Studies on the Thermal Behavior of Inorganic Phosphates Containing Nitrogen as Ammonium Ions or Amino Groups

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平成５年１月

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（アンモニウムイオンあるいはアミノ基として
窒素を含む無機リン酸塩の熱挙動に関する研究）

平成５年１月

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Chapter 1 Introduction

1-1 Introduction

There are many polymers among the inorganic compounds. In general, they are not dissolved in any solvents.[1] Even if dissolved, they are occasionally decomposed. Therefore, studies on them are difficult. On the contrary, inorganic condensed phosphates are an exception. They have usually chain, cyclic, or branched structures.[2-8] They are comparatively easily dissolved in water or aqueous solutions with little decomposition.[1] Therefore, they are expected to be a good example for the studies of so-called "inorganic polymers."[9,10]

Of all the inorganic phosphates, there are many species including the salts of lower-oxy acids of phosphorus.[3,5,11] These salts are strongly reductive.[3,5,12] While, the phosphates in this thesis are those having fully oxidized phosphorus atoms, i. e., their oxidation number of + 5. They are stable,[1,3,12] and classified based on the ratio of M^I_2O/P_2O_5 (=R), where M^I means monovalent-metal present in them, as shown in Table 1·1.[7] Polyphosphates involve di-, tri-, tetraphosphates, and so forth.[2-5,7] They may be also classified as middle-chain-, i. e., oligophosphates, and long-chain-, i. e., poly- or highpolyphosphates.[6]

Strictly speaking, metaphosphates have cyclic-structure ions.[5, 13, 14] Of all them, cyclo-tri-,[15] cyclo-tetra-,[16] cyclo-hexa-,[17] and cyclo-octaphosphates[18] are well-known.

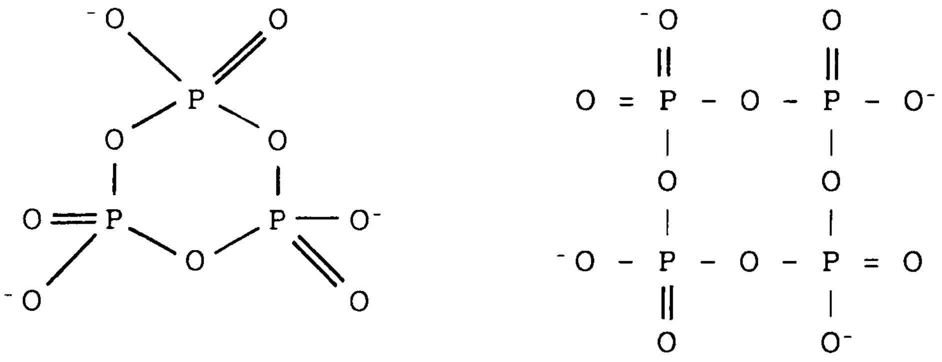
Table 1·1. Classification of Condensed Phosphates Based on the Ratio of $M^I{}_2O$ to P_2O_5 (=R)

$M^I{}_2O/P_2O_5$ (=R)[a]	Designation	General Formula
$R = 3$	Monophosphate	M_3PO_4
$1 < R \leqq 2$	Polyphosphate	$M_{n+2}P_nO_{3n+1}$
$R = 1$	Metaphosphate	$(MPO_3)_n$
$0 < R < 1$	Ultraphosphate	$xM_2O \cdot yP_2O_5$ $(0<x/y<1)$
$R = 0$	Phosphorus Pentoxide	P_2O_5

a) M^I stands for monovalent metal.

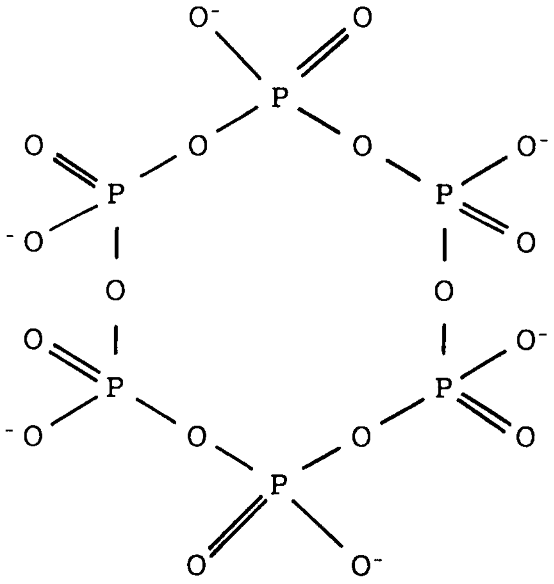
Figure 1·1 shows the ionic structures of cyclo-tri-, cyclo-tetra-, and cyclo-hexaphosphates.

As the condensed phosphates are comparatively easily dissolved in water or aqueous solutions, paper chromatography (PC),[19] thin-layer chromatography (TLC),[20] and liquid chromatography (LC)[21] have been used for separating and determining of their anions. Recently, high-performance liquid chromatography connected with flow-injection analysis (HPLC-FIA) has been developed.[22] Therefore, it was used in this work. X-Ray diffractometry is available, in a similar manner to that used in the studies of other inorganic compounds.[23, 24] IR spectrophotomery[25, 26] and nuclear magnetic resonance



cyclo-
Triphosphate Ion

cyclo-
Tetraphosphate Ion



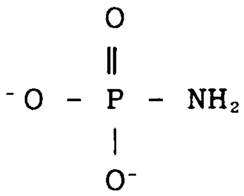
cyclo-
Hexaphosphate Ion

Fig. 1·1. Ionic structures of cyclo-tri-, cyclo-tetra-, and cyclo-hexaphosphates.

analysis[23,24] are effective analytical methods for the studies of inorganic phosphates.

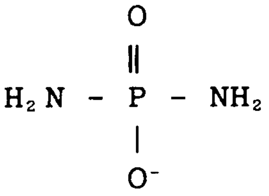
Well, some of inorganic phosphates have nitrogen atoms in the formula. Especially, ammonium bivalent-metal (mono)phosphates are well-known.[11,23,27,28] Their thermal behavior has been reported from the analytical chemical point of view.[29] Other ammonium bivalent-metal phosphates occasionally appear in the course of the manufacture of chemical fertilizers.[30] Their precipitation conditions and X-ray diffraction patterns were reported.[31-33] The nitrogen in inorganic phosphates can exist in another form, i. e., as phosphorus-nitrogen bonds. The inorganic phosphates with phosphorus-nitrogen bonds can be classified in regard with the number of phosphorus atoms and that of amino ($-NH_2$) and imino ($=NH$) groups ($=N-$).[34] The structures of the typical phosphates with phosphorus-nitrogen bonds and their ions are shown in Fig. 1·2. They have attracted our attention as a new class of chemical fertilizer and flame-proofing materials.[34-36]

Condensed inorganic phosphates can be prepared through thermal dehydration-condensation of lower-condensed phosphates.[2,7,9,37,38] Their formation and structures depend on the nature of constituent cation, the temperature and the time of heating, the cooling rate of the melts, and the atmosphere of heating, e. g., the partial pressure of



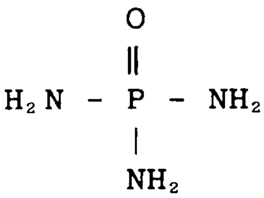
$${}^{-}\mathrm{O}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}^{-}}{|}}{\mathrm{P}}}-\mathrm{NH_2}$$

Amidophosphate Ion



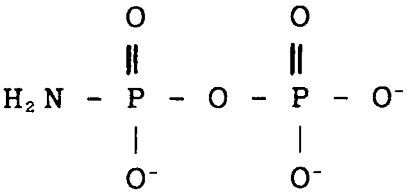
$$\mathrm{H_2N}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}^{-}}{|}}{\mathrm{P}}}-\mathrm{NH_2}$$

Diamidophosphate Ion



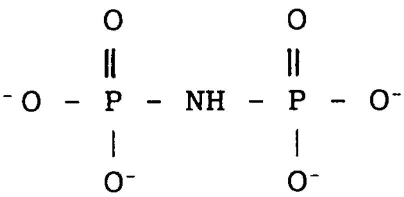
$$\mathrm{H_2N}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{NH_2}}{|}}{\mathrm{P}}}-\mathrm{NH_2}$$

Phosphoryl triamide



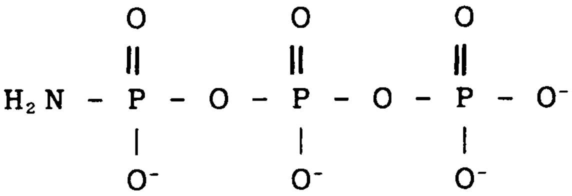
$$\mathrm{H_2N}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}^{-}}{|}}{\mathrm{P}}}-\mathrm{O}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}^{-}}{|}}{\mathrm{P}}}-\mathrm{O}^{-}$$

Amidodiphosphate Ion



$${}^{-}\mathrm{O}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}^{-}}{|}}{\mathrm{P}}}-\mathrm{NH}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}^{-}}{|}}{\mathrm{P}}}-\mathrm{O}^{-}$$

Imidodiphosphate Ion



$$\mathrm{H_2N}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}^{-}}{|}}{\mathrm{P}}}-\mathrm{O}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}^{-}}{|}}{\mathrm{P}}}-\mathrm{O}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}^{-}}{|}}{\mathrm{P}}}-\mathrm{O}^{-}$$

Amidotriphosphate Ion

Fig. 1·2. Structures of Typical Phosphate Ions with Phosphorus-Nitrogen Bonds.

water vapor present in the atmosphere.[7,12,39] Therefore, reversely speaking, changing of the constituent cation or the atmosphere is thought to be available for the investigation of the reaction mechanisms of the thermal behavior of inorganic phosphates. Although many workers have studied the thermal behavior of inorganic phosphates,[40] the thermal behavior of the phosphates containing nitrogen atoms has been reported comparatively a little. Therefore, its investigation is significant.

Inorganic phosphates are used as chemical fertilizers,[30,41-44] flame-proofing materials,[34-36] detergents,[42,44] food additives,[42,44] inorganic ion exchangers,[1,45-47] laser materials,[42] ionic conductor,[42,48] and so forth.[42,44] As some of them are occasionally prepared by thermal processes, the studies on the thermal behavior of the phosphates including nitrogen atoms is also expected to be utilized for the development of the inorganic-phosphate materials. Therefore, this work has been carried out in order to clarify some mechanisms for the formation of inorganic polymers.

Chapter 1 of this thesis shows the introduction to the studies on the thermal behavior of the inorganic phosphates including nitrogen atoms.

