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The Synthesis and Thermal Behavior of Barium Bis(hydrogenphosphoramidate) and Barium Phosphoramidate

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Barium bis(hydrogenphosphoramidate) monohydrate and barium phosphoramidate monohydrate were made by mixing a solution of potassium hydrogenphosphoramidate and a solution of barium chloride at pH 6.1—6.4 and 10.0—10.5 respectively. Both products were stable at room temperature. Barium bis(hydrogenphosphoramidate) monohydrate was decomposed by water to produce the orthophosphate. This was condensed to make polyphosphates above 100 °C and finally formed barium metaphosphate above 500 °C. The thermal products of the hydrogenphosphoramidate did not produce any phosphate with imino groups. Barium phosphoramidate produced ortho-, di-, imidodi-, and triphosphates when it was heated above 200 °C. These thermal products were converted to dibarium diphosphate in air above 500 °C.

Among many phosphorus–nitrogen compounds, phosphazenes are probably the best-known and the most intensively investigated compounds. Some of them are already used as industrial materials and products. There are a series of phosphorus–nitrogen compounds which have amino groups on a P atom. These compounds can be used as a new type of chemical fertilizer with a P-N covalent bond and as flameproof materials because they produce polyphosphates having imino and amino groups when they are heated. They can also be used as starting materials for the preparation of many organic and inorganic phosphorus compounds.

In our previous papers,[1–4] the synthesis and the thermal behavior of magnesium and calcium phosphoramidates and hydrogenphosphoramidates were reported. Both the hydrogenphosphoramidates were unstable even at room temperature and decomposed to polyphosphates, while the phosphoramidates were stable at room temperature. These phosphoramidates and hydrogenphosphoramidates were decomposed to polyphosphates above room temperature in air. This paper will describe the synthesis and the thermal behavior of barium bis(hydrogenphosphoramidate) and phosphoramidate.

Experimental

Preparation of Barium Bis(hydrogenphosphoramidate). Potassium hydrogenphosphoramidate was made by the method described in a previous paper;[5] 0.08 mol of the phosphoramidate was dissolved in 85 cm^3 of water. The aqueous solution of barium chloride, which was made by dissolving 0.04 mol of barium chloride dihydrate in 40 cm^3 of water, was added to the phosphoramidate solution below 5 °C to prevent the hydrolysis of the phosphoramidate. The pH of the solution was 6.1—6.4 during the treatment. A white precipitate was filtered off and washed with cold water, ethanol, and then acetone. The product was dried at 50 °C for 1 d under reduced pressure.

Preparation of Barium Phosphoramidate. Potassium hydrogenphosphoramidate(0.04 mol) was dissolved in 400 cm^3 of water. Barium chloride dihydrate (0.04 mol) was dissolved in 120 cm^3 of water. The solution was poured into the phosphoramidate solution and the resulting solution was stirred for 5—10 min. During the treatment, the temperature of the phosphoramidate solution was kept below 5 °C to prevent the hydrolysis of the phosphoramidate; the pH of the solution was kept at 10.0—10.5 with aqueous ammonia. The white precipitate thus obtained was removed by filtration. Acetone was added to the mother liquor and the white product was filtered off, washed with 50-V% aqueous ethanol, ethanol, and then acetone. The product was dried at 25 °C for 1 d under reduced pressure.

Chemical Analysis. Phosphorus in a sample was determined colorimetrically by dissolving about 0.2 g of the sample in 100 cm^3 of a 6%-EDTA (disodium dihydrogen ethylenediaminetetraacetate dihydrate) aqueous solution. Barium and nitrogen in a sample were estimated by the gravimetric technique and the Kjeldahl method respectively.

Paper Chromatography and Colorimetry of Phosphates. The thermal products of barium hydrogenphosphoramidate were dissolved in a 6%-EDTA aqueous solution and those of barium phosphoramidate were dissolved in the EDTA solution of pH 9—10 controlled with aqueous ammonia. The one-demensional paper-chromatographic separation and the colorimetric determination of the phsophate species in the EDTA solutions were made by the method described in our previous paper.[1]

X-Ray Diffractometry. An X-ray diffraction diagram of a powder sample was taken with nickel-filtered Cu *Kα* radiation using a Toshiba X-ray diffractometer, ADG-102.

