Thermal Decomposition of Silver Amidotriphosphate $Ag_4P_3O_9NH_2$

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Synopsis. Silver amidotriphosphate, $Ag_4P_3O_9NH_2$, was heated at a rate of 5 K min^{-1} in a stream of dry air, humid air, or dry HCl. When heated to 245°C in a stream of dry air, $Ag_4P_3O_9NH_2$ was decomposed mainly to oligophosphates with some phosphorus-nitrogen bonds. Condensation of $Ag_4P_3O_9NH_2$ by the action of HCl took place even at room temperature.

It was reported that ammonium amidotriphosphate ($(NH_4)_4P_3O_9NH_2 \cdot H_2O$) cyclized thermally to ammonium *cyclo*-triphosphate in a solid state.[1] The cyclization was promoted by HCl at lower temperatures. In contrast, barium amidotriphosphate ($Ba_2P_3O_9NH_2 \cdot 3.5H_2O$) was not cyclized thermally even in the presence of HCl.[2]

The constituent cation is one of the factors which affect the composition and structure of thermal products of inorganic phosphates.[3] Since *cyclo*-triphosphates were formed from $(NH_4)_4P_3O_9NH_2 \cdot H_2O$, we expected that amidotriphosphates having monovalent cation would also cyclize to *cyclo*-triphosphates on heating. In view of this, thermal decomposition of silver amidotriphosphate ($Ag_4P_3O_9NH_2$) has been examined in the present work.

Experimental

Silver amidotriphosphate $Ag_4P_3O_9NH_2$ was prepared according to Ref. 4. HPLC-FIA showed that more than 93.9% of phosphorus atoms were present as amidotriphosphate ions in the products. Phosphorus, total nitrogen, and nitrogen present as ammonium ions, $N(NH_4^+)$, were analyzed as in Refs. 1 and 2. The nitrogen content present as amino, imino, and nitrilo groups ($N(NH_2^-)$) was calculated by subtracting the $N(NH_4^+)$ content from the total nitrogen content.[1,2] The silver content was determined by atomic absorption spectrophotometry. Found: Ag, 61.78; P, 13.23; $N(NH_4^+)$, 0.01; $N(NH_2^-)$, 1.82%. Calcd for $Ag_4P_3O_9NH_2$: Ag, 63.04; P, 13.57; $N(NH_2^-)$, 2.05%.

About 10 mg of the product was placed in a platinum pan. Thermal analyses (TG-DTA) were carried out at a heating rate of 5 K min^{-1} in quiescent air or in a stream of dry air with a flow rate of 50 cm^3 min^{-1}, using a MAC SCIENCE TG-DTA 2020 apparatus. The dry air was prepared by passing of air through molecular sieves.

A 0.1-g portion of the product was heated in a cylindrical electric furnace at the same heating 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} was prepared with an Ace Constant-humidity Generator Model AHC-1 (Ace Scientific Laboratory Co., Ltd.).[1,2] HCl was obtained as previously.[1] Before heating, the electric furnace was purged with the required gas of about twice its volume. As soon as the temperature of the sample reached the predetermined value, the sample was taken out and cooled in a silica gel desiccator, and then subjected to further analyses.

A 20-mg portion of a sample was dissolved in a mixture of 2 cm^3 of a 1 mol dm^{-3} NaCl aqueous solution and 2 cm^3 of a 0.1 mol dm^{-3} NaOH aqueous solution. AgCl was filtrated out from the solution. The filtrate was diluted to 500 cm^3 with distilled water, and immediately analyzed with a JASCO HPLC-FIA system.[1,2]

IR spectra were recorded with a JASCO IR-700 spectrophotometer by means of mull methods. The measurements of the spectra in the ranges 4000—2000 cm^{-1} and 1550—1300 cm^{-1} were carried out using HCB (hexachlorobutadiene) as dispersant. The spectra for 2000—1550 cm^{-1} and 1300—700 cm^{-1} were obtained using Nujol instead of HCB.

X-Ray diffraction patterns were measured by use of nickel-filtered Cu $K\alpha$ radiation.

Results and Discussion

Thermal Decomposition in Quiescent Air. The DTA curve of $Ag_4P_3O_9NH_2$ measured in quiescent air shows an exothermic peak at about 210°C (Fig. 1). A TG-gain was observed corresponding to the exothermic peak. When the thermal analyses (TG-DTA) were performed in a stream of dry air, the exothermic peak was weakened and the corresponding TG-gain was not detectable. Therefore the exothermic peak and the TG-gain must be attributable to absorption of water vapor from the atmosphere.