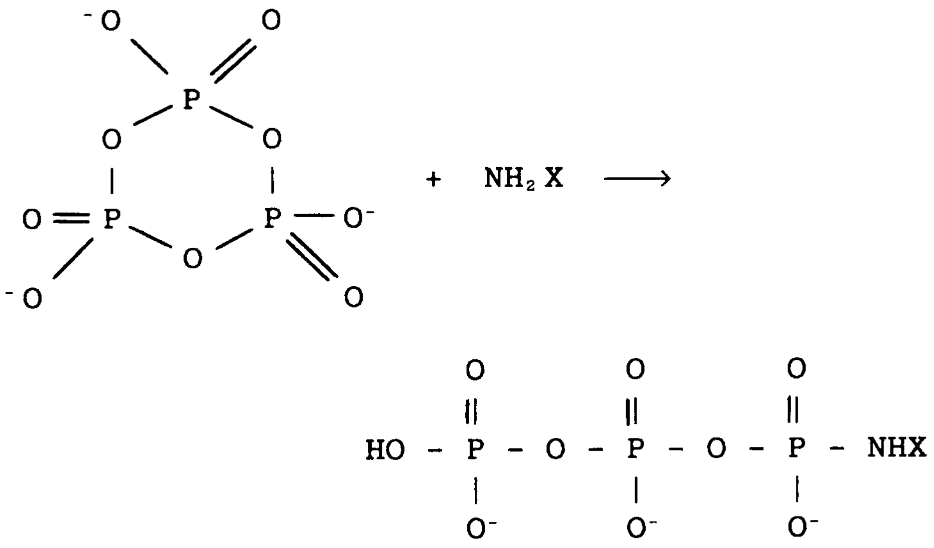
Although the thermal condensation of ammonium dihydrogen phosphate, $NH_4H_2PO_4$, and diammonium hydrogenphosphate, $(NH_4)_2HPO_4$, has been studied repeatedly,[49] the present author has reinvestigated it. The results are described in Chapter 2 from the standpoint of fundamental polymerization.

In Chapter 3, the thermal condensation of ammonium bivalent-metal hydrogenbis(phosphates), i. e., $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$ and $(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$, is described.[50, 51]

In Chapter 4, a new ammonium cyclo-hexaphosphate, $(NH_4)_6P_6O_{18} \cdot 1.5H_2O$, is reported.[52] There is discussed the thermal decomposition and subsequent radical polymerization of the $(NH_4)_6P_6O_{18} \cdot 1.5H_2O$ and ammonium cyclo-tetraphosphate, $(NH_4)_4P_4O_{12}$, to ammonium polyphosphates.[52]

Several new ammonium bivalent-metal cyclo-phosphates, i. e., $Sr_2(NH_4)_2P_6O_{18} \cdot 7H_2O$, $Cu_2(NH_4)_2P_6O_{18} \cdot 8.5H_2O$, $Ca_2(NH_4)_2P_6O_{18} \cdot 7H_2O$, and $Sr(NH_4)P_3O_9 \cdot 3H_2O$, were prepared by wet methods.[53, 54] The thermal decomposition and polymerization of these cyclo-phosphates and ammonium strontium cyclo-tetraphosphate, $Sr(NH_4)_2P_4O_{12}$, is discussed in Chapter 5.[53, 54]

Of all the inorganic phosphates with phosphorus-nitrogen bonds, amido(mono)phosphates are mostly known and have been studied by many workers in regard with their thermal decomposition.[55] On the other hand, an amidotriphosphate ion, $P_3O_9NH_2{}^{4-}$, has such a structure that the terminal oxygen atom of triphosphate ion, $P_3O_{10}^{5-}$, is replaced with an amino group.[56-58] N-methyl- and N-ethylamidotriphosphates were also reported as the triphosphate derivatives.[59] Both of them are formed by a reaction of cyclo-triphosphates with ammonia or the corresponding alkyl amines in aqueous solutions,[56-59] as expressed by Eq. 1·1 where X stands



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-NHX \qquad (1\cdot 1)$$

for H, CH_3, or C_2H_5. Chapter 6 shows that ammonium amidotriphosphate, $(NH_4)_4P_3O_9NH_2 \cdot H_2O$, is condensed through zwitterions.[60] A new phase of ammonium cyclo-triphosphate, $(NH_4)_3P_3O_9$, is reported.[60]

Chapter 7 expresses the thermal condensation of silver amidotriphosphate, $Ag_4P_3O_9NH_2$,[61] and barium amidotriphosphate, $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$.[62]

Chapter 8 shows the summary.

This work is thought to clarify some mechanisms, other than dehydration-condensation, for the thermal polymerization of inorganic phosphates containing nitrogen atoms.

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Chapter 2 Thermal Condensation of Ammonium Dihydrogenphosphate $NH_4H_2PO_4$ and Diammonium Hydrogenphosphate $(NH_4)_2HPO_4$

2-1 Introduction

It is well-known that formation and structure of condensed inorganic phosphates depend on the nature of constituent cation, the temperature and the time of heating, the cooling rate of the melts, and the atmosphere of heating.1) Therefore, reversely speaking, changing of the heating atmosphere was thought to be available for the study on the thermal behavior of the inorganic phosphates.

Although the thermal behavior of ammonium dihydrogenphosphate, $NH_4H_2PO_4$ [MAP], and diammonium hydrogenphosphate, $(NH_4)_2HPO_4$ [DAP], has been studied widely, 2-17) the thermal condensation of MAP and DAP tried by changing of water-vapor pressure in atmosphere is reported from the standpoint of fundamental polymerization.

2-2 Experimental

2-2-1 Chemicals

Unless otherwise stated, guaranteed-grade reagents were used without further purification. Ammonium dihydrogen phosphate, $NH_4H_2PO_4$ [MAP], and diammonium hydrogenphosphate, $(NH_4)_2HPO_4$ [DAP], were ground and sieved to obtain particles of uniform size (100-200 mesh). The

MAP and DAP were identified by X-ray diffractometry.18,19)

2-2-2 X-Ray Diffractometry

The X-ray powder diffraction patterns were recorded on a Rigaku Denki Geigerflex X-ray diffractometer, RAD-IA, using nickel-filtered Cu Kα radiation.

2-2-3 Thermal Analysis

An appropriate amount of MAP or DAP was placed in a platinum pan. The thermal analyses (TG-DTA) were carried out at a heating rate of 5 K min^{-1} using a MAC SCIENCE TG-DTA 2020 system. The measurements were performed in static air or in a stream of dry air at 50 cm^3 min^{-1}. The dry air was prepared by passing of the compressed air through the columns filled with molecular sieves. The TG-DTA system was purged by the dry air for 30 min before measurements.

2-2-4 HPLC-Flow Injection Analysis (HPLC-FIA)

A JASCO LC-800 Liquid Chromatograph connected with a JASCO flow-injection analysis unit, FIU-300N, was used. A polystyrene-based anion exchanger (TSK gel SAX, d_p = 10 μm, Toyo Soda Co., Ltd.) was packed in the column (I. D. × L: 4.6 × 250 mm). The eluent was an aqueous potassium chloride solution including 0.1 % (w/v) of tetrasodium ethylenediaminetetraacetate tetrahydrate.20) It was flowed through at 1.0 cm^3 min^{-1}. Table 2·1 shows the changes in concentration of the KCl solution with the passage of time. After the eluent was exchanged with a 1.0 mol dm^{-3} KCl aqueous solution at a given time, polyphosphates with long-chain ions were eluted.

Table 2·1. Concentration of an Aqueous Potassium Chloride Solution Used in the Gradient Method of HPLC-FIA

Period/ min	Initial Concenration/ mol dm^{-3}	Final Concentration/ mol dm^{-3}
0 - 12.8	0.200	0.200
12.8 - 25.6	0.200	0.293
25.6 - 38.4	0.293	0.345
38.4 - 51.2	0.345	0.378
51.2 - 64.0	0.378	0.398
64.0 - 76.8	0.398	0.415
76.8 - 89.6	0.415	0.425
89.6 - 102.4	0.425	0.433
102.4 - 115.2	0.433	0.443
115.2 - 128.0	0.443	0.448

The Mo(V)-Mo(VI) reagent was prepared according to the method reported by Hirai et al.21) At a flow rate of 0.8 cm^3 min^{-1}, it was introduced continuously into the stream of effluent. Then, the mixed solution was heated to 140°C by passing it through 15 m of 2.0 × 0.5 mm (O.D. × I.D.) PTFE tube in an air bath. The heteropoly blue thus formed was measured at 830 nm in a flow cell.21, 22) Figure 2·1 shows an HPLC-FIA chromatogram of an inorganic-phosphate mixture.

About ten-mg portion of a sample was dissolved in distilled water and diluted to 25 cm^3. After this solution was 20-fold diluted with distilled water, a 100-μ l portion of the resultant solution was injected

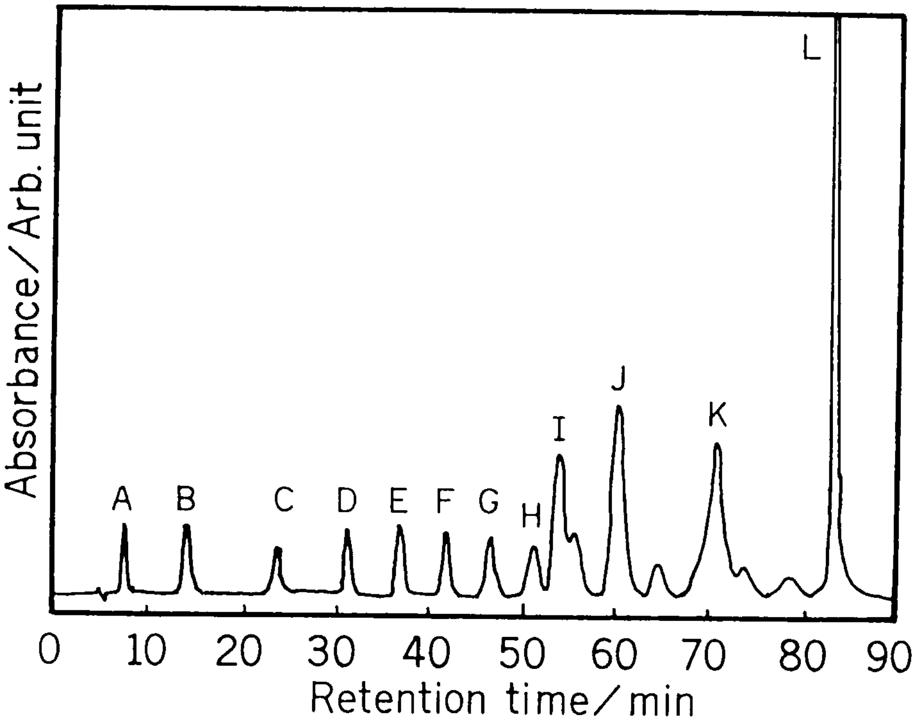

Fig. 2·1. HPLC-FIA chromatogram of an inorganic-phosphate mixture. A: Mono-, B: di-, C: tri-, D: tetra-, E: penta-, F: hexa-, G: hepta-, H: octa-, I: cyclo-hexa-, J: cyclo-tetra-, K: cyclo-tri-, L: polyphosphates.

into the HPLC-FIA system to determine the composition of phosphates in the sample.

2-2-5 Thermal Reaction

Since the amounts of the samples heated with the TG-DTA system were too little to be used for further analyses, the samples were prepared with a cylindrical electric furnace (I.D.× L: 40× 420 mm). A 0.2-g portion of $NH_4H_2PO_4$ [MAP] or $(NH_4)_2HPO_4$ [DAP] was spread on a porcelain boat. The boat was placed in a quartz tube, which was set in the electric furnace. It was heated at the same rate of 5 K min^{-1} as that used in the TG-DTA measurements. As soon as the temperature of the sample reached the predetermined value, the sample was taken out and cooled to room temperature in a silica gel dessicator, and then subjected to further analyses.

