The Syntheses and Decompositions of Strontium and Barium Tetraphosphates

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Strontium and barium tetraphosphates were made by hydrolyzing *cyclo*-tetraphosphate in a 5 mol dm^{-3} solution of sodium hydroxide, neutralizing the phosphate solution with 1 mol dm^{-3} hydrochloric acid, and then adding an aqueous solution of strontium or barium chloride to the solution. The P/M (M: Sr or Ba) ratio of the tetraphosphates was 1.3. The strontium and barium tetraphosphates were X-ray diffractometrically amorphous and contained about 23—14 and 14—8% of bound water depending on the washing conditions. They decomposed to phosphates having shorter chain lengths with the bond water in air at 25—30 °C or at a higher temperature. The decomposed phosphates were polymerized again above 150 °C and the products were mixtures of diphosphate and other polyphosphates.

The usual syntheses of polyphosphates have been made by some heating process. Organic acid anhydride, trichloroacetonitrile, and dicyclohexylcarbodiimide have been used as dehydrating agents.[1—6] It is still difficult to produce oligophosphates having chain lengths longer than the triphosphate by these methods. The compounds with the composition of $3MO\cdot 2P_2O_5$ (M: Sr, Ba, or Pb) were made by a heating method.[7—11] The barium and lead phosphates were confirmed to be tetraphosphate by paper chromatography. The strontium compound is not characterized yet. These compounds were slightly soluble in solvents, except for strongly acidic aqueous solutions, and the phosphates are readily hydrolyzed to phosphates having shorter chain lengths in the acidic solutions at room temperature. So it is difficult to use the phosphates for studying chemical properties. The present authors have reported the syntheses of calcium and magnesium tetraphosphates by a wet chemical process and have discussed the stability of the products.[12,13] The tetraphosphates were soluble in an aqueous disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA) solution and can be used for studying chemical properties of the phosphates in an aqueous reaction system. This paper describes the syntheses of strontium and barium tetraphosphates by a wet chemical process and the thermal stability of the products.

Experimental

Synthetic Method. All the chemicals were of commercial reagent grade and were used without further purification. Sodium *cyclo*-tetraphosphate tetrahydrate was made by hydrolyzing α-P_2O_5 in water cooled below 15 °C with vigorous stirring and then by adding sodium chloride to the solution.[14] About 10 g of sodium *cyclo*-tetraphosphate tetrahydrate was added to 25 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 *cyclo*-phosphate was not dissolved in the sodium hydroxide solution, while the tetraphosphate produced by the hydrolysis of the *cyclo*-phosphate was well dissolved in the alkaline solution. Accordingly, the progress of the hydrolysis of the *cyclo*-phosphate to tetraphosphate was observed visually by the clarification of the solution. After being filtered, the solution was neutralized with 1 mol dm^{-3} hydrochloric acid to pH 10 at a temperature below 3 °C to prevent the hydrolysis of the tetraphosphate. An aqueous solution of strontium chloride or barium chloride, which was made by dissolving 20 g of strontium and barium chlorides in 20 and 50 cm^3 of water respectively, was added to the tetraphosphate solution. A white precipitate was filtered off, washed with cold water, ethanol, and acetone, and then dried under reduced pressure at 25 °C.

Paper Chromatography. One-dimensional paper chromatography was used for the identification of phosphates with acidic and basic developing solvents.[15] The acidic and basic solvents were used for the separation of chain and ring phosphates respectively. About 0.5 g of a sample was dissolved in 50 cm^3 of a 6% aqueous EDTA solution. About 8 mm^3 of the solution was spotted on Toyo No. 51A filter paper (2 by 50 cm). The development was carried out in a thermostat at 5 °C for 2 d. The determination of the phosphate on the chromatogram was made by the method described in our previous paper.[13]

Determination of Phosphorus, Strontium, and Barium in the Products. About 0.2 g of the strontium tetraphosphate and about 0.75 g of EDTA was dissolved in water and diluted to the mark by using a 100-cm^3 volumetric flask. About 0.5 g of the barium tetraphosphate was dissolved in a diluted hydrochloric acid solution and the total volume was made 100 cm^3 with water. The determination of phosphorus in the sample solutions was made by means of the molybdenum-blue method with Lucena-Conde and Prat's reagent.[16] The amounts of strontium and barium in the sample solutions were determined by the EDTA back titration and the gravimetric technique respectively.

