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Thermal Decomposition of Barium Amidotriphosphate $Ba_2P_3O_9NH_2{\cdot}3.5H_2O$

Atsushi Takenaka,* Hiromu Yamasaki, Itaru Motooka,† and Hiroyuki Nariai†
Department of Industrial Chemistry, Yonago National College of Technology,
4448, Hikona-cho, Yonago, Tottori 683
† Department of Chemistry, Faculty of General Education, Kobe University,
Tsurukabuto, Nada-ku, Kobe 657

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Synopsis. Barium amidotriphosphate ($Ba_2P_3O_9NH_2{\cdot}3.5H_2O$) was heated at 5 K min^{-1} in streams of dried air, humid air, and dried hydrogen chloride. *cyclo*-Triphosphates were not observed in any products, unlike in the pyrolysis of $(NH_4)_4P_3O_9NH_2{\cdot}H_2O$. Water vapor or hydrogen chloride hydrolyzed phosphorus–nitrogen and phosphorus–oxygen bonds of the products.

As a new type of fertilizer and as flame-proofing materials, interest has been focused on inorganic phosphates with phosphorus–nitrogen bonds.[1] Of all the phosphorus–nitrogen phosphates, amidotriphosphates are known to be formed by ammonolyses of *cyclo*-triphosphates in aqueous solution.[2–4]

In the preceding work, we studied the thermal decomposition of ammonium amidotriphosphate $(NH_4)_4P_3O_9NH_2{\cdot}H_2O$.[5] The amidotriphosphate cyclized again to form a kind of ammonium *cyclo*-triphosphate.

Although the thermal products of inorganic phosphates partially depend on their constituent cation,[6] it was not clear whether amidotriphosphates other than $(NH_4)_4P_3O_9NH_2{\cdot}H_2O$ were thermally changed to *cyclo*-triphosphates or not. As barium amidotriphosphate ($Ba_2P_3O_9NH_2{\cdot}3.5H_2O$) could be obtained easily from $(NH_4)_4P_3O_9NH_2{\cdot}H_2O$, we have studied the thermal decomposition of $Ba_2P_3O_9NH_2{\cdot}3.5H_2O$ in the present work, especially with interest in the formation of *cyclo*-triphosphates. Since hydrogen chloride acted as an accelerating agent for the cyclization of $(NH_4)_4P_3O_9NH_2{\cdot}H_2O$,[5] $Ba_2P_3O_9NH_2{\cdot}3.5H_2O$ was also heated in a stream of dried hydrogen chloride as well as streams of dried air and humid air.

Experimental

Eight mmol (2.617 g) of ammonium amidotriphosphate ($(NH_4)_4P_3O_9NH_2{\cdot}H_2O$)[3] was dissolved in 30 cm^3 of distilled water. This solution was mixed with 7 cm^3 of a 0.5 mol dm^{-3} barium chloride aqueous solution. The precipitate was removed by filtration. A 25-cm^3 portion of the barium chloride solution was added to the filtrate. The product was filtered off and washed sequentially with water, acetone, and ether, and then air-dried. The product was characterized by HPLC-FIA and by determinations of nitrogen,[5] barium,[7] and phosphorus.[8] Ammonium nitrogen[5] was not detected in the product. Found: P, 15.17; Ba, 43.78; N, 2.24%. Calcd for $Ba_2P_3O_9NH_2{\cdot}3.5H_2O$: P, 15.73; Ba, 46.50; N, 2.37%. Fifteen mg of the product was dissolved in 20 cm^3 of a 0.1 mol dm^{-3} aqueous tetrasodium ethylenediaminetetraacetate solution. As soon as it was diluted to 500 cm^3 with distilled water, the solution was analyzed with an HPLC-FIA system.