Since the thermal condensation of MAP or DAP is accompanied by dehydration, it was expected to be affected by humidity in the atmosphere of heating. So, MAP or DAP was also heated in streams of dry air and of humid air(relative humidity 90 % at 25°C) at 50 cm^3 min^{-1}. The dry air was obtained as described in Section 2-2-3. The humid air stream was prepared by the use of an Ace Constant-humidity Generator Model AHC-1 (Ace Scientific Laboratory Co., Ltd.).[22]

2-3 Results and Discussion

2-3-1 Thermal Condensation of Ammonium Dihydrogenphosphate $NH_4H_2PO_4$

Figure 2·2 shows TG and DTA curves of $NH_4H_2PO_4$ [MAP] measured in static air and in a stream of dry air at 50 cm^3 min^{-1}. An endothermic peak at 200°C reflects the decomposition of the sample.

Table 2·2 represents the percentage of phosphorus atoms present as mono-, di-, tri-, oligo-(chain length n=4-13), and polyphosphates in the products obtained by heating of MAP at 5 K min^{-1} to the temperatures indicated by arrows in Fig. 2·2. Since condensed phosphates with the chain length more than two were observed in the products heated up to 210°C, the endothermic reaction at 200°C is also attributable to partial condensation of MAP. The X-ray diffraction patterns of the products heated up to 210°C also show the weak diffraction lines of diammonium dihydrogendiphosphate $(NH_4)_2H_2P_2O_7$.[23]

As temperature rose, the chain lengths and the amounts of the condensed phosphates produced increased. The composition of phosphates in the products was not apparently affected by water vapor present in atmosphere.

2-3-2 Thermal Condensation of Diammonium Hydrogenphosphate $(NH_4)_2HPO_4$

Figure 2·3 shows TG and DTA curves of $(NH_4)_2HPO_4$ [DAP] measured at 5 K min^{-1} in static air and in a stream of dry

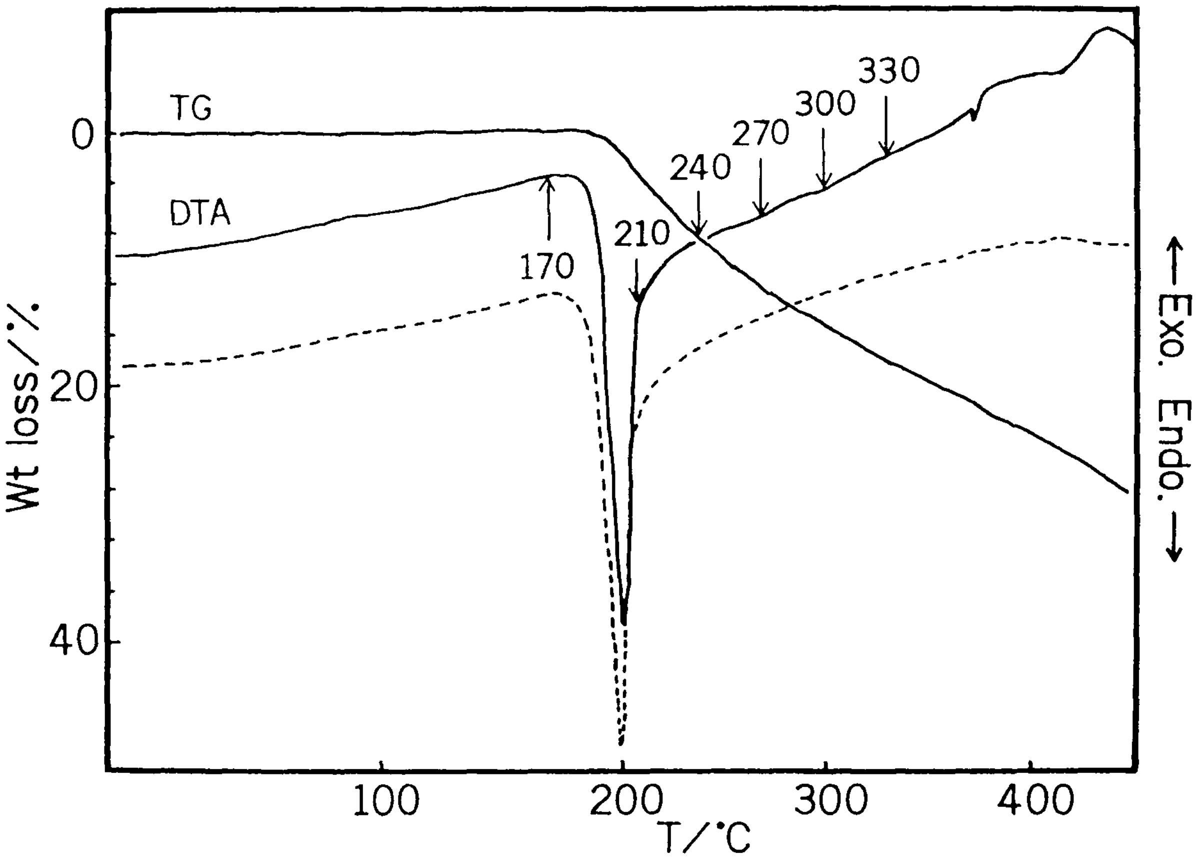

Fig. 2·2. TG and DTA curves of $NH_4H_2PO_4$ measured in static air and in a stream of dry air. Solid line (——): TG and DTA curves in static air, dashed line (---): DTA curve in a stream of dry air. Heating rate: 5 K min^{-1}.

Table 2·2. Composition of the phosphates in the products obtained by heating of $NH_4H_2PO_4$ in different atmospheres up to the temperatures indicated by arrows in Fig. 2·2

T/°C	Atmosphere	Composition/ P %				
		mono-	di-	tri-	oligo-[a]	poly-
170	Static air	100.0				
	Dry air stream	100.0				
	Humid air stream[b]	100.0				
210	Static air	66.9	25.0	6.4	1.6	
	Dry air stream	63.3	24.9	9.0	2.8	
	Humid air stream	63.6	28.2	6.8	1.4	
240	Static air	33.5	39.6	16.0	10.9	
	Dry air stream	33.2	39.4	16.9	10.5	
	Humid air stream	36.2	39.9	15.7	8.2	
270	Static air	18.0	31.5	21.8	28.7	
	Dry air stream	19.5	34.0	21.5	25.3	
	Humid air stream	20.9	34.1	21.2	23.8	
300	Static air	11.5	24.3	20.2	44.1	
	Dry air stream	9.7	21.6	19.6	49.1	
	Humid air stream	8.8	20.8	18.7	51.7	
330	Static air	5.5	15.5	15.3	62.7	1.0
	Dry air stream	5.8	14.5	13.7	63.5	2.4
	Humid air stream	4.7	14.1	14.0	65.5	1.7

a) Chain length from 4 to 13.

b) Relative humidity 90 % at 25°C.

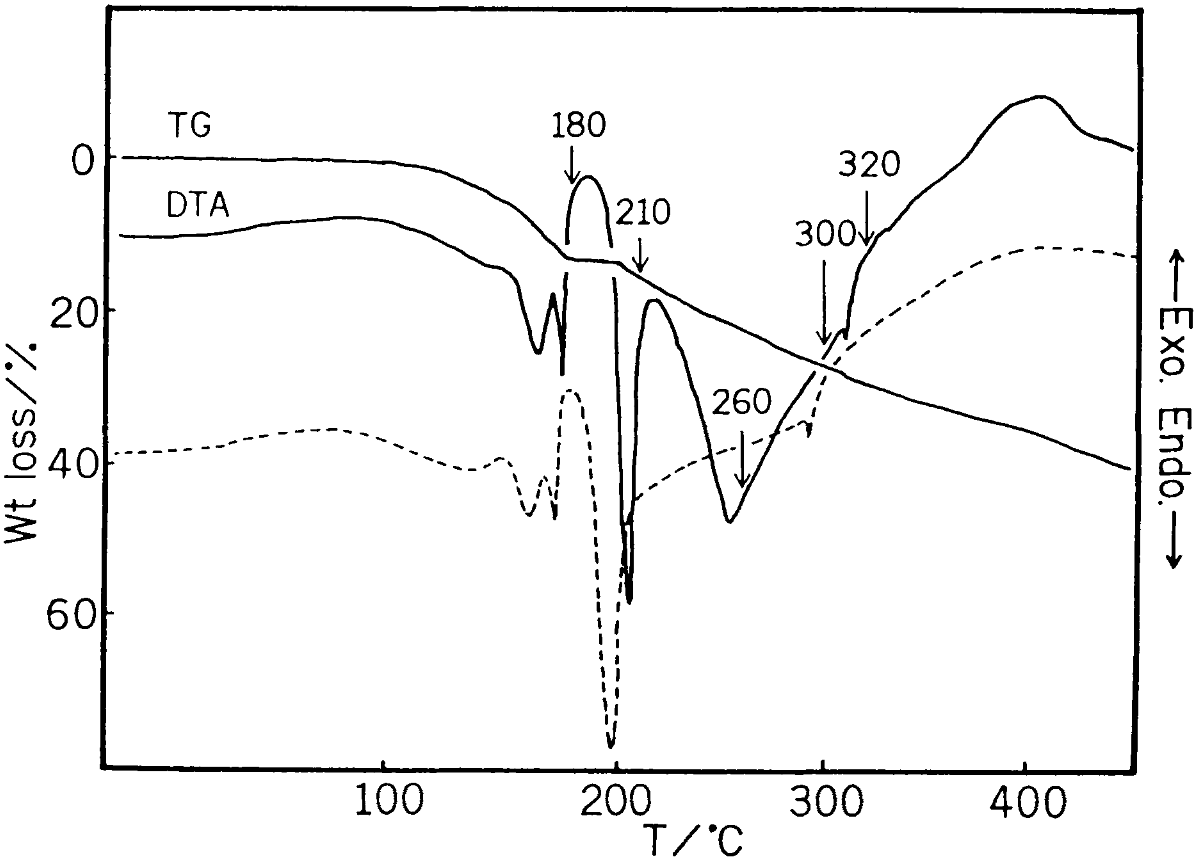

Fig. 2·3. TG and DTA curves of $(NH_4)_2HPO_4$ measured in static air and in a stream of dry air. Solid line (—): TG and DTA curves in static air, dashed line (---): DTA curve in a stream of dry air. Heating rate: 5 K min^{-1}.

air.

Table 2·3 represents the percentage of phosphorus atoms present as mono-, di-, tri-, oligo-(n=4-13), and polyphosphates in the products heated to the temperatures indicated by arrows in Fig. 2·3.

When DAP was heated to 180°C, the X-ray diffraction lines of the products agreed with those of MAP.[18) Therefore, the endothermic peaks below 180°C reflect the elimination of ammonia from DAP. A TG-loss observed up to 180°C (ca. 12.8 %) is very close to that calculated according to the following equation (12.90 %):

$$(NH_4)_2HPO_4 \rightarrow NH_4H_2PO_4 + NH_3 \qquad (2\cdot1)$$

Since DAP is changed to MAP at 180°C, DAP behaves like MAP above 180°C. Indeed, the products of DAP heated to 210 or 300°C resembled those of MAP heated to 210 or 300°C, respectively (Tables 2·2 and 2·3).

Table 2·3 shows no appreciable effect of humidity on the thermal condensation of DAP, as was the case for MAP.

