Thermal Decomposition of Ammonium Copper(II) *cyclo*-Hexaphosphate $Cu_2(NH_4)_2P_6O_{18} \cdot 8.5H_2O$ and Ammonium Calcium *cyclo*-Hexaphosphate $Ca_2(NH_4)_2P_6O_{18} \cdot 7H_2O$

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Ammonium copper(II) and ammonium calcium *cyclo*-hexaphosphates, $Cu_2(NH_4)_2P_6O_{18} \cdot 8.5H_2O$ and $Ca_2(NH_4)_2P_6O_{18} \cdot 7H_2O$, were prepared by a wet method. TG-DTA, HPLC-FIA, and X-ray diffraction method were used to investigate the thermal decomposition of the *cyclo*-hexaphosphates. The effect of humidity on the pyrolysis was also examined by the use of dry N_2 gas and humid air. $Cu_2(NH_4)_2P_6O_{18} \cdot 8.5H_2O$ was mainly decomposed to oligophosphates by hydrolysis. Parts of the oligophosphates were changed to poly- (n=7—13) and highpolyphosphates through a condensation. The poly- and the highpolyphosphates were more abundant under the dried conditions. Above 280 °C ammonia was liberated. As the crystalline products, $Cu_2P_2O_7$ was identified at 380 °C, and $Cu_2P_4O_{12}$ above 430 °C. $Ca_2(NH_4)_2P_6O_{18} \cdot 7H_2O$ lost almost all its water of crystallization by 177 °C. As ammonia was evolved from 270 to 420 °C, accelerated by humidity, amorphous highpolyphosphates were formed. The formation of the highpolyphosphates was considered to proceed through a radical polymerization, since oligophosphates were scarcely detected in the course of the thermal reaction.

Ammonium calcium *cyclo*-triphosphate and its hydrates have been studied in regard to their formation,[1–4] crystal structures,[5–7] thermal behavior,[5,8] and other properties.[9] Ammonium calcium *cyclo*-tetraphosphate and its hydrate were also investigated mainly in terms of their crystal structures.[10,11] On the other hand, of all the ammonium copper(II) *cyclo*-phosphates, only the *cyclo*-octaphosphate was reported;[12] no ammonium calcium nor ammonium copper(II) *cyclo*-hexaphosphates has been reported in literature.

In the preceding study,[13] the thermal decomposition of ammonium strontium *cyclo*-phosphates was carried out in order to clarify whether a radical polymerization, like the thermal change of ammonium *cyclo*-phosphates to ammonium polyphosphate,[14] took place or not. Finally, it was concluded that the ammonium strontium *cyclo*-phosphates were decomposed to polyphosphates through dehydration-condensation rather than through radical polymerization. Therefore, the dehydration-condensation was supposed to also take place over the course of the thermal decomposition of another ammonium bivalent metal *cyclo*-phosphates.

Several experiments were attempted for the purpose of preparing some ammonium bivalent metal *cyclo*-hexaphosphates, but only the following salts were obtained: Ammonium copper(II) *cyclo*-hexaphosphate $Cu_2(NH_4)_2P_6O_{18} \cdot 8.5H_2O$ and ammonium calcium *cyclo*-hexaphosphate $Ca_2(NH_4)_2P_6O_{18} \cdot 7H_2O$.

The purpose of this series of studies has been to investigate the thermal decomposition of the ammonium bivalent metal *cyclo*-phosphates, especially with regard to the mechanism of the formation of the poly- and/or the highpolyphosphates from the ammonium bivalent metal *cyclo*-phosphates. Since the ammonium copper(II) and the ammonium calcium *cyclo*-hexaphosphates were prepared by wet methods, we studied the thermal decomposition of the two *cyclo*-hexaphosphates in the present work.

The ammonium copper(II) *cyclo*-hexaphosphates were decomposed to oligophosphates through hydrolysis, and polyphosphates generating through the dehydration-condensation of the oligophosphates. However, against our expectation, the ammonium calcium *cyclo*-hexaphosphate was thought to change to the highpolyphosphates via radical polymerization, which was accelerated by the humidity of the atmosphere.