Figure 2 shows the percentage of phosphorus atoms present as amidotri-, mono-, di-, and tri-, oligo- (chain length=4—13), and polyphosphates in the products heated at a rate of 5 K min^{-1} to the temperatures indicated on the DTA curve of Fig. 1. Two peaks other than those of the above-mentioned phosphates were detected on the HPLC-FIA chromatograms of the products heated to 150°C. The one was located just before the peak of monophosphate, and the other just before that of diphosphate. In view of the short retention time, both

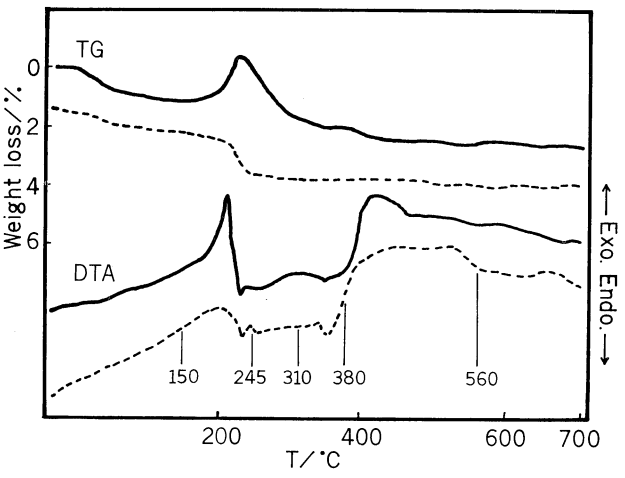

Fig. 1. TG and DTA curves for $Ag_4P_3O_9NH_2$. Solid curve (——): in quiescent air, dashed curve (---): in a stream of dry air.

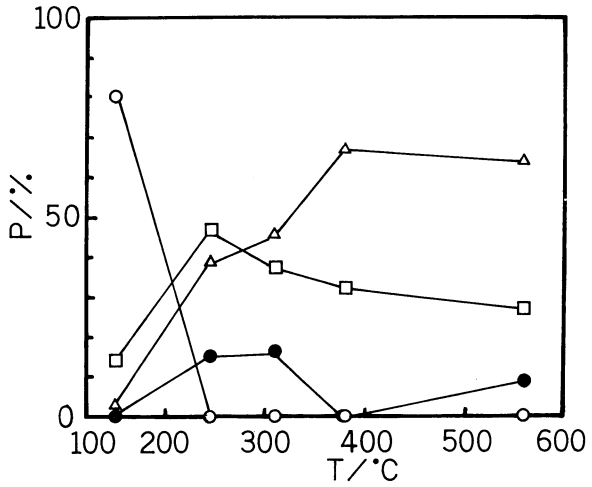

Fig. 2. Changes in the amounts of phosphates in the samples heated at a rate of 5 K min^{-1} in quiescent air. ○: amidotri-, ●:poly-, □: mono-, di-, and tri-, △: oligo- (chain length=4—13).

peaks are attributable to short-chain phosphates with one or several phosphorus(P)–nitrogen(N) bonds. Although a 3-% portion of phosphorus atoms was present as these phosphates with P–N bonds, the value was not plotted in Fig. 2. When heated to 150 °C, $Ag_4P_3O_9NH_2$ remained mostly undecomposed, as was recognized by X-ray diffractometry. Figure 2 indicates that $Ag_4P_3O_9NH_2$ was decomposed at a temperature above 245 °C.

Effect of Atmosphere on the Thermal Decomposition. Although $Ag_4P_3O_9NH_2$ was not converted to *cyclo*-triphosphates in quiescent air, we expected that its cyclization would be caused by HCl, as was the case for $(NH_4)_4P_3O_9NH_2 \cdot H_2O$.[1] Since water absorption took place at about 210 °C, $Ag_4P_3O_9NH_2$ was heated in a stream of dry air or humid air to examine the effect of humidity.

Some peaks other than those of amidotri-, mono-, di-, and tri-, oligo-, and polyphosphates were occasionally detected on the HPLC-FIA chromatograms of products. Judging from their locations, they are assignable to short or middle-chain phosphates with one or several P–N bonds, and are denoted as "other" in Table 1. Table 1 lists the percentage of phosphorus atoms present as the respective phosphate in the products heated to 150, 245, 310, and 380 °C at a rate of 5 K min^{-1}.

The fractions of phosphorus atoms present as oligophosphates in the products, heated to 150 °C in a stream of dry HCl, were higher than those in the products heated to 150 °C in a stream of dry air or humid air (Table 1). Therefore the oligophosphates might have resulted from the condensation of zwitterions, as was the case for the cyclization of $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ by HCl.[1] If the condensation of oligophosphates by HCl took place through the zwitterions, $Ag_4P_3O_9NH_2$ was expected to be condensed even at room temperature. In view of this, $Ag_4P_3O_9NH_2$ was reacted with dry HCl for 1 or 3 h. Indeed, the fraction of phosphorus atoms existing then as oligophosphates were 32 and 27 % in the products, respectively. Hence the condensation of $Ag_4P_3O_9NH_2$ to the oligophosphates by HCl must take place through the zwitterions.