2-4 Conclusion

$NH_4H_2PO_4$ [MAP] and $(NH_4)_2HPO_4$ [DAP] were heated at 5 K min^{-1} in different atmospheres. The products were characterized by HPLC-flow injection analysis (HPLC-FIA) and X-ray powder diffraction analysis. MAP decomposed and partly condensed through an endothermic reaction at 200°C. As the temperature rose, the condensed phosphates produced

Table 2·3. Composition of the phosphates in the products obtained by heating of $(NH_4)_2HPO_4$ in different atmospheres up to the temperatures indicated by arrows in Fig. 2·3

T/°C	Atmosphere	Composition/ P %				
		mono-	di-	tri-	oligo-[a]	poly-
180	Static air	97.6	2.4			
	Dry air stream	98.1	1.9			
	Humid air stream[b]	99.0	1.0			
210	Static air	65.1	24.9	7.5	2.5	
	Dry air stream	61.9	29.1	7.0	2.0	
	Humid air stream	59.8	30.7	7.1	2.4	
260	Static air	27.1	38.0	19.8	15.0	
	Dry air stream	25.3	35.7	19.6	19.4	
	Humid air stream	22.2	35.5	20.3	22.0	
300	Static air	12.1	24.8	19.7	43.3	
	Dry air stream	9.1	21.4	18.6	50.9	
	Humid air stream	10.6	22.1	19.0	48.1	
320	Static air	9.2	20.1	17.5	52.7	0.5
	Dry air stream	8.8	17.6	15.5	57.0	1.1
	Humid air stream	11.3	19.2	15.6	53.3	0.6

a) Chain length from 4 to 13.

b) Relative humidity 90 % at 25°C.

from MAP increased in their chain lengths and amounts. Since DAP was changed to MAP at 180°C, DAP behaved like MAP above 180°C.

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Chapter 3 Thermal Condensation of Ammonium Zinc Trihydrogenbis(phosphate) Monohydrate $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$ and Diammonium Magnesium Dihydrogenbis(phosphate) Tetrahydrate $(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$

3-1 Introduction

As shown in Chapter 2, chain phosphates are formed from $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$. The nature of constituent cation is one of the factors which affect the structure of condensed phosphates.1) It is well-known that zinc and magnesium metaphosphates consist of eight-membered ring anions.1-3) Zinc bis(dihydrogenphosphate) dihydrate $Zn(H_2PO_4)_2 \cdot 2H_2O$ and magnesium bis(dihydrogenphosphate) dihydrate $Mg(H_2PO_4)_2 \cdot 2H_2O$ are condensed to zinc cyclo-tetraphosphate $Zn_2P_4O_{12}$ and magnesium cyclo-tetraphosphate $Mg_2P_4O_{12}$ with eight-membered ring anions, respectively.2,3) Since the molar ratio of zinc or magnesium to phosphorus of ammonium zinc trihydrogenbis(phosphate) monohydrate $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$ [NZHP] or diammonium magnesium dihydrogenbis(phosphate) tetrahydrate $(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$[NMHP] is 1/2, like that of $Zn(H_2PO_4)_2 \cdot 2H_2O$ or $Mg(H_2PO_4)_2 \cdot 2H_2O$, NZHP and NMHP are thought to produce zinc and magnesium metaphosphates with eight-membered ring anions.

Although a few reports have been published on the thermal condensation of NZHP and NMHP,[4,5] they were inadequate, e. g., regarding analytical methods used. In this chapter, therefore, the thermal condensation of NZHP and NMHP is discussed by controlling of the humidity in atmosphere. Deammoniation accompanied by their condensation was also checked by means of a neutralization titrimetry.

3-2 Experimental

Unless noted particularly, experimental procedures were similar to those described in Chapter 2.

3-2-1 Analyses of Phosphorus, Nitrogen, and Zinc

Total phosphorus was determined colorimetrically.[6,7] Nitrogen content was obtained by means of an ammonia-distillation method.[8] Zinc was determined by gravimetry.[9]

3-2-2 Thermal Analysis

NZHP or NMHP was placed in a platinum pan. The thermal analyses (TG-DTA) were carried out at a heating rate of 2.5 or 5 K min^{-1}, respectively, using a Rigaku Thermal Analyzer 8076 D1. The measurements were performed in static air or in a stream of dry N_2 gas at 50 cm^3 min^{-1}. The nitrogen gas (purity: 99.95 %) was flowed directly from the cylinder.

3-2-3 HPLC-Flow Injection Analysis (HPLC-FIA)

A JASCO TRIROTER V Liquid Chromatograph connected with a JASCO flow-injection analysis unit, FIU-300, was used.

Sample of NZHP and NMHP were dissolved in a 0.1 mol dm^{-3} aqueous Na_2H_2edta (disodium dihydrogen ethylenediaminetetraacetate) solution. After dilution with distilled water, the sample solution was injected into the HPLC-FIA system.

3-2-4 Preparation of Ammonium Zinc Trihydrogenbis(phosphate) Monohydrate $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$ and Diammonium Magnesium Dihydrogenbis(phosphate) Tetrahydrate $(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$

$(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$ [NZHP] was prepared as follows. Forty grams of phosphoric acid (85%) were mixed with 80 cm^3 of distilled water. Two grams of zinc oxide were added to the diluted phosphoric acid solution to dissolve. The pH of the solution was adjusted to three,[10] with concentrated ammonium hydroxide, and then it was allowed to stand for four days at room temperature. The precipitate was filtered off, and washed with cold water, 50%(V/V) ethanol-water, and then acetone. The product was air-dried. It was chracterized by X-ray diffractometry.[10] Found: Zn, 21.64; N, 4.50; P, 21.02 %. Calcd for $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$: Zn, 22.21; N, 4.76; P, 21.04 %.

Samples of $(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$[NMHP] were given by Dr. A. W. Frazier (Chemical Research Department, National Fertilizer Development Center, Tennessee Valley Authority, USA). Before use, it was identified by X-ray diffractometry.[11]

3-2-5 Thermal Reaction

Samples of NZHP or NMHP were heated at the same rate of 2.5 or 5 K min^{-1} as that used in the corresponding TG-DTA measurements. Isothermal experiments were occasionally carried out at a fixed reaction time of 5 h.

NZHP or NMHP was heated in streams of dry N_2 gas and of humid air at 50cm^3 min^{-1}. For heating of NZHP, two kinds of humid air were employed. The one of humid air (relative humidity 90 % at 25°C) contained ca. 1.0 mg of water vapor per 50 cm^3, and the other (relative humidity 90 % at 36°C) ca. 1.9 mg. For NMHP, a stream of the former humid air was only used.

Thermal condensation of NZHP and NMHP was also accompanied by deammoniation. The amount of ammonia evolved was determined as follows.[12] The effluent gas (dry nitrogen) was introduced continuously at 50 cm^3 min^{-1} into an appropriate amount of 0.01 mol dm^{-3} sulfuric acid. When heating was over, the sample was moved to the edge of the furnace, cooled quickly, and then the nitrogen was passed into the acid for a further 10 min to absorb any ammonia remaining in the furnace. The ammonia absorbed in the solution was determined by means of a back-titration technique, using a 0.02 mol dm^{-3} sodium hydroxide solution and Methyl Red as an indicator.

3-3 Results and Discussion

3-3-1 Thermal Condensation of Ammonium Zinc Trihydrogenbis(phosphate) Monohydrate $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$

Figure 3·1 shows an example of TG and DTA curves measured in static air. The notches of the DTA curve observed between 150 and 450°C changed for each measurements, which must be due to the tendency of NZHP to sputter. A weight loss up to 600°C was ca. 23.7 %, which was close to that calculated according to the following equation(24.15 %):

$$(NH_4)ZnH_3(PO_4)_2 \cdot H_2O \rightarrow Zn(PO_3)_2 + NH_3 + 3H_2O \qquad (2\cdot 1)$$

Figures 3·2 and 3·3 represent the percentage of phosphorus atoms present as mono-(P_1), di-(P_2), and oligophosphates (chain length n= 3-9: P_{oligo}) in the products, obtained by heating of NZHP at 2.5 K min^{-1} to the temperatures indicated by arrows in Fig. 3·1. The products heated below 380°C were dissloved well in a 0.1 mol dm^{-3} Na_2H_2edta solution, while those heated to above 450°C were not dissolved completely in the Na_2H_2edta solution. Therefore, since the HPLC-FIA data of the products heated to above 450°C were not thought to show accurate percentage of phosphates present in the products, the results were not illustrated in Figs. 3·2 and 3·3.

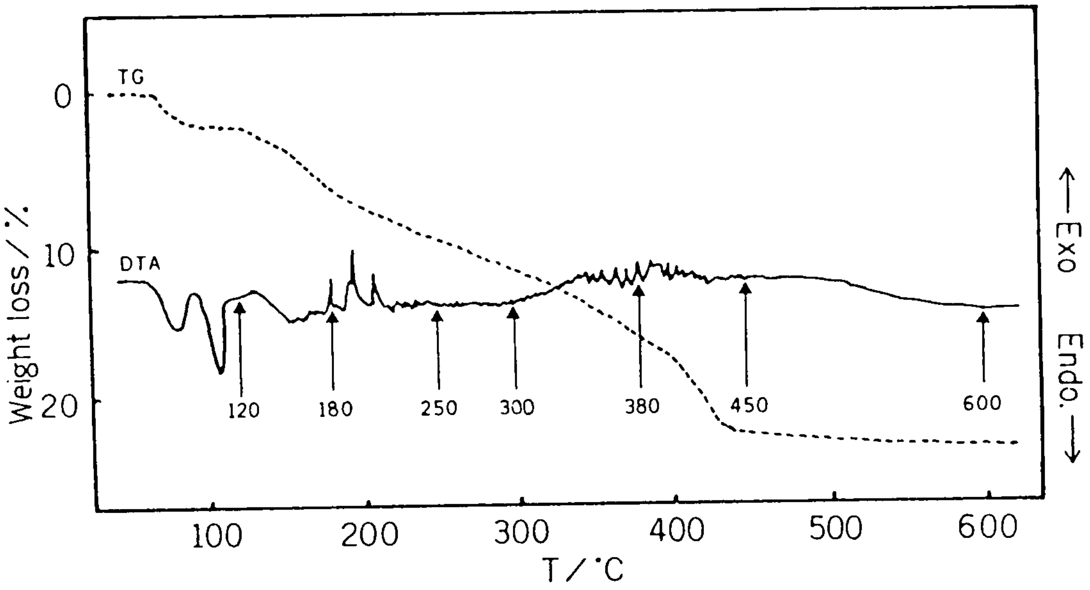

Fig. 3·1. TG and DTA curves of $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$ measured in static air. Heating rate: 2.5 K min^{-1}.