Experimental

The ammonium bivalent metal *cyclo*-hexaphosphates, $Cu_2(NH_4)_2P_6O_{18} \cdot 8.5H_2O$ and $Ca_2(NH_4)_2P_6O_{18} \cdot 7H_2O$, were prepared by wet methods similar to those described in the literature.[13] HPLC-flow injection analyses (HPLC-FIA) for the samples of $Cu_2(NH_4)_2P_6O_{18} \cdot 8.5H_2O$ were carried out after metathesis by the use of a 1% (w/w) sodium sulfide aqueous solution, as reported by Nariai et al.[15] The other analytical procedures were essencially the same as those mentioned in the literature.[13]

$Cu_2(NH_4)_2P_6O_{18} \cdot 8.5H_2O$ was observed to consist only of *cyclo*-hexaphosphate ions. At least 99.9% of the phosphorus atoms were found to be present as *cyclo*-hexaphosphate ions in $Ca_2(NH_4)_2P_6O_{18} \cdot 7H_2O$.

Results and Discussion

Thermal Decomposition of Ammonium Copper(II) *cyclo*-Hexaphosphate $Cu_2(NH_4)_2P_6O_{18} \cdot 8.5H_2O$. Figure

1 shows thermal analyses (TG-DTA) in stationary air and in a stream of dry N_2 gas. Since ammonia was not evolved until 280 °C, the water of crystallization caused a large endothermic peak below 150 °C accompanying a loss in weight.

Figure 2 represents the percentage of phosphorus atoms present as *cyclo*-hexa-, oligo- (n=1—6), and polyphosphates (n=7—13) in the products which were obtained by heating to the temperature indicated by arrows in Fig. 1. Figure 2 shows that the amounts of the oligophosphates were obviously larger under the humid conditions than under the dry conditions—these, humid and dry, conditions were the same as those described in Ref. 13. The oligophosphates were found abundantly even under the dry conditions; thus, $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$ was thought to be hydrolyzed mainly by its water of crystallization. The amounts of the polyphosphates were less under the humid conditions, and the highpolyphosphates were not observed at all under the humid conditions. The polyphosphates and highpolyphosphates were formed in largest amounts at 280 °C under the dry conditions. Since the primitive products were the oligophosphates, the poly- and the highpolyphosphates were thought to be produced by dehydration-condensation of the oligophosphates. The smaller amounts of polyphosphates and the absence of the highpolyphosphates under the humid conditions must be attributed to a retardation of the dehydration-condensation, caused by an enhanced partial pressure of the water vapor.

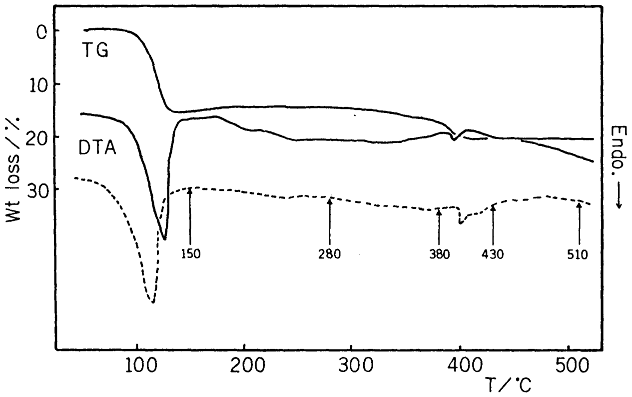

Fig. 1. Thermal analyses of $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$ measured in the two different atmospheres. Solid line (——): in stationary air, dotted line (----): DTA in a stream of dry N_2 gas, heating rate: 2.5 K min^{-1}.

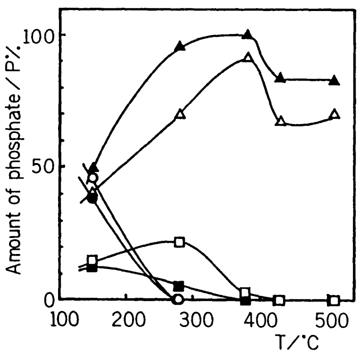

Fig. 2. Amount of phosphates in the decomposition products of $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$.
○ and ●: *cyclo*-Hexaphosphate observed under the dried and the humid conditions, respectively; △ and ▲: oligophosphates (chain length, n=1—6) observed under the dried and the humid conditions, respectively; □ and ■: polyphosphates (n=7—13) under the dried and the humid conditions, respectively.