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

DTA and TG. The samples were heated at a heating rate of 5 °C min^{-1} with a Cho Balance TRDA$_1$-H-type apparatus.

IR Measurement. IR spectra of samples were recorded on a JASCO IR spectrophotometer, A-3, using the KBr disk method.

Determination of Bound Water. The amount of bound water in a sample was determined by the Karl Fisher method with an MK-AII apparatus by Kyoto Denshi.

Decomposition in Air. The decomposition of the product at 25—30 °C in air was studied by paper chromatography, X-ray diffractometry, and IR spectrometry as described above.

Results and Discussion

Composition of the Product. The paper-chromatographic identification of the products showed that the products were composed of tetraphosphate. Strontium and barium ions had no serious effect on the development of the phosphates. The P/M (M:

Sr or Ba) ratios of the products were 1.30 and 1.33 for the strontium and barium salts respectively. Accordingly, the products were strontium tetraphosphate, $Sr_3P_4O_{13}$, and barium tetraphosphate, $Ba_3P_4O_{13}$. The strontium and barium phosphates contained about 23—14 and 14—8% of water respectively depending on the washing condition with ethanol and acetone. The products were X-ray diffractometrically amorphous.

Decomposition in Air at 25—30 °C. The stability of the tetraphosphates was studied in air at 25—30 °C. As Table 1 shows, the strontium tetraphosphate decomposed to phosphates having shorter chain lengths. The water contents in the decomposition product decreased as the passage of time, so the decomposition seemed to be caused by the bound water. The IR spectra of the decomposition products of the strontium tetraphosphate are shown in Fig. 1. The assignment of the absorptions is listed in Table 2. The intensity of the absorptions due to a $(PO_2)^-$ group decreased with the elapse of reaction time and finally disappeared. The result agrees well with that in Table 1. The following degradation process can be concluded from these results:

$$\begin{tikzcd}
& \text{Ortho} + \text{Tri} \arrow[r] & 2(\text{Ortho}) + \text{Di} \arrow[dd] \\
\text{Tetra} \arrow[ur] \arrow[dr] & & \\
& 2(\text{Di}) \arrow[r] & 4(\text{Ortho}).
\end{tikzcd}$$

The decomposition product was amorphous even after 30 d. Since a part of the decomposition product of the barium tetraphosphate seemed to be insoluble in an aqueous EDTA solution, the decomposition of the phosphate could not be studied by the paper chromatography method. The IR spectra of the decomposition products of the barium tetraphosphate are shown in Fig. 2. The intensity of the absorption due to a $(PO_2)^-$ group decreased with time so the tetraphosphate seemed to decompose to phosphates with shorter chain lengths. The X-ray diffraction diagrams of the decomposition products of the phosphate are shown in Fig. 3. The decomposition product gave weak peaks at 16 d, and the intensity of the peaks increased with time. These peaks are all assigned to those of barium diphosphate–water (5/12), which is made by adding an aqueous barium chloride solution to an aqueous sodium diphosphate solution. The result agrees well with that of IR spectra. The water used for the decomposition of the phosphate may be the bound water in the product because, as Table 3 shows, the water content of the product decreased

Table 1. COMPOSITION OF THE SELF-DECOMPOSITION PRODUCTS OF THE STRONTIUM TETRAPHOSPHATE IN AIR AT 25—30 °C

Reaction time/d	H_2O(%)	Phosphates/P(%)			
		Ortho	Di	Tri	Tetra
0	22.9	0.7	5.1	6.2	88.0
5	21.0	12.0	31.8	26.1	30.1
9	19.4	20.0	41.2	22.7	16.1
21	17.9	31.1	51.4	12.7	4.8
30	16.7	43.3	44.5	10.2	2.0