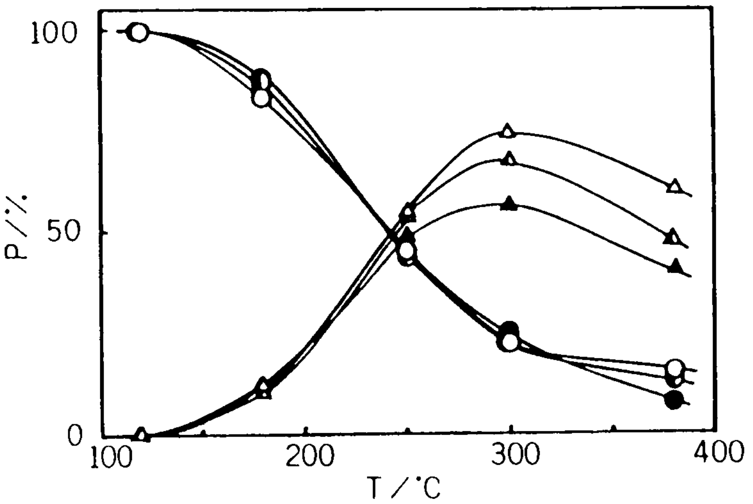

Fig. 3·2. Amounts of mono-(P_1) and diphosphates(P_2) in the products obtained by heating of $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$ to the temperatures indicated in Fig. 3·1 in streams of dry nitrogen and two kinds of humid air. Heating rate: 2.5 K min^{-1}. ○ and △ : P_1 and P_2 in dry N_2 gas, ◐ and ◭ : P_1 and P_2 in ca. 1.0 mg- H_2O, ● and ▲ : P_1 and P_2 in ca. 1.9 mg- H_2O.

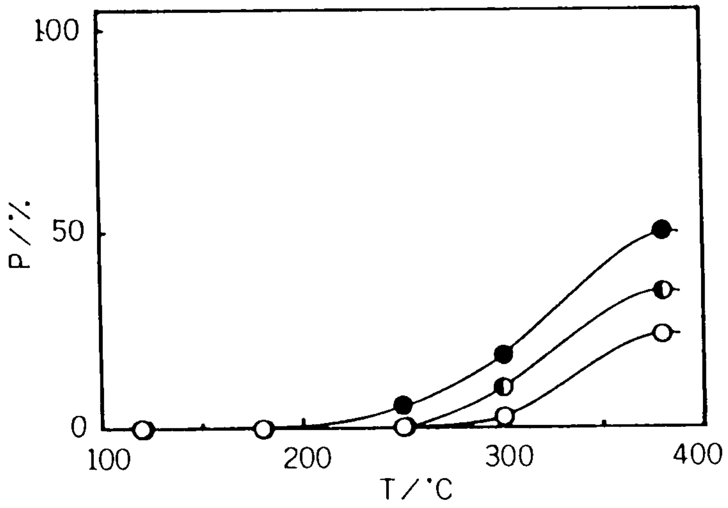

Fig. 3·3. Amounts of oligophosphates (n=3-9) in the products obtained by heating of $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$ to the temperatures indicated in Fig. 3·1 in streams of dry nitrogen and two kinds of humid air. Heating rate: 2.5 K min^{-1}. ○ : dry N_2 gas, ◐ : ca. 1.0 mg- H_2O, ● : ca. 1.9 mg- H_2O.

And a peak due to polyphosphates sometimes was seen even on the HPLC-FIA chromatograms of the products heated to the temperatures below 380°C. Since the percentage of phosphorus atoms present as polyphosphates in the products was less than ca. 4.7 %, the data were not neglected in Figs. 3·2 and 3·3.

Figures 3·2 and 3·3 show that humidity decreased the amounts of diphosphates(P_2) between 250 and 380°C, while it increased those of oligophosphates(P_{oligo}); thus, the formation of P_{oligo} probably involved a partial hydrolysis of -P-O-P- linkages of P_2. McGilvery and Scott reported such a hydrolytic effect of water vapor.[13] The hydrolysis of P_2 produces acidic monophosphates (P_1). In other words, it results in an increase in the hydroxyl groups. Reasonably, as indicated by Thilo and Seemann,[14] the increase causes more chances that the hydroxyl groups of the P_1 encounter those of other phosphates ($n \geqq 2$). It is certainly favorable for a heterogeneous solid-state reaction through which P_{oligo} is formed, i. e., condensation. As shown in Fig. 3·2, the humidity hardly made any apparent differences in the disappearance of monophosphates(P_1), which implies that the condensation of the acidic P_1 with the phosphates ($n \geqq 2$) took place immediately, independent of humidity. Therefore, in the temperature range (250-380°C), humidity is thought to be more effective for the hydrolysis of the -P-O-P-linkages than for the retardation of liberation of the water vapor produced by condensation.

Although the products heated to 450 and 600°C were not dissolved completely in a 0.1 mol dm^{-3} Na_2H_2edta aqueous solution as above-mentioned, they were found to consist of a zinc polyphosphate β-$Zn(PO_3)_2$ by X-ray diffractometry.[15] Preliminary isothermal experiments in static air gave the formation of β-$Zn(PO_3)_2$ even at 350°C.

Figure 3·4 shows X-ray diffraction patterns of isothermal products heated at 250, 300 and 500°C under dry conditions. The products at 170°C was amorphous, while those at 250°C could not be characterized. The diffraction lines of the products heated at 300°C under dry conditions, agreed with those due to γ-$Zn_2P_2O_7$ (Fig. 3·4 b).[16] Although humidity gave some lines other than those of γ-$Zn_2P_2O_7$ for the products heated at 300°C, γ-$Zn_2P_2O_7$ was formed as an intermediate, and changed to β-$Zn(PO_3)_2$ through reorganization at higher temperature (above 350°C).

X-Ray diffraction patterns showed isothermal products at 500°C to consist of long-chain β-$Zn(PO_3)_2$ and cyclo-tetraphosphate α_2-$Zn_2P_4O_{12}$.[17] The humidity did not cause any difference in the patterns. Beucher and Grenier[17] reported that α_2-$Zn_2P_4O_{12}$ with an eight-membered ring anion had strong diffraction lines at 13.8, 19.9, and 30.7° (d(A) reported are converted to 2θ

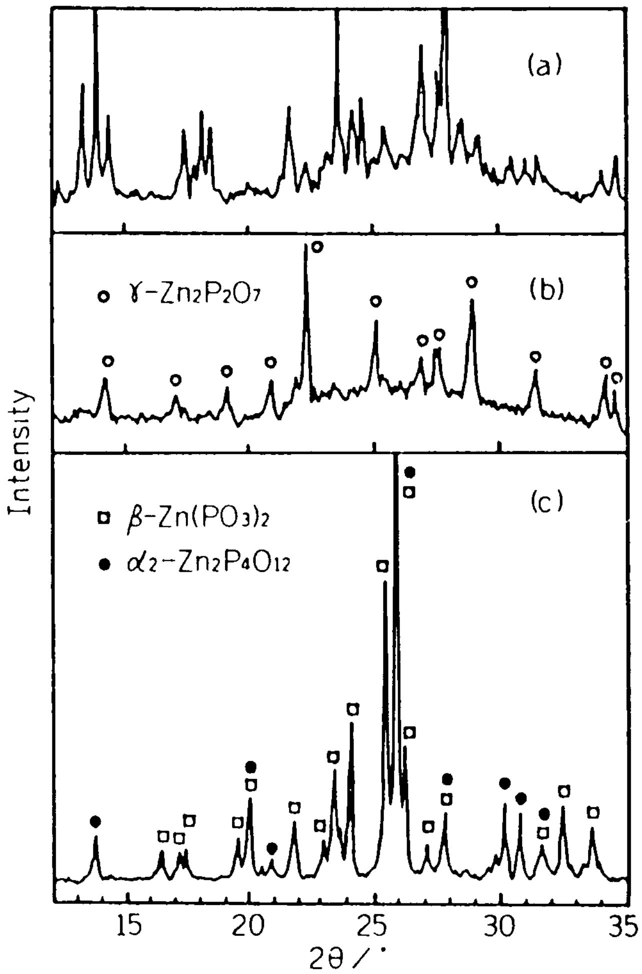

Fig. 3·4. X-Ray diffraction patterns of the isothermal products obtained by heating of $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$ in a stream of dry nitrogen. (a): at 250°C for 5 h, (b): at 300°C for 5 h, (c): at 500°C for 5 h.

(deg): Cu Kα radiation). Comparing the corresponding lines in Fig. 3-4 c with the strongest line of β-$Zn(PO_3)_2$ at 25.8°,[15] α_2-$Zn_2P_4O_{12}$ was thought to be a minor component. The products were allowed to stand in a 0.1 mol dm^{-3} Na_2H_2edta solution for three days at room temperature. They were apparently fairly dissolved in the Na_2H_2edta solution. If the solubility of α_2-$Zn_2P_4O_{12}$ was the same as that of β-$Zn(PO_3)_2$, and if these phosphate ions were not hydrolyzed, the HPLC-FIA for the supernatant solution showed that ca. 90 % and ca.5 % of phosphorus atoms in the products were present as polyphosphate ions and cyclo-tetraphosphate ions, respectively. And HPLC-FIA by the use of a rapid metathesis for 5 min, with a 10 %(w/w) sodium sulfide aqueous solution, also gave results that there were hardly any cyclo-tetraphosphate ions. Therefore, it should be concluded that the $Zn(PO_3)_2$ formed was not $Zn_2P_4O_{12}$ but β-$Zn(PO_3)_2$.

3-3-2 Thermal Condensation of Diammonium Magnesium Dihydrogenbis(phosphate) Tetrahydrate $(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$

Figure 3-5 shows TG and DTA curves measured in static air at a heating rate of 5 K min^{-1}. A loss in weight at 580°C was 42.9 %, and that at 660°C was 43.6 %. These losses are close to a weight loss expressed by

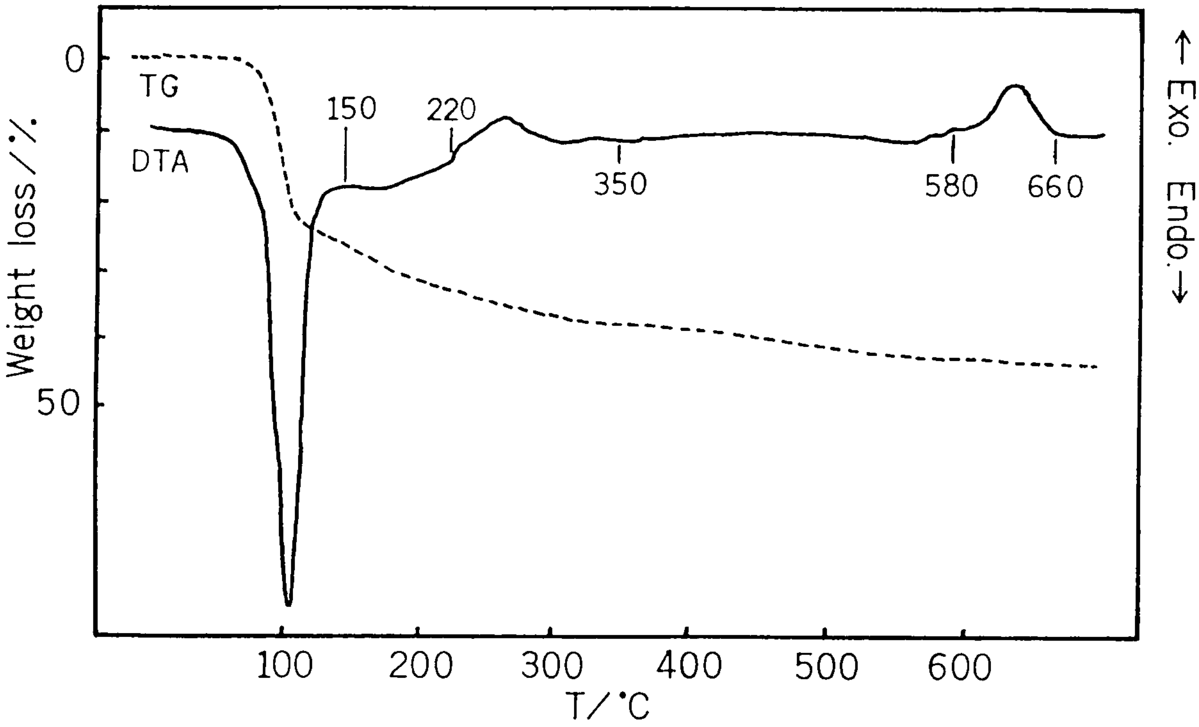

Fig. 3·5. TG and DTA curves of $(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$ measured in static air at a heating rate of 5 K min^{-1}.

the following equation (43.83 %):

$$(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O \rightarrow Mg(PO_3)_2 + 2NH_3 + 6H_2O \quad (2\cdot 2)$$

Figure 3·6 shows the X-ray diffraction patterns of the products heated in a stream of dry nitrogen to the temperatures indicated on the DTA curve of Fig. 3·5.