Since ammonia gradually evolved for temperatures above 280 °C, several reactions, such as a deammoniation and a dehydration (and besides a liberation of diphosphorus pentaoxide), were considered to take place simultaneously. We therefore could not clarify the process of the decomposition. The products obtained by heating until 150 and 280 °C were amorphous, while the X-ray diffraction patterns of the products heated to 380 °C were those of $Cu_2P_2O_7$. Copper(II) *cyclo*-tetraphosphate, $Cu_2P_4O_{12}$, was the only crystalline material at 430 and 510 °C. The oligophosphates fell off from 380 to 430 °C, which was accompanied with a large weight loss. The endothermic peak at 400 °C can probably be attributed to the formation of *cyclo*-tetraphosphate from the oligophosphates, as reported by Thilo and Grunze.[16] Only under the dry conditions was the *cyclo*-triphosphate anion $P_3O_9{}^{3-}$ detected at 430 °C. Although the phosphorus present as $P_3O_9{}^{3-}$ was ca. 16%, there were no X-ray diffraction lines except for those of $Cu_2P_4O_{12}$. Therefore, the *cyclo*-triphosphate was considered to be in the form of an amorphous phase.

Thermal Decomposition of Ammonium Calcium *cyclo*-Hexaphosphate $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$. Figure 3 shows thermal analyses in stationary air and in a stream of dry nitrogen gas. Figure 4 represents the

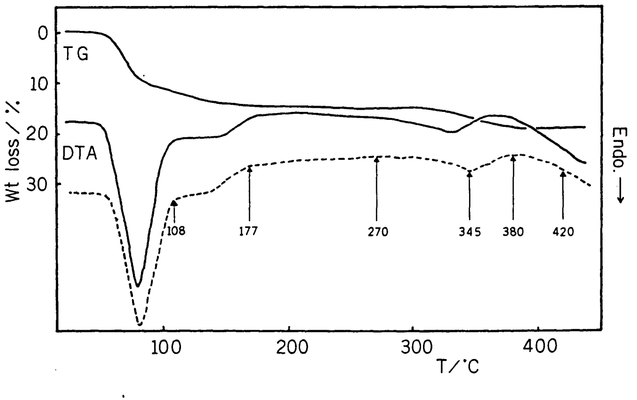

Fig. 3. Thermal analyses of $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ measured in the two different atmospheres. Solid line (——): in stationary air, dotted line (----): DTA in a stream of dry N_2 gas, heating rate: 2.5 K min^{-1}.

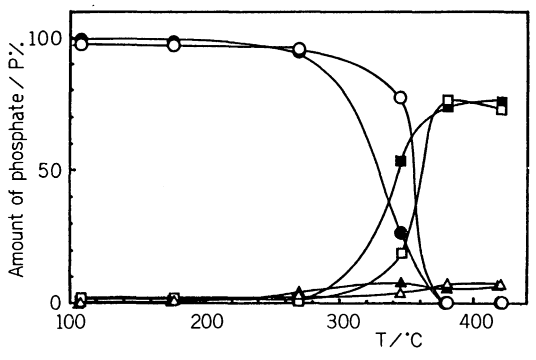

Fig. 4. Amount of phosphates in the decomposition products of $Ca_2(NH_4)_2P_6O_{18}\cdot7H_2O$.
○ and ●: *cyclo*-Hexaphosphate observed under the dried and the humid conditions, respectively; △ and ▲: oligophosphates (n=1—6) under the dried and the humid conditions, respectively; □ and ■: highpolyphosphates under the dried and the humid conditions, respectively.

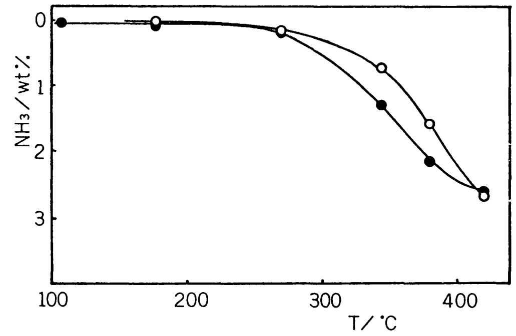

Fig. 5. Amount of ammonia evolved by heating $Ca_2(NH_4)_2P_6O_{18}\cdot7H_2O$.
○: in the dried atmosphere, ●: in the humid atmosphere.

percentage of phosphorus atoms present as *cyclo*-hexa-, oligo- (n=1—6), and highpolyphosphates, in the products obtained by heating up to the temperature indicated by arrows in Fig. 3.