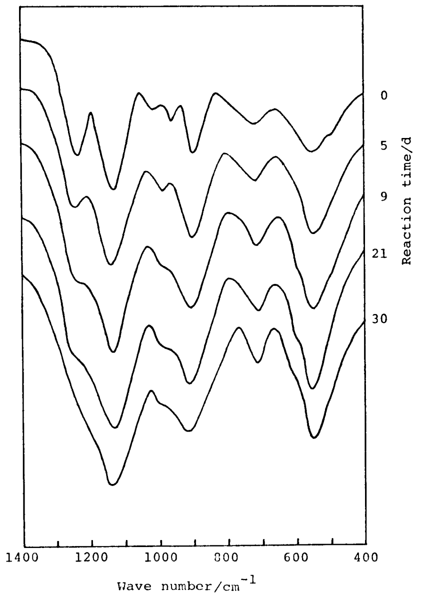

Fig. 1. IR spectra of the self-decomposition products of the strontium tetraphosphate in air at 25—30 °C.

Table 2. ASSIGNMENT OF THE SPECTRA OF THE PRODUCTS

Position of absorption maxima/cm^{-1}	Assignment[a]
1240	$\nu_{as}(PO_2)^-$
1130	$\nu_{as}(PO_3)^{2-}$
1010	$\nu_s(PO_2)^-$
990—960	$\nu_s(PO_3)^{2-}$
900	ν_{as}P-O-P
720	ν_sP-O-P
550	$\delta(PO_2)^-$ and/or $\delta(PO_3)^{2-}$

a) The assignment was made on the basis of Refs. 17 and 18.

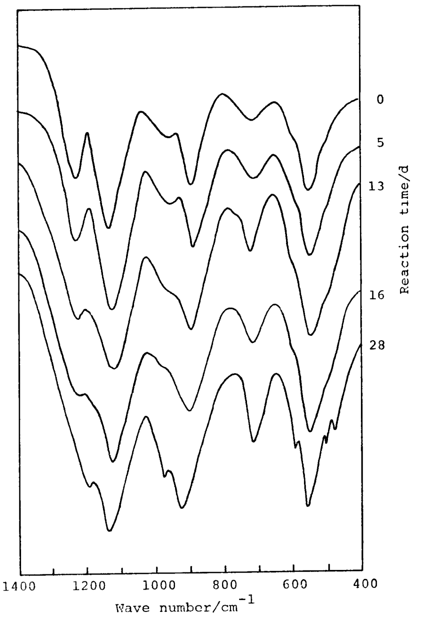

Fig. 2. IR spectra of the self-decomposition products of the barium tetraphosphate in air at 25—30 °C.

with time.

DTA and TG. DTA and TG curves of the strontium tetraphosphate are given in Fig. 4. The samples as numbered on Fig. 4 were removed from a furnace, cooled in a silica-gel desiccator, and subjected to further analysis. The results are presented in Table 4 and Figs. 5 and 6. Samples No. 1 and No. 2 were soluble in water, but No. 3 was insoluble in water. So the composition of phosphates in No. 3 could not be studied by paper chromatography. A rapid weight loss of the product and a corresponding big endothermic peak were observed below 150 °C. This reaction seemed to be caused by removing the bound water and, as Table 4 shows, the decomposition of the tetraphosphate to phosphates having shorter chain lengths occurred at the same time. The succeeding gradual weight loss of the product from 150—380 °C is the condensation reaction of the decomposition product. Samples No. 1 and No. 2 were X-ray diffractometrically amorphous, but, as Fig. 6 shows, sample No. 3 gave X-ray diffraction peaks of α-$Sr_2P_2O_7$ (ASTM card, No. 24-1011) and $Sr_3P_4O_{13}$ (ASTM card, No. 20-1207). So the exothermic peak at about 540 °C may be due to the crystallization of the amorphous phosphates.