About 13 mg of the product was placed in a platinum pan. Thermal analyses (TG-DTA) were carried out at 5 K min^{-1} in stationary air and in a stream of dried air at 50 cm^3 min^{-1}. The dried air used was prepared by the passage of air through molecular sieves.[5]

A 0.1-g portion of the product was heated in a cylindrical electric furnace at the same rate of 5 K min^{-1} as that used in TG-DTA. A stream of humid air (relative humidity 90% at 25 °C) at 50 cm^3 min^{-1} and a stream of dried hydrogen chloride were prepared as reported in Ref. 5. Before heating, the electric furnace was purged with a volume of these gases about twice the volume of the furnace. As soon as the sample reached the required temperature, it was taken out and cooled to room temperature in a desiccator, and immediately analyzed by HPLC-FIA, X-ray diffractometry, and IR spectrophotometry. HPLC-FIA was performed as mentioned above. X-Ray diffraction patterns were obtained by the use of nickel-filtered Cu *Kα* radiation. IR spectra were measured with a KBr disc method.

Results and Discussion

Thermal Decomposition in Stationary Air. Figure 1 shows thermal analysis (TG-DTA) measured in stationary air and the DTA measured in a stream of dried air at 50 cm^3 min^{-1}. The endothermic peaks at 60 °C and at 90 °C in stationary air overlapped to appear as one peak at about 70 °C in a stream of dried atmosphere, which implied that the endothermic peaks were caused by the elimination of bound water (the water of crystallization).

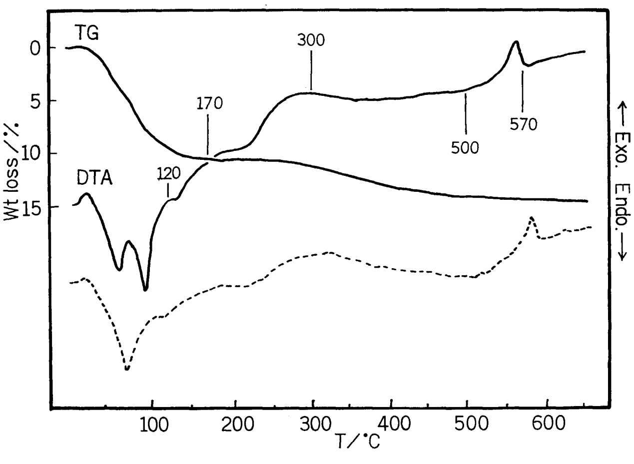

Fig. 1. Thermal analyses of $Ba_2P_3O_9NH_2{\cdot}3.5H_2O$ measured at a heating rate of 5 K min^{-1}. Solid line (—): TG and DTA measured in stationary air, dashed line (---): DTA measured in a stream of dried air.

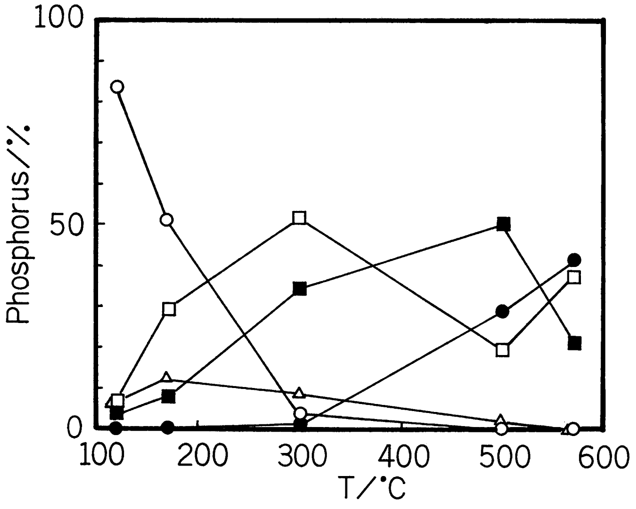

Fig. 2. Changes in amounts of phosphates in the samples heated at 5 K min^{-1} in stationary air. ○: amidotri-, ●: poly-, □: mono-, di-, and tri-, ■: oligo- (chain length=4—11), △: other (the phosphates were thought to have short or middle chain structures with one or several phosphorus-nitrogen bonds).