Figure 3·7 represents the percentage of phosphorus atoms present as mono-(P_1), di-(P_2), tri-(P_3), oligo-(chain length=4-11: P_{oligo}), and polyphosphates(P_{poly}) in the products heated in a stream of dry nitrogen to the temperatures indicated on the DTA curve of Fig. 3·5. Even when the product heated to 580°C was allowed to stand in a 0.1 mol dm^{-3} Na_2H_2edta aqueous solution for some days at room temperature, it was not dissolved completely. However, the composition for the supernatant solution was plotted in Fig. 3·7, by assuming that all the phosphates in the product were dissolved in the same manner and no hydrolytic reaction took place during their dissolution. Since the product heated to 660°C consisted of $Mg_2P_4O_{12}$ 3) and was hardly dissolved in the Na_2H_2edta solution, its composition was neglected in Fig. 3·7.

When measured in a stream of dry nitrogen, the TG and DTA curves were not changed compared with those measured in static air. Although NMHP was heated in a stream of humid air (relative humidity 90% at 25°C), the X-ray patterns of the products were the same as those

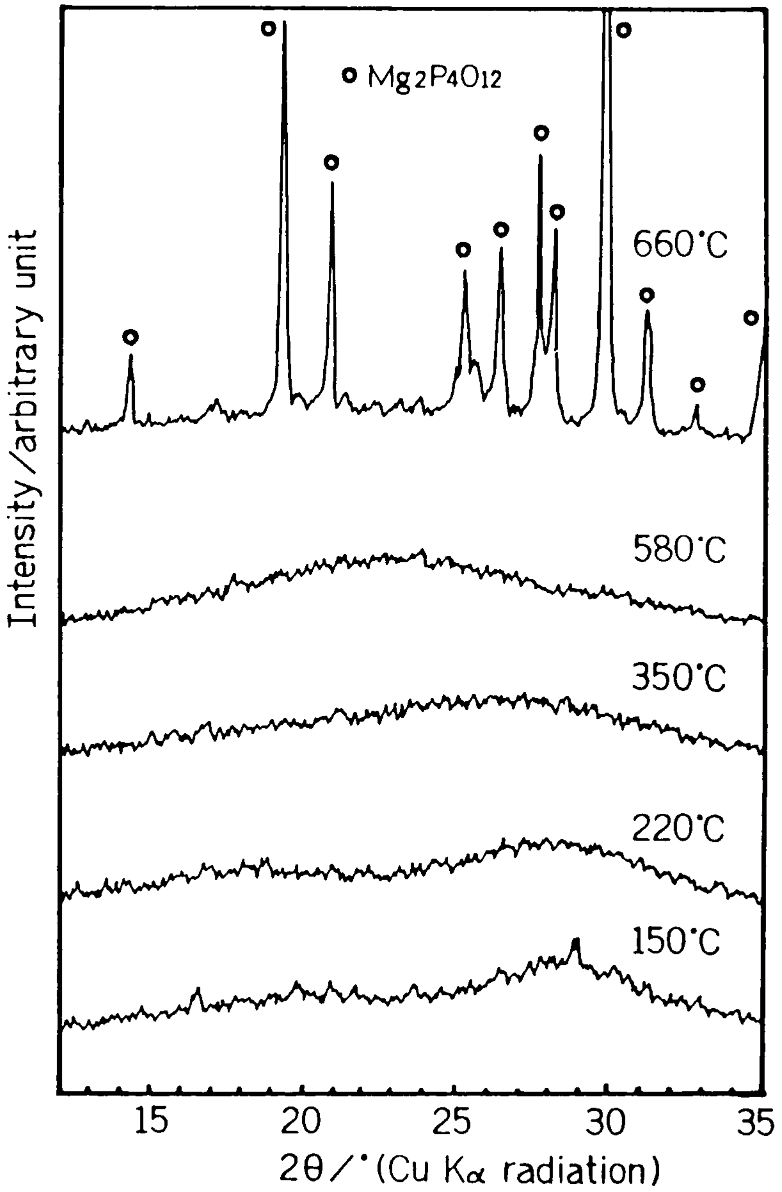

Fig. 3·6. X-Ray diffraction patterns of the products obtained by heating of $(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$ in a stream of dry nitrogen to the temperatures indicated on the DTA curve of Fig. 3·5. Heating rate: 5 K min^{-1}.

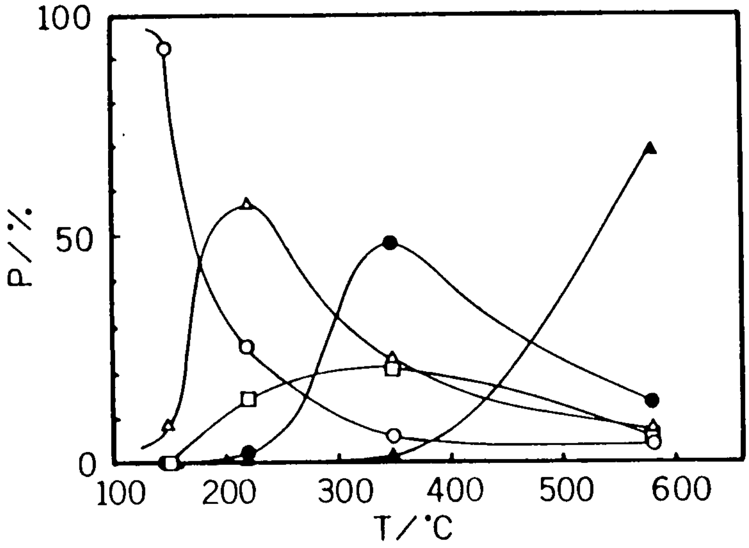

Fig. 3·7. Amounts of phosphates in the products obtained by heating of $(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$ in a stream of dry nitrogen to the temperatures indicated on the DTA curve of Fig. 3·5. Heating rate: 5 K min^{-1}. ○ : Mono-, △ : di-, □ : tri-, ● : oligo- (chain length=4-11), ▲ : polyphosphates.

obtained in a stream of dry nitrogen. A slight amount (ca. 3.7%) of cyclo-tetraphosphates(P_{4m}) exsisted in the product heated to 580°C in a stream of humid air; while, in the product heated to 580°C in a stream of dry nitrogen gas, P_{poly} was present more abundantly than in the humid atmosphere. Except for these slight differences, the thermal condensation of NMHP was concluded to proceed independent of humidity. Therefore, the results obtained in the dry atmosphere are described below.

Figure 3·8 shows the amount of ammonia evolved in a stream of nitrogen. Up to 150°C, a TG-loss was ca. 26.7 % and ca. 2.5 % of ammonia was evolved. The difference between the two values(ca. 24.2 %) corresponds to the amount of water evolved. Although it is somewhat larger than the weight loss due to the dehydration of the water of crystallization (22.22 %), the following dehydration took place at 105°C where an endothermic peak appeared:

$$(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O \rightarrow (NH_4)_2MgH_2(PO_4)_2 + 4H_2O \quad (2\cdot 3)$$

Ammonia was evolved gradually with rising temperature, which did not apparently cause any DTA peaks. Between 150 and 220°C, P_1 fell off rapidly, while P_2 and P_3 were formed. A broad endothermic effect from 150 to 250°C was thought to correspond to the dehydration of structural water. P_{oligo} and P_{poly} appeared above 220°C and above 350°C, respectively. When heated to 660°C, the product was magnesium cyclo-tetraphosphate $Mg_2P_4O_{12}$ (Fig. 3·6).[31]

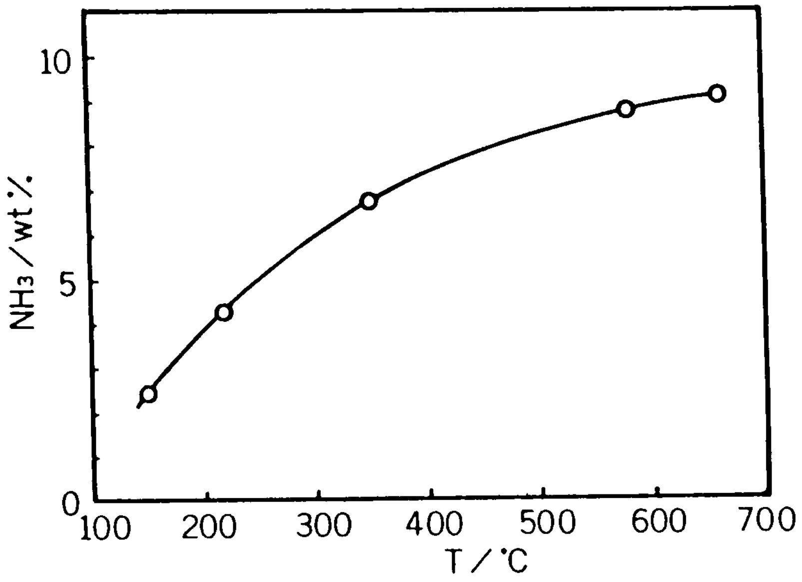

Fig. 3·8. Amounts of ammonia evolved by heating of $(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$ in a stream of dry nitrogen to the temparatures indicated on the DTA curve of Fig. 3·5. Heating rate: 5 K min^{-1}.

3-4 Conclusion

Ammonium zinc trihydrogenbis(phosphate) monohydrate $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$ [NZHP] was gradually condensed to di-(P_2) and oligophosphates (chain length n=3-9: P_{oligo}). A part of the formation of P_{oligo} involved hydrolysis of the -P-O-P- linkages of the P_2, which was accelerated by humidity. γ-$Zn_2P_2O_7$ was formed at 300°C as an intermediate. Above 350°C, NZHP was condensed to a zinc polyphosphate β-$Zn(PO_3)_2$ with long-chain anion.

The water of crystallization evolved at 105°C from diammonium magnesium dihydrogenbis(phosphate) tetrahydrate $(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$ [NMHP]. Oligo-(n=4-11: P_{oligo}) and polyphosphates(P_{poly}) were formed above 220°C and above 350°C, respectively. The P_{poly} was converted to crystalline magnesium cyclo-tetraphosphate $Mg_2P_4O_{12}$ above 640°C.