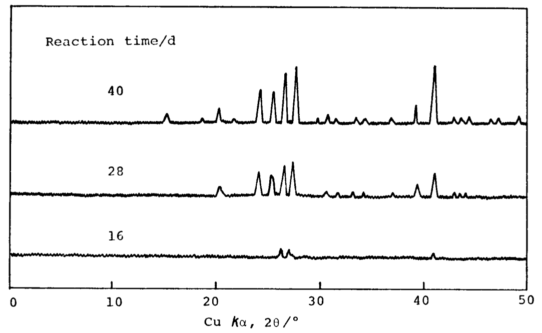

Fig. 3. X-Ray diffraction diagrams of the self-decomposition products of the barium tetraphosphate in air at 25—30 °C.

Table 3. The water contents of the decomposition products of the barium tetraphosphate in air at 25—30 °C

Reaction time/d	H_2O(%)
0	14.4
5	12.1
13	10.0
16	8.4
28	7.1

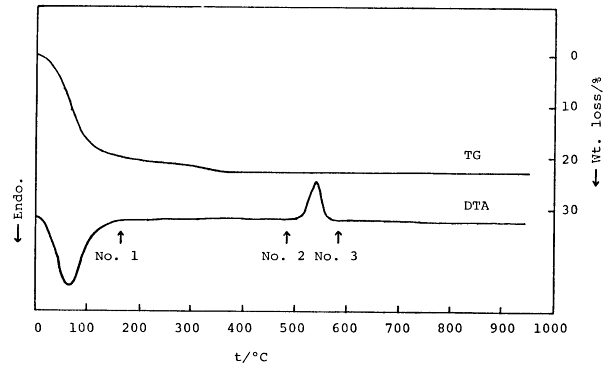

Fig. 4. DTA and TG curves of the strontium tetraphosphate in air.

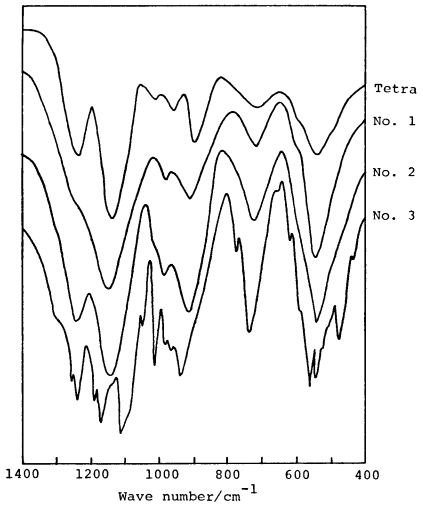

Fig. 5. IR spectra of the thermal decomposition products (Nos. 1—3) of the strontium tetraphosphate in air.

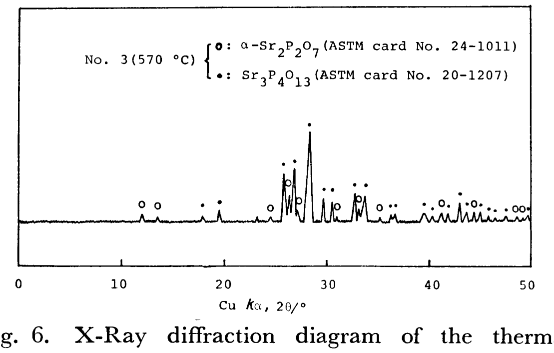

Fig. 6. X-Ray diffraction diagram of the thermal decomposition product (No. 3) of the strontium tetraphosphate in air.

Table 4. Composition and weight loss of the thermal decomposition products of the strontium tetraphosphate

Sample	Phosphates/P(%)					Wt. loss/%
	Ortho	Di	Tri	Tetra	Higher	
No. 1	26.1	47.2	18.5	8.2	—	21.2
No. 2	18.8	30.2	16.8	34.2		22.9

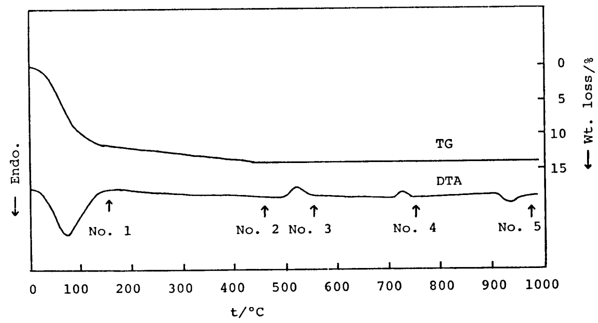

Fig. 7. DTA and TG curves of the barium tetraphosphate in air.