IR Spectrophotometry. An IR spectrum of a sample was recorded on a JASCO IR spectrophotometer, A-3, using the KBr disc method.

^{31}P NMR Measurement. The nuclear magnetic resonance data were taken with a JNM-GX270 spectrograph on the aqueous solutions of the thermal products located by paper chromatography. As is customary, the NMR chemical shifts are reported relative to external 85%-orthophosphoric acid with positive shifts being downfield.

DTA and TG. A sample was heated at a rate of 5 °C min^{-1} in air by means of a Cho Balance TRDA$_1$-H apparatus.

Results and Discussion

Barium Bis(hydrogenphosphoramidate). The yield of the product was about 10.2 g. Found: P, 18.4; N, 7.9; Ba, 38.5%. Calcd for $Ba(HPO_3NH_2)_2 \cdot H_2O$: P, 17.8; N, 8.1; Ba, 39.5%. In this manner, the product was

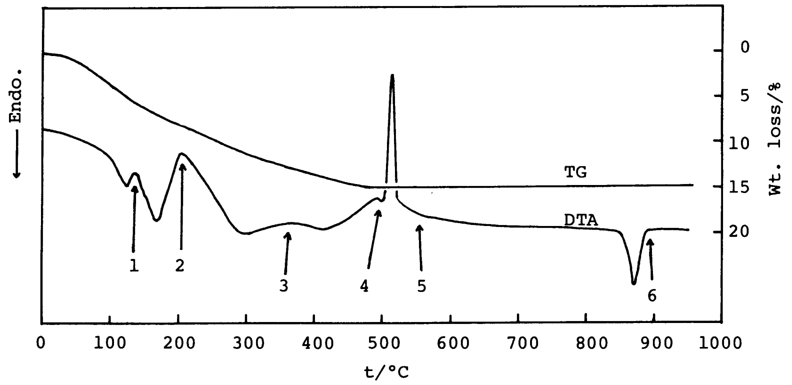

Fig. 1. DTA and TG curves of $Ba(HPO_3NH_2)_2 \cdot H_2O$ in air.

TABLE 1. WEIGHT LOSS AND COMPOSITION OF THE THERMAL PRODUCTS OF $Ba(HPO_3NH_2)_2 \cdot H_2O$

Sample	Total N/%	N/% as NH_4^+	Wt. loss /%	X-Ray dif.	Ortho & Amido	Di & Imidodi	Tri	Higher
Amido[a]	7.9	—	—	—	100	—	—	—
1	5.8	2.2	4.1	Am[b]	47.3	24.7	12.9	15.1
2	2.4	2.2	7.7	Am	10.3	15.8	16.4	57.5
3	0.6	—	11.7	Am	—	—	—	—
4	0	0	13.9	Am	—	—	—	—
5	0	0	15.0	$Ba(PO_3)_2$ JCPDS card 20-141	—	—	—	—
6	0	0	15.1	Am	—	—	—	—

a) $Ba(HPO_3NH_2)_2 \cdot H_2O$. b) Amorphous.

found to be barium bis(hydrogenphosphoramidate) monohydrate. The X-ray diffraction diagram of the product was the same as that of $Ba_{1/2}HPO_3NH_2 \cdot H_2O$ (JCPDS card, No. 18—170), but the careful measurement of the heating weight loss of the product, as will be shown later, also supported the above conclusion. Magnesium and calcium bis(hydrogenphosphoramidate) slowly decomposed to polyphosphates at room temperature,[1,2] while the product obtained in this work was very stable and did not decompose at room temperature. To study the thermal behavior of the product, DTA and TG curves of the product were taken with the result shown in Fig. 1. The samples as numbered on Fig. 1 were removed from a furnace, cooled in a silica-gel desiccator, and subjected to further analysis. The results are shown in Table 1, and Figs. 2 and 3. The hydrogenphosphoramidate showed two endothermic peaks accompanying weight loss below 200 °C. The following dehydration reaction may be written for the endothermic process:

$$Ba(HPO_3NH_2)_2 \cdot H_2O \longrightarrow Ba(HPO_3NH_2)_2 + H_2O. \quad (1)$$

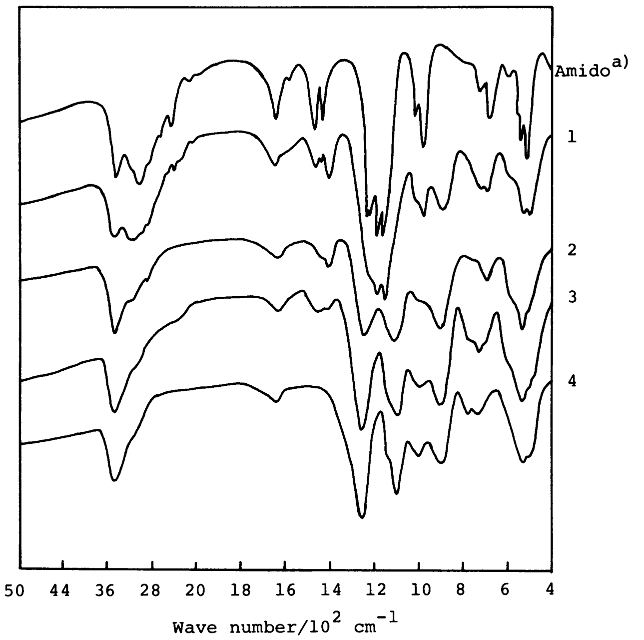

Fig. 2. IR spectra of the thermal products of $Ba(HPO_3NH_2)_2 \cdot H_2O$.
a): $Ba(HPO_3NH_2)_2 \cdot H_2O$.

As Table 1 shows, the thermal product 1 exhibited less N content than that of $Ba(HPO_3NH_2)_2$ and contained ammonium ions. The N content of the product 2 was less than that of the product 1. Almost all the nitrogen of the product 2 was present as ammonium ions. The IR spectra of the thermal products 1 and 2 showed peaks of NH_4^+ at 1400 cm^{-1}, P–O–P and/or P–N(H)–P at 900 cm^{-1}, and $(PO_2)^-$ at 1220—1250 cm^{-1}. The paper-chromatographic analysis of the thermal products 1 and 2 agreed well with these results. Since the thermal

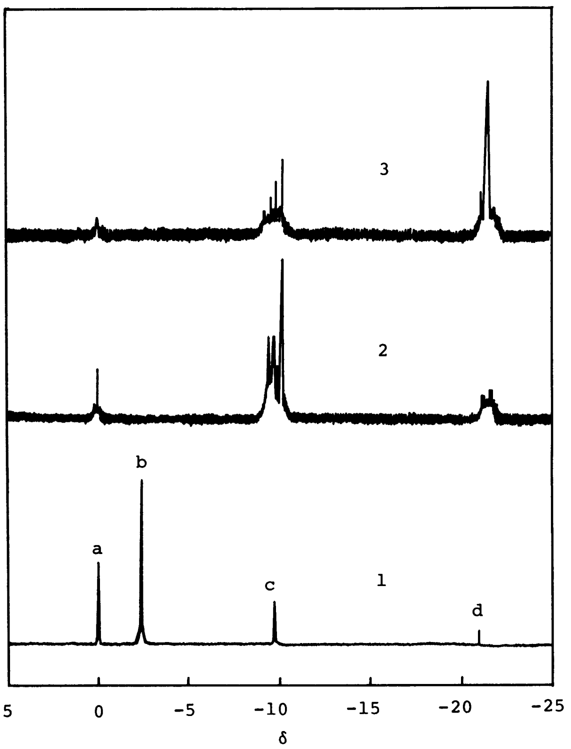

Fig. .3 ^{31}P NMR spectra of the thermal products of $Ba(HPO_3NH_2)_2 \cdot H_2O$ in air.
a: Orthophosphate, b: phosphoramidate, c: end-PO_4 group, d: middle-PO_4 group.

products other than 1 and 2 contained insoluble material and the separation of the phosphate species was poor, the paper-chromatographic analysis of the products was not possible. The above results do not indicate clearly that $P-NH_2$ linkages thermally decompose to form P-N(H)-P linkages with the elimination of ammonia as follows:

$$-\overset{|}{\underset{|}{P}}-NH_2 + NH_2-\overset{|}{\underset{|}{P}}- \longrightarrow -\overset{|}{\underset{|}{P}}-N(H)-\overset{|}{\underset{|}{P}}- + NH_3. \quad (2)$$