Figure 2 presents the percentage of phosphorus atoms present as amidotri-, from mono- to tri-, oligo- (chain length=4—12), and polyphosphates in the products obtained by heating to the temperatures indicated on the DTA curve of Fig. 1. Several peaks other than those of the above phosphate ions appeared before the peak of octaphosphate on the HPLC-FIA chromatograms. On the basis of their retention times, they were thought to be short or middle chain phosphates with one or several phosphorus-nitrogen bonds. They are also plotted in a group in Fig. 2 and expressed as "other".

Figure 3 shows the X-ray diffraction patterns of the products. The sample heated to 570 °C contained a crystalline material. The sample mainly consisted of poly- and triphosphates. Its X-ray diffraction data did not agree with any data of barium polyphosphates reported on the JCPDS cards. Therefore, perhaps, the crystalline material might have been a kind of triphosphate.

Figure 4 shows that absorptions at 1475 and at 1428 cm^{-1} appeared on the IR spectrum of the sample heated to 170 °C. Corbridge and Lowe suggested that two absorptions near 1400 cm^{-1} could be ascribed to the ammonium ion.[9] Therefore, the product heated to

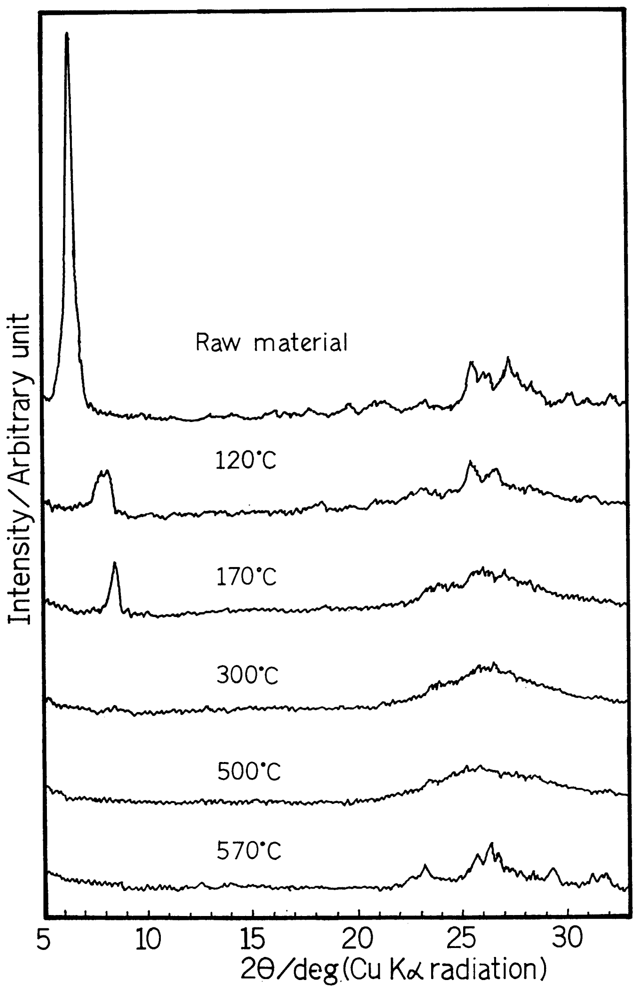

Fig. 3. X-Ray diffraction patterns of the samples heated at 5 K min^{-1} in stationary air.