Absorption of water vapor at about 210 °C is corroborated by the observation that the total amount of mono-, di-, and triphosphates in the products heated to 245 °C in a stream of humid air was higher than that in a stream of dry air. In the dry atmosphere, hydrolysis hardly takes place and an imino or a nitrilo group may be formed by the elimination of NH_3 from two or three amino groups of $Ag_4P_3O_9NH_2$. We thus analyzed the product heated to 245 °C in a stream of dry air to obtain P, 13.32; $N(NH_4^+)$, 0.01; $N(NH_2^-)$, 0.52 %. As shown in Table 1, only a small portion of phosphorus atoms was present as amidotriphosphates with P–N bonds in the product. The content of $N(NH_2^-)$, which reflects the existence of P–N bonds,[4] in the product was more than that calculated for the small amount of amidotriphosphates. Polyphosphates in the product hence must have some P–N bonds, because the other phosphates have no P–N bonds.

An absorption band at 3180 cm^{-1} in the IR spectrum of $Ag_4P_3O_9NH_2$ is assigned to the N–H asymmetric stretching vibration of $-NH_2$ groups, and that at 3090 cm^{-1} to the N–H symmetric stretching vibration (Fig. 3).[5,6] An absorption band at 1570 cm^{-1} may be assigned to the (P)–N–H deformation.[5,6] These absorption are not seen in

Table 1. Effect of the Atmosphere on the Phosphate Composition in the Products Obtained by Heating of $Ag_4P_3O_9NH_2$

T/°C	Atmosphere	Composition/P%				
		Amidotri-	Mono-, di-, and tri-	Oligo-[a]	Poly-	Other[b]
150	Dry air	80	13	2	—	5
	Humid air	82	14	2	—	2
	Dry HCl	—	68	32	—	—
245	Dry air	3	20	14	63	—
	Humid air	—	64	36	—	—
	Dry HCl	—	75	25	—	—
310	Dry air	—	15	36	47	2
	Humid air	—	36	48	16	—
380	Dry air	—	12	44	43	1
	Humid air	—	26	72	2	—

a) Chain lengths from 4 to 13. b) These anions were thought to have short or middle chain structures with one or several phosphorus-nitrogen bonds.

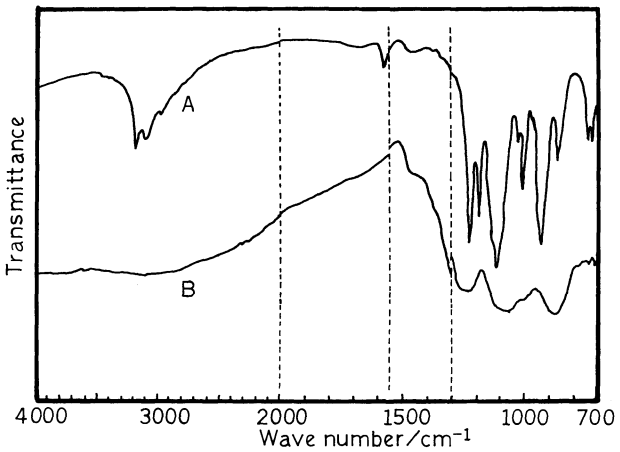

Fig. 3. IR spectra of $Ag_4P_3O_9NH_2$ and the sample heated at a rate of 5 K min^{-1} to 245 °C in a stream of dry air. The spectra for 4000—2000 cm^{-1} and for 1550—1300 cm^{-1} were obtained with mull methods by use of HCB (hexachlorobutadiene) as dispersant. The spectra for 2000—1550 cm^{-1} and for 1300—700 cm^{-1} were obtained by use of Nujol. A: $Ag_4P_3O_9NH_2$, B: product heated to 245 °C.

the spectrum of the product heated to 245 °C. Although the absorptions at about 730 cm^{-1} are assigned to the P–N stretching or to the (P)–O–P stretching (or bending),[5,7] they are not clearly detectable in the spectrum of Fig. 3 B. Thus, IR spectra do not demonstrate the presence of P–N bonds in the product.

To the contrary of our expectation, $Ag_4P_3O_9NH_2$ was not converted thermally to *cyclo*-triphosphates even by the action of HCl as was the case for $(NH_4)_4P_3O_9NH_2 \cdot H_2O$.[1]

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