Accordingly, a ^{31}P NMR study of the thermal products was made. The ^{31}P NMR spectrum of the thermal product 1 showed peaks due to orthophosphate (0 ppm), phosphoramidate (−2.4 ppm), an end-PO_4 group (−9.8 ppm), and a middle-PO_4 group (−20.9 ppm). The thermal product 2 showed the NMR peaks of orthophosphate, an end-PO_4 group, and a middle-PO_4 group. Accordingly, these thermal products did not contain any substance with P-N(H)-P linkages. The hydrogenphosphoramidate did not form thermal products with imino groups. According to the above results, one can write the following reactions for the thermal decomposition of the hydrogenphosphoramidate to orthophosphate and condensation of the orthophosphate to polyphosphates:

$$Ba_{1/2}HPO_3NH_2 + H_2O \longrightarrow Ba_{1/2}NH_4HPO_4, \quad (3)$$

$$2Ba_{1/2}NH_4HPO_4 \begin{cases} \nearrow Ba(HO_3POPO_3H) + 2NH_3 + H_2O, & (4) \\ \searrow Ba(HO_3POPO_3NH_4) + NH_3 + H_2O, & (5) \end{cases}$$

$$Ba(HO_3POPO_3H) + Ba_{1/2}NH_4HPO_4 \longrightarrow Ba_{3/2}[HO_3POP(O_2)OPO_3H] + NH_3 + H_2O. \quad (6)$$

The thermal product 3 contained only a small amount of nitrogen and the product 4 contained no nitrogen. The IR spectra of these products were similar to that of polyphosphate with a meta composition. The ^{31}P NMR spectrum of the product 3 showed a small orthophosphate peak and peaks of end- and middle-PO_4 groups. Therefore, the successive broad endothermic peaks were found to be caused by the condensation of ortho- and polyphosphates to polyphosphate with a meta composition. The thermal products 1-3 showed weak unknown X-ray diffraction peaks and the product 4 was amorphous by X-ray diffractor. The product 5 showed X-ray diffraction peaks of barium metaphosphate(JCPDS card, No. 20—141). The large exothermic peak at about 510 °C is responsible for the conversion of amorphous barium metaphosphate into the crystalline form. The measured weight losses of the products 5 and 6 were close to the calculated one according to the following reaction:

$$Ba(HPO_3NH_2)_2 \cdot H_2O \longrightarrow Ba(PO_3)_2 + 2NH_3 + H_2O. \quad (7)$$

The last endothermic peak at about 870 °C was found to be caused by the melting of the barium metaphos-

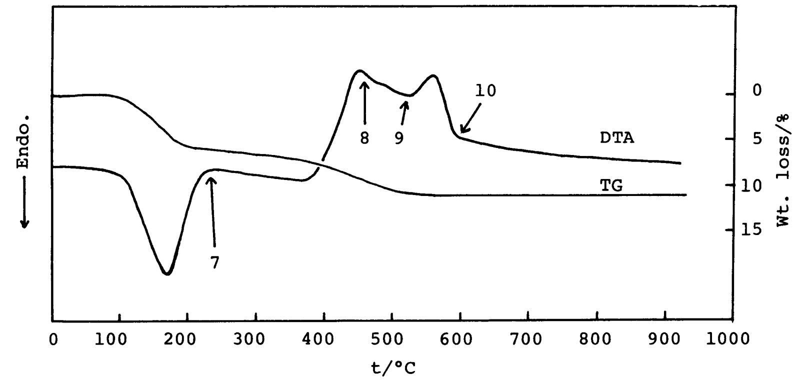

Fig. 4. DTA and TG curves of $BaPO_3NH_2 \cdot H_2O$ in air.

Table 2. Weight loss and composition of the thermal products of $BaPO_3NH_2 \cdot H_2O$

Sample	Total N/%	N/% as NH_4^+	Wt. loss /%	X-Ray dif.	Ortho & Amido	Di & Imidodi	Tri
Amido[a]	5.4	—	—	—	100	—	—
7	5.2	1.8	6.6	Un[b]	78.1	21.9	0
8	4.0	1.8	7.9	Un	56.2	37.3	6.5
9	0.5	0.3	10.1	Am[c]	11.4	77.2	11.4
10	0	0	10.8	$Ba_2P_2O_7$ JCPDS card 9-45	2.3	97.7	0

a) $BaPO_3NH_2 \cdot H_2O$. b) Unknown pattern. c) Amorphous.