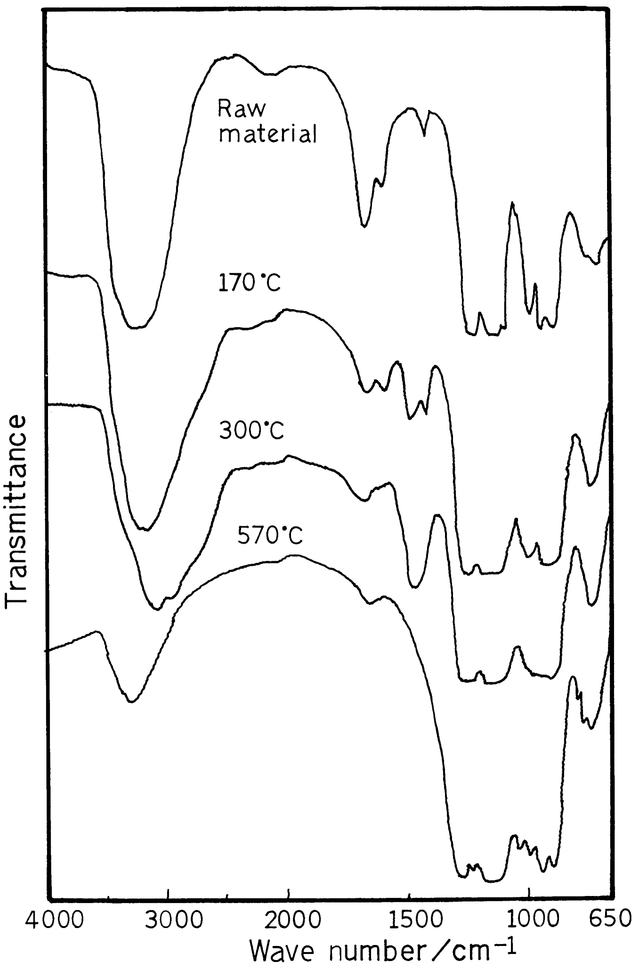

Fig. 4. IR spectra of $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$ and the samples heated at 5 K min^{-1} to 170, 300, and 570 °C in stationary air.

Table 1. Effect of the Atmosphere on the Phosphates Composition in the Products Obtained by Heating of $Ba_2P_3O_9NH_2\cdot3.5H_2O$

T/°C	Atmosphere	Composition/P%				
		amidotri-	mono-, di-, and tri-	oligo-[a)]	poly-	other[b)]
120	Dried air	69.7	9.9	6.2	6.3	8.0
	Humid air	72.3	10.1	5.0	7.3	5.4
	Dried HCl	—	78.9	12.4	8.6	—
170	Dried air	44.0	23.8	13.8	4.5	14.0
	Humid air	40.8	31.5	10.8	4.5	12.3
	Dried HCl	—	88.5	5.1	6.4	—
300	Dried air	6.4	38.7	29.1	4.7	21.0
	Humid air	—	55.1	36.8	4.0	4.1
500	Dried air	—	24.5	47.2	17.7	10.6
	Humid air	—	18.6	52.1	25.3	4.0
570	Dried air	—	19.5	38.6	36.3	5.6
	Humid air	—	37.5	24.9	35.2	2.4

a) The chain length was from four to twelve. b) These anions were thought to have short or middle chain structures with one or several phosphorus-nitrogen bonds.

170 °C contained ammonium ions, which must have been formed from amino groups. The spectrum of $Ba_2P_3O_9NH_2\cdot3.5H_2O$ showed a small absorption at 1602 cm^{-1}. The absorption probably arose from amino groups.[9,10)] It disappeared in the IR spectrum of the sample heated to 300 °C, which agreed with the result that amidotriphosphate ions were almost cleaved below 300 °C (Fig. 2).

Effect of Atmosphere on the Thermal Decomposition. The samples were heated at 5 K min^{-1} to the respective temperatures in three different atmospheres. Table 1 shows the percentage of phosphorus atoms present as the respective phosphates in the thermal products. *cyclo*-Triphosphates were observed in the thermal decomposition of ammonium amidotriphosphate ($(NH_4)_4P_3O_9NH_2\cdot H_2O$), as reported in the preceding paper.[5)] Hydrogen chloride accelerated the cyclization of the amidotriphosphate to the *cyclo*-triphosphate at lower temperatures. However, in the present work, *cyclo*-triphosphate ions could not be detected in any products. It might be attributed to the lack of formation of zwitterions reported in Ref. 5.

Table 1 shows that the above-mentioned "other" phosphates were not present and mono-, di-, and triphosphates were abundant in the samples heated in dried hydrogen chloride, which revealed that the hydrogen chloride did not act as an accelerating agent for the cyclization, but as a hydrolyzing agent for the phosphorus–nitrogen and the phosphorus–oxygen bonds. Water vapor in the atmosphere also hydrolyzed the phosphorus–nitrogen and the phosphorus–oxygen bonds present in the products.

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