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Chapter 4 Thermal Decomposition and Polymerization of Ammonium cyclo-Hexaphosphate $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$ and Ammonium cyclo-Tetraphosphate $(NH_4)_4P_4O_{12}$

4-1 Introduction

Ammonium cyclo-tri- and cyclo-tetraphosphates are known in regard to several properties.[1-10] Although their thermal behavior has been also reported,[1,3,6,10] ammonium cyclo-hexaphosphates with twelve-membered ring anion have not been studied regarding the thermal behavior. In this chapter, the thermal decomposition and the subsequent polymerization of ammonium cyclo-hexaphosphate $(NH_4)_6P_6O_{18}\cdot 1.5H_2O[P_{6m}]$ and ammonium cyclo-tetraphosphate $(NH_4)_4P_4O_{12}[P_{4m}]$ are discussed.

Since, as shown in the preceding chapters, the thermal behavior of inorganic phosphates is occasionally affected by the heating atmosphere, the thermal decomposition of P_{6m} and P_{4m} were examined by controlling of the vapor pressure of water or ammonia.

4-2 Experimental

Unless otherwise noted, the procedures were similar to those described in the preceding chapters.

4-2-1 Analysis of Phosphorus

With an HPLC-flow injection analysis (HPLC-FIA) system, total phosphorus was determined colorimetrically (see 4-2-3).

4-2-2 Thermal Analysis

The thermal analyses (TG-DTA) were carried out at a heating rate of 2.5 K min^{-1}, by means of a Rigaku 8002SD Thermal Analyzer. The measurements were performed in static air or in a stream of dry nitrogen at 100 cm^3 min^{-1}. The flow rate did not influence the temperatures assigned to DTA peaks. If required, an atmosphere of static dry nitrogen was also used. It was attained by the evacuation of the furnace of the TG-DTA device, followed by introduction of the dry nitrogen. This procedure was repeated three times.

4-2-3 HPLC-Flow Injection Analysis (HPLC-FIA)

The HPLC-FIA system was the same as that described in Chapter 3. The system was equipped with two injection ports called as loop-valve sampler. One loop-valve sampler, placed ahead of a column, is used for the separation and determination of phosphates. The other, available for the determination of total phosphorus, is situated after the column.

Samples were dissolved in water. If their dissolution was inadequately or not, they were dissolved by addition of an NaCl aqueous solution. After dilution with distilled water, the sample solution was injected into the HPLC-FIA system. If the chain length of polyphosphates existing in the solution becomes longer, hydrolysis of the polyphosphates to monophosphates by Mo(V)-Mo(VI) reagent is not enough to form the heteropoly blue complex completely (see Chapter 2). The composition of the sample turns out to be incorrect. To prevent it, a diluted hydrochloric acid was added to the sample solution, and allowed to stand at 70°C for 1 h. After neutralization, the solution was diluted and then injected into the loop-valve sampler located after the column. According to the procedure, total phosphorus atoms existing in the solution were determined. The amount of phosphorus atoms present as the phosphates, excluding polyphosphates, divided by that of the total phosphorus atoms gives the accurate percentage of these phosphates. The percentage of polyphosphates could be obtained by subtracting the total percentage of all the phosphates excluding polyphosphates from one-hundred %.

4-2-4 Preparation of Ammonium cyclo-Hexaphosphate $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$ and Ammonium cyclo-Tetraphosphate $(NH_4)_4P_4O_{12}$

Ammonium cyclo-hexaphosphate was obtained as follows. Sodium cyclo-hexaphosphate hexahydrate, $Na_6P_6O_{18}\cdot 6H_2O$, was obtained according to Ref. 11. The H^+-type of cation exchanger was changed to its NH_4^+-type by the passage of 1.5 dm^3 of ca. 3.5 mol dm^{-3} aqueous ammonia. A solution of 15 g of $Na_6P_6O_{18}\cdot 6H_2O$ in 200 cm^3 of water was passed at ca. 5 cm^3 min^{-1} through the column, as reported by Coates and Woodard.[10] The effluent was collected, and mixed with its 5-fold volume of methanol. The product was filtered off, washed with methanol and acetone, and air-dried. At least 98.5 % of phosphorus atoms was present as cyclo-hexaphosphate ions. Impurities were mainly highly-condensed phosphate ions. As shown in Table 4·1, the X-ray diffraction pattern of the product was slightly different from that of ammonium cyclo-hexaphosphate monohydrate prepared by Vol'fkovich et al.[12] Found: P, 30.55; N, 13.87 %. Calcd for $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$: P, 30.54; N, 13.79 %.

Sodium cyclo-tetraphosphate tetrahydrate, $Na_4P_4O_{12}\cdot 4H_2O$, was obtained according to Ref. 13. About 20 g of $Na_4P_4O_{12}\cdot 4H_2O$ was dissolved in 250 cm^3 of distilled water. The solution was flowed through a column packed with about 500 cm^3 of the NH_4^+-type cation exchanger. The effluent was collected, and mixed with its 5-fold volume of methanol. The precipitate of ammonium cyclo-tetraphosphate, $(NH_4)_4P_4O_{12}$, was filtered off, washed with methanol and acetone, and air-dried. It was identified by X-ray diffractometry.[10]

4-2-5 Thermal Reaction

Samples were heated in an electric furnace at the same heating rate of 2.5 K min^{-1} as that used in the TG-DTA measurements. A stream of dry air at 50 cm^3 min^{-1} was prepared by passing air through the columns, filled with molecular sieves, of a Heatless Air Drier HF 200-9-30 (Nippon

Table 4·1. X-Ray Diffraction Data for Ammonium cyclo-Hexaphosphate

The present work		Vol'fkovich et al.	
d(A)	Intensity[a]	d(A)	Intensity
6.55	VS	6.56	100
		4.99	10
4.44	S	4.46	80
4.19	S	4.20	10
3.81	M	3.86	60
3.62	M		
3.26	W	3.28	40
3.05	M	3.06	60
3.01	M	3.02	10
2.91	S	2.919	20
2.83	M	2.843	70
2.63	S	2.645	90
2.56	W	2.576	40
2.51	W	2.520	30
		2.503	10
		2.400	20
2.38	W	2.381	40
2.28	W		
2.22	VW	2.229	50
2.18	W	2.192	20
2.13	W	2.142	80
2.10	W	2.110	80
2.02	W	2.026	30

a) VS: Very strong, S: strong, M: medium, W: weak, VW: very weak.

Pure Gas Co., Ltd.).[14] A stream of humid air (relative humidity 90 % at 25°C) at 50 cm^3 min^{-1} was prepared as described in Chapter 2. Ammonia gas (purity: 99.9 %) was flowed at 50 cm^3 min^{-1} directly from the cylinder.

4-3 Results and Discussion

4-3-1 Thermal Decomposition and Polymerization of Ammonium cyclo-Hexaphosphate $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$

Thermal analyses (TG-DTA) of $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$ [P_{6m}] in static air and in a stream of dry nitrogen are shown in Figs. 4·1 a and b, respectively. Three endothermic peaks at about 180, 195, and around 300°C were observed in both of atmospheres. An exothermic peak appeared at 205°C. The endothermic peak at around 300°C reflects the melting of the products.

In order to investigate the thermal processes causing TG changes and DTA peaks, P_{6m} was heated at 2.5 K min^{-1} to 100, 150, 180, 195, 205, and 215°C in streams of dry air, humid air, and ammonia gas. The percentage of phosphorus atoms present as cyclo-hexaphosphates and polyphosphates in the products was plotted in Fig. 4·2.

Thilo and Grunze reported that lithium tetra- and octaphosphates were formed selectively in the course of thermal decomposition of lithium cyclo-tetraphosphate tetrahydrate. They supposed that their formation was

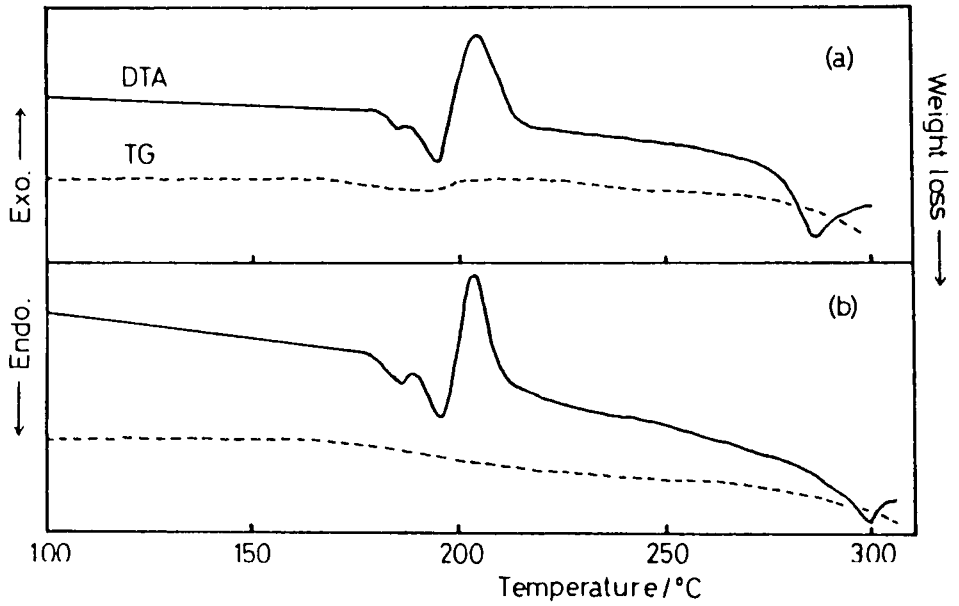


Fig. 4·1. TG-DTA analyses of ammonium cyclo-hexaphosphate $(NH_4)_6P_6O_{18}\cdot1.5H_2O$ measured at 2.5 K min^{-1}. (a): In static air, (b): in a stream of dry nitrogen at 100 cm^3 min^{-1}.

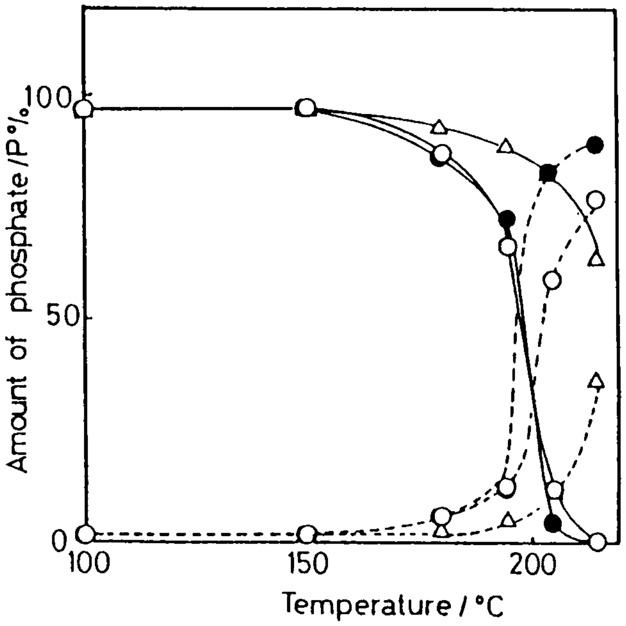


Fig. 4·2. Amounts of cyclo-hexa- and polyphosphates in the products of $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$ heated at 2.5 K min^{-1}. Solid line (———): cyclo-Hexaphosphate, dashed line (----): polyphosphates. ○ : In a stream of humid air at 50 cm^3 min^{-1}, ● : in a stream of dry air at 50 cm^3 min^{-1}, △ : in a stream of ammonia at 50 cm^3 min^{-1}.

caused by the polymerization of "radicals", which were produced thermally.[11] Since the decomposition of P_{6m} was scarcely affected by humidity (Fig. 4·2), the P_{6m} rings are considered not to suffer hydrolysis, but to be decomposed to "radicals." Immediately, the radicals must polymerize to polyphosphates.