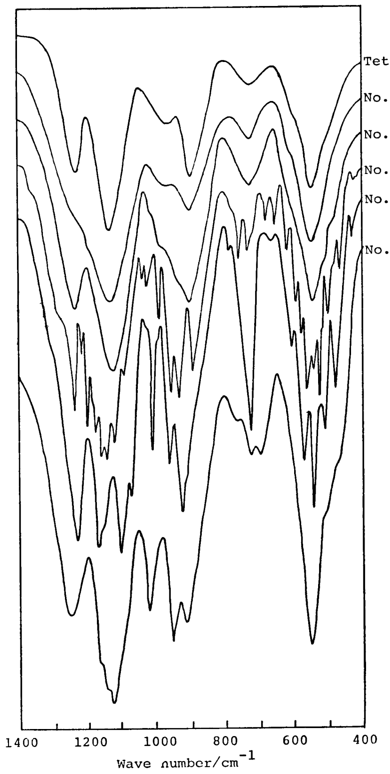

Fig. 8. IR spectra of the thermal decomposition products (Nos. 1—5) of the barium tetraphosphate in air.

The curves of DTA and TG measurements of the barium tetraphosphate are shown in Fig. 7. The tetraphosphate showed a rapid weight loss accompanied by a big endothermic peak. The process was considered to be caused by the elimination of the bound water. As Fig. 8 shows, the absorption of a $(PO_2)^-$ group disappeared in the IR spectrum of No. 2, while the sample still showed the absorptions of a P–O–P linkage. This means that the tetraphosphate decomposes to phosphates with shorter chain lengths and the main decomposition product is diphosphate. The gradual weight loss seemed to be due to the condensation of the decomposed phosphates since, as Fig. 8 shows, sample No. 3 showed the IR absorption of a $(PO_2)^-$ group at about 1240 cm^{-1}. Samples No. 1 and No. 2 were amorphous and No. 3 gave the unknown X-ray diffraction peaks shown in Fig. 9. So the exothermic peak around 520 °C is attributable to the crystallization of the phosphates. After the second exothermic peak, the sample gave different X-ray diffraction peaks. The small endothermic peak at about 930 °C was caused by melting of a part of the phosphates because the product was sintered after the endothermic reaction. The last product gave the X-ray diffraction pattern of barium diphosphate (ASTM card, No. 9-45), while the IR spectrum of No. 5 gave the absorption associated with a $(PO_2)^-$ group. Therefore, sample No. 5 was considered to be a mixture of crystalline barium diphosphate and amorphous polyphosphates having a middle-PO_4 group.

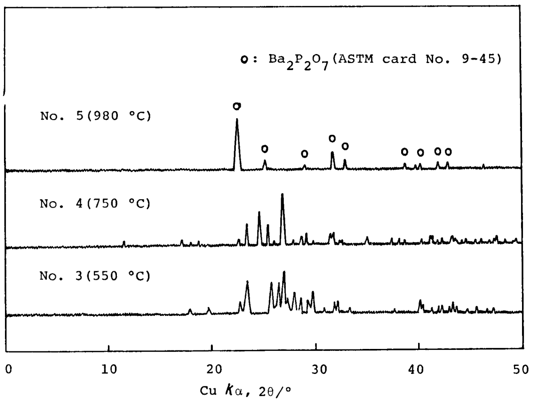

Fig. 9. X-Ray diffraction diagrams of the thermal decomposition products (Nos. 3—5) of the barium tetraphosphate in air.

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