Ammonia was evolved, as shown in Fig. 5. Until 270 °C, the *cyclo*-hexaphosphate ions were not cleaved and ammonia was hardly evolved. There was little change in weight from 177 to 270 °C. Therefore, the weight loss until 170 °C was attributed to the liberation of the water of crystallization, which caused a series of the endothermic peaks below 177 °C, as expressed by the following equation (Eq. 1):

$$Ca_2(NH_4)_2P_6O_{18}\cdot7H_2O \rightarrow Ca_2(NH_4)_2P_6O_{18}+7H_2O. \quad (1)$$

Figure 4 shows that highpolyphosphates were produced more rapidly under the humid conditions than under the dry conditions—these conditions were also the same as those mentioned in Ref. 13— in proportion to the disappearance of a *cyclo*-hexaphosphate. Although the *cyclo*-hexaphosphate was decomposed more rapidly under the humid conditions than under the dry conditions, there were only small amounts of oligophosphates, which are the primitive hydrolytic products of the *cyclo*-hexaphosphate, even under the humid conditions. If the highpolyphosphates were produced by a dehydration-condensation, as in the pyrolysis of $Cu_2(NH_4)_2P_6O_{18}\cdot8.5H_2O$, they should have been present more abundantly under the dry conditions than under the humid conditions. Therefore, however, the larger amount of the highpolyphosphates under the humid conditions suggests that they were not produced through the dehydration-condensation of the oligophosphates, but through another thermal change.

The TG-curve shows a plateau around 420 °C (Fig. 3). A weight loss of ca. 3.7% from 270 to 420 °C in the dry atmosphere was estimated from the ammonia evolved in this range (ca. 2.6%) and the water remaining at 270 °C in the products (ca. 1.1%). The loss (ca. 3.7%) was close to that actually observed by thermogravimetry (ca. 4.0%); thus, dehydration-condensation was more unlikely as a thermal formation of the highpolyphosphates.

We reported a radical polymerization on the thermal decomposition of ammonium *cyclo*-tetra- and *cyclo*-hexaphosphates.[14] Then, ammonium oligophosphates were yielded little or a little. And it was the "trigger reaction" in the decomposition of the ammonium *cyclo*-phosphates that a small amount of ammonia was liberated.

$Ca_2(NH_4)_2P_6O_{18}$, formed according to Eq. 1, was converted to amorphous highpolyphosphates at between 270 and 420 °C. The conversion was accompanied by a liberation of ammonia (Figs. 4 and 5), as in the case of the pyrolysis of the ammonium *cyclo*-phosphates.[14] The amounts of oligophosphates were small, as shown in Fig. 4, as in the case of the pyrolysis of the ammonium *cyclo*-phosphates.[14] Therefore, it might be concluded that the amorphous highpolyphosphates were produced through a polymerization of the oligophosphate radicals. The thermal change of $Ca_2(NH_4)_2P_6O_{18}$ to the highpolyphosphates can be described according to the following equation (Eq. 2):

$$Ca_2(NH_4)_2P_6O_{18}[\text{crystalline}] \rightarrow$$
$$2Ca(NH_4)_{1-x}H_x(PO_3)_3[\text{amorphous}]+2xNH_3. \quad (2)$$

As shown in Fig. 5, ammonia evolved more abundantly under the humid conditions than under the dry conditions, called the "catalytic effect" of humidity in the literature.[13] The evolution of ammonia caused an endothermic peak at 345 °C (Figs. 3 and 5). The catalytic effect was also shown by a shift in the endothermic peak to a lower temperature by the presence of water vapor.

Figure 3 shows neither an increase in the weight nor a corresponding exothermic peak, resulting from the water-incorporation of oligophosphate radicals, unlike in the pyrolysis of $(NH_4)_4P_4O_{12}$.[14] Perhaps, otherwise, the water molecules supplied by the humid air might form some weak bondings with the ammonium ions, so accelerating the liberation of ammonia.

It was reported in the literature[13] that ammonium strontium *cyclo*-triphosphate is decomposed to poly- ($n\geq 4$) and oligophosphates (n=1—3), e.g., from 250 to 380 °C under humid conditions. Because no observation was made of either an increase in weight nor of a corresponding exothermic peak, we concluded that the formation of the polyphosphates took place through dehydration-condensation. However, some part of the formation must proceed via oligophosphate radicals, especially within the initial temperature range (250—335 °C), since in this range there were hardly any oligophosphates which should appear as the primitive hydrolytic products of the ammonium strontium *cyclo*-triphosphate.

In the thermal decomposition of $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$ at higher temperature, a white sublimable material—which was probably diphosphorus pentaoxide—adhered to the inner surface at the outlet of a glass tube placed in a furnace. Although Feldmann reported that ammonium calcium *cyclo*-triphosphate $Ca(NH_4)P_3O_9\cdot aq$ liberated diphosphorus pentaoxide,[8] $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ did not apparently produce this material under the present conditions.

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