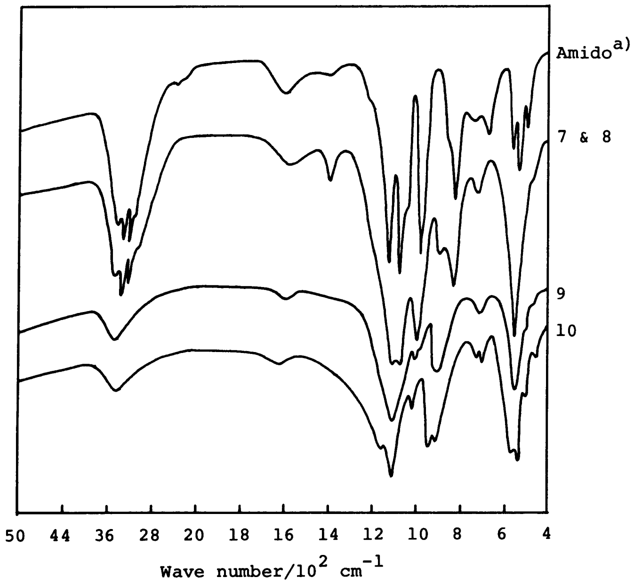

Fig. 5. IR spectra of the thermal products of $BaPO_3NH_2 \cdot H_2O$.
a): $BaPO_3NH_2 \cdot H_2O$.

phate.

Barium Phosphoramidate. The yield of the product was about 8.5 g. Found: P, 12.3; N, 5.4; Ba, 54.7%. Calcd for $BaPO_3NH_2 \cdot H_2O$: P, 12.4; N, 5.6; Ba, 54.2%. Accordingly, the product is barium phosphoramidate monohydrate. As will be described in the later part of this section, the study of the heating weight loss of the product supported this conclusion. The phosphoramidate was stable and did not decompose at room temperature. To study the thermal behavior of the product, DTA and TG curves of the product were taken with the result in Fig. 4. The chemical analysis data, the IR spectra, and the ^{31}P NMR spectra of the thermal products are shown in Table 2, and Figs. 5 and 6 respectively. The first large endothermic reaction accompanied by rapid weight loss seemed to be caused mainly by removal of the bound water because the measured weight loss was close to the calculated one according to the reaction:

$$BaPO_3NH_2 \cdot H_2O \longrightarrow BaPO_3NH_2 + H_2O. \qquad (8)$$

As Table 2 shows, the nitrogen content of the thermal product 7 was less than that of $BaPO_3NH_2$. The product contained ammonium ions and ortho-, and diphosphate and/or imidodiphosphate other than the phosphoramidate. The IR spectrum of the product 7 exhibited absorptions of NH_4^+ at 1400 cm⁻¹ and P–O–P and/or P–N(H)–P linkages at 900 and 720 cm⁻¹. These results indicate that barium phosphoramidate monohydrate reacts at this stage according to the following processes other than reaction 8:

