scission of the end P–O–P group of tetraphosphate takes place faster than that of the middle P–O–P group in an aqueous solution. This tendency is the reverse of that of the decomposition of the product at 300 °C. The same results were obtained for the hydrolysis at 60 and 50 °C. The rate constants at 60 and 50 °C were 1.5×10^{-3} and 4.3×10^{-4} min^{-1} respectively. The activation energy was determined to be 105 kJ mol^{-1} by means of the least-squares method.

References

1) K. N. Bell, L. F. Audrieth, and O. F. Hill, *Ind. Eng. Chem.*, **44**, 568 (1952).

2) S. Ohashi, *Kagaku To Kogyo*, **21**, 878 (1968). The A_2 and B_2 solvents in Table 3 were used.

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