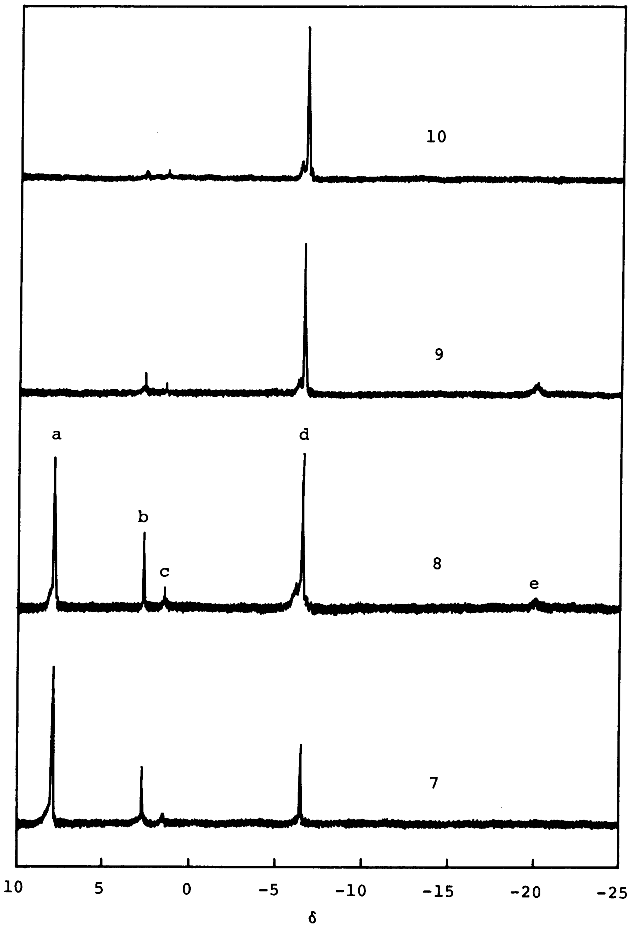

Fig. 6. ^{31}P NMR spectra of the thermal products of $BaPO_3NH_2 \cdot H_2O$ in air.
a: Phosphoramidate, b: orthophosphate, c: imidodiphosphate,[6] d: end-PO_4 group, e: middle-PO_4 group.

$$BaPO_3NH_2 + H_2O \longrightarrow BaNH_4PO_4, \qquad (9)$$

$$BaNH_4PO_4 \longrightarrow BaHPO_4 + NH_3, \qquad (10)$$

$$2BaHPO_4 \longrightarrow BaO_3POPO_3Ba + H_2O, \qquad (11)$$

$$2BaPO_3NH_2 \longrightarrow BaO_3PN(H)PO_3Ba + NH_3. \qquad (12)$$

As Fig. 6 shows, the product 7 contained phosphoramidate, orthophosphate, imidodiphosphate, and diphosphate. (Barium phosphoramidate, tribarium bis(phosphate), and dibarium diphosphate showed ^{31}P NMR peaks at about 7.8—8.0, 2.8, and −5.6—−6.3 ppm respectively in a 6%-EDTA solution of pH 9—10 controlled with aqueous ammonia). So all the above reactions 9—12 take place at this stage. The intensity of the imidodiphosphate peak was weak and the rate of the Reaction 12 seemed to be much slower than those of the other reactions. According to Table 2, successive slow weight loss was due to the elimination of ammonia. Since the NMR spectrum of the product 8 exhibited peaks with stronger intensity than that of the product 7 at the same δ, the above reactions 9—12 may take place rapidly over the temperature range of 400—500 °C. The total energy of the reactions was considered to be exothermal. As Table 2 and Fig. 6 show, the thermal products 8 and 9 contained triphosphate. It is not probable that orthophosphate with Ba/P ratio of 1.0 would form triphosphate over this low temperature range. The problem can be solved by taking into account the following reorganization or disproportionation reaction in this system:

$$2BaNH_4PO_4 \longrightarrow Ba_{3/2}PO_4 + Ba_{1/2}(NH_4)_2PO_4. \qquad (13)$$

The chemical species, $Ba_{1/2}(NH_4)_2PO_4$, can form triphosphate according to the reaction as follows:

$$Ba_{1/2}(NH_4)_2PO_4 + 2BaNH_4PO_4 \longrightarrow Ba_{5/2}[O_3POP(O_2)OPO_3] + 4NH_3 + 2H_2O. \qquad (14)$$

The product 10 contained small amounts of ortho- and imidodiphosphates other than diphosphate and did not contain higher polyphosphates, so the reorganization or the decomposition of the triphosphate to diphosphate may occur according to the reaction:

$$Ba_{5/2}[O_3POP(O_2)OPO_3] + Ba_{3/2}PO_4 \longrightarrow 2Ba_2(O_3POPO_3). \qquad (15)$$

The NMR data also showed that imidodiphosphate gradually converted to diphosphate. The reaction written below can be responsible for the conversion:

$$BaO_3PN(H)PO_3Ba + H_2O \longrightarrow BaO_3POPO_3Ba + NH_3. \qquad (16)$$

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