A TG-increase from 195 to 205°C is probably due to an incorporation of water molecules, as stated by Thilo and Grunze.[11] The products included only oligophosphates (chain length $n = 1-6$) other than cyclo-hexa- and polyphosphates. Figure 4·3 shows that the oligophosphates were found more in the humid atmosphere than in the dry atmosphere. Therefore, the incorporation of water molecules must inhibit the polymerization of the radicals.

As indicated in Fig. 4·2, P_{6m} remained undecomposed up to high temperatures in a stream of ammonia, which suggests that the departure of ammonia from P_{6m} is a "trigger" reaction for the cleavage of P_{6m} to oligophosphate radicals.

4-3-2 Thermal Decomposition and Polymerization of Ammonium cyclo-Tetraphosphate $(NH_4)_4P_4O_{12}$

Figures 4·4 a, b, and c show TG and DTA curves of $(NH_4)_4P_4O_{12}$ [P_{4m}] measured at 2.5 K min^{-1} in static air, in a stream of dry nitrogen, and in static dry nitrogen, respectively. An exothermic peak at 238°C is seen in the DTA curve in static air, while the DTA curve in a stream of dry

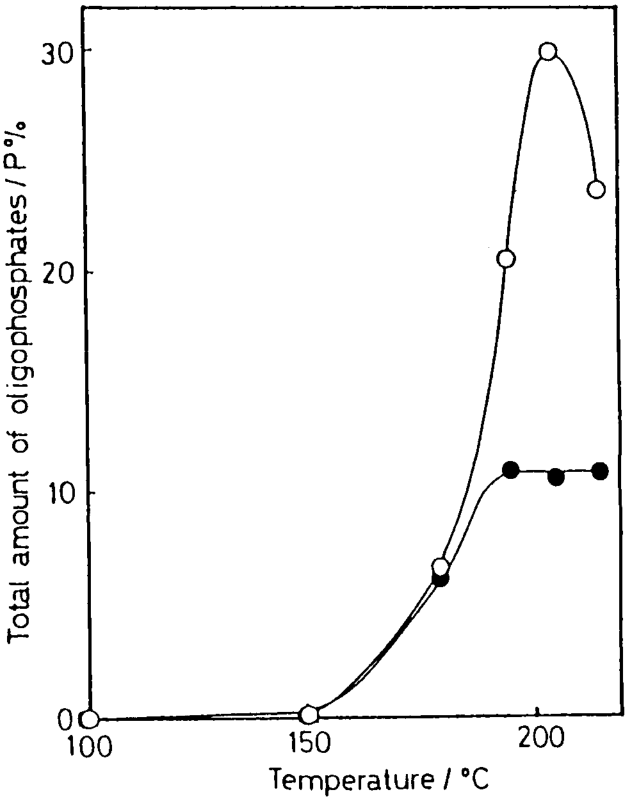


Fig. 4·3. Total amounts of oligophosphates (chain length = 1-6) in the products obtained by heating of $(NH_4)_6P_6O_{18}\cdot1.5H_2O$ at 2.5 K min^{-1}. ○ : In a stream of humid air at 50 cm^3 min^{-1}, ● : in a stream of dry air at 50 cm^3 min^{-1}.

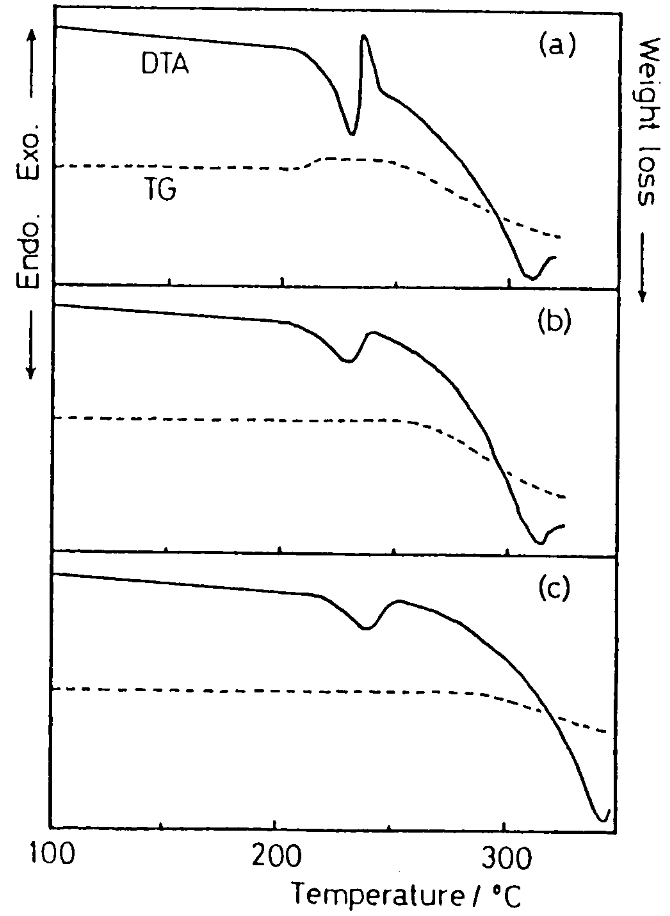


Fig. 4·4. TG-DTA analyses of ammonium cyclo-tetraphosphate $(NH_4)_4P_4O_{12}$ measured at 2.5 K min^{-1}. (a): In static air, (b): in a stream of dry nitrogen at 100 cm^3 min^{-1}, (c) in static dry nitrogen.

nitrogen shows no exothermic peak. These curves show endothermic peaks at 233 and 230°C, respectively. An endothermic peak at 240°C is seen in the DTA curve measured in static dry nitrogen.

P_{4m} was heated at 2.5 K min^{-1} to 150, 200, 233, 238, and 244°C (and sometimes 258°C as well). As seen in Fig. 4·5, the amount of P_{4m} in the products decreases rapidly between 200 and 238°C independent of humidity. Therefore, the P_{4m} rings did not suffer hydrolysis. If polyphosphates are produced by condensation of acidic ammonium oligophosphates, the TG curve will show a weight loss. The amount of polyphosphates in the products heated in a stream of dry air increases rapidly from 200 to 238°C (Fig. 4·5). However, the TG curves in the dry atmospheres show no weight change (Figs. 4·4 b and c). Therefore, the polyphosphates probably resulted from the polymerization of the "radicals" decomposed from P_{4m}, as was the case for P_{6m}.

Only when measured in static air, the DTA curve has an exothermic peak at 238°C, as shown in Fig. 4·4 a. Corresponding to the exothermic peak, a TG gain is observed. Therefore, the exothermic peak at 238°C is thought to be attributed to the bonding of radicals with water molecules. Heat of formation of the phosphates brought about by the binding of the radicals with water molecules(ΔH; kJ mol^{-1}) can be calculated based on the

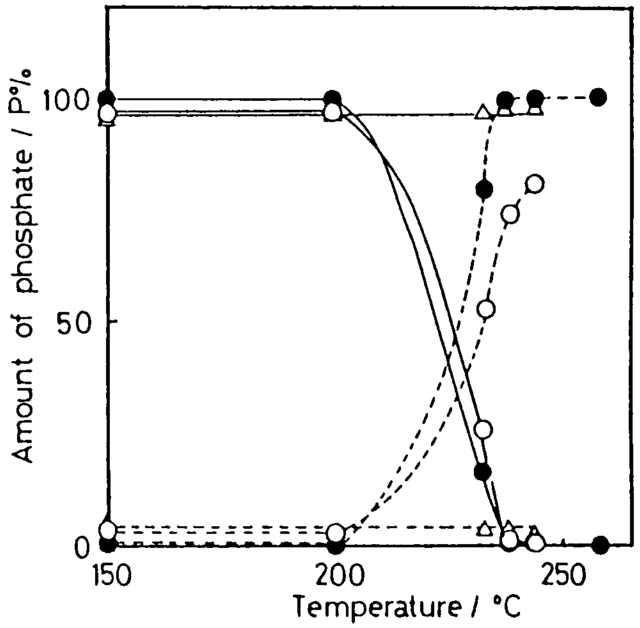
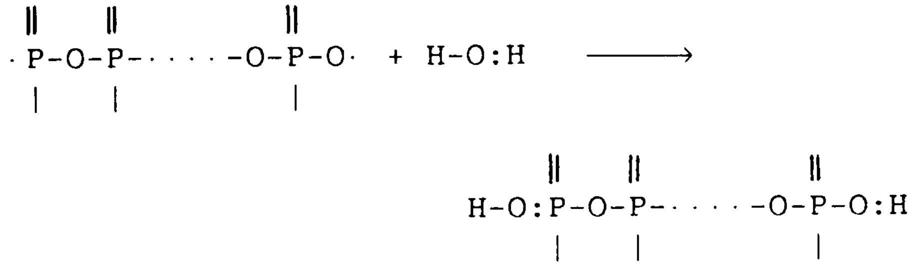


Fig. 4·5. Amounts of cyclo-tetra- and polyphosphates in the products of $(NH_4)_4P_4O_{12}$ heated at 2.5 K min^{-1}.

Solid line (———): cyclo-Tetraphosphate,

dashed line (----): polyphosphates. ○ : In a stream of humid air at 50 cm^3 min^{-1}, ● : in a stream of dry air at 50 cm^3 min^{-1}, △ : in a stream of ammonia at 50 cm^3 min^{-1}.

following scheme:



$$\cdot\overset{\|}{\underset{|}{P}}-O-\overset{\|}{\underset{|}{P}}-\cdots-O-\overset{\|}{\underset{|}{P}}-O\cdot + H-O{:}H \longrightarrow H-O{:}\overset{\|}{\underset{|}{P}}-O-\overset{\|}{\underset{|}{P}}-\cdots-O-\overset{\|}{\underset{|}{P}}-O{:}H$$

According to the scheme, ΔH should be given as follows:

$$\Delta H = (O\text{-}H)aq. + [-\{(O\text{-}H) + (P\text{-}O)\}] \fallingdotseq -(P\text{-}O) \quad (4\cdot 1),$$

where (O-H)aq. is the oxygen-hydrogen bond energy of water molecules, (O-H) is the oxygen-hydrogen bond energy of phosphates, and (P-O) is the phosphorus-oxygen bond energy of phosphates of ca. 359.8 kJ mol^{-1}.15) Therefore, the heat of formation of the phosphates(ΔH) amounts to a negative value of -359.8 kJ mol^{-1}, which accounts for the exothermic reaction at 238°C.

The products included oligophosphates (chain length=1-5) other than cyclo-tetra- and polyphosphates. Figure 4·6 shows that the percentage of phosphorus atoms present as the oligophosphates was higher in the products heated in a stream of humid air than in a stream of dry air. While, polyphosphates were found more abundantly in the products heated in the dry atmosphere than in the humid atmosphere (Fig. 4·5). This result indicates that the water molecules exsisting in atmosphere combined with the oligophosphate radicals and inhibited their polymerization.

Since P_{4m} was stable from 150 to 244°C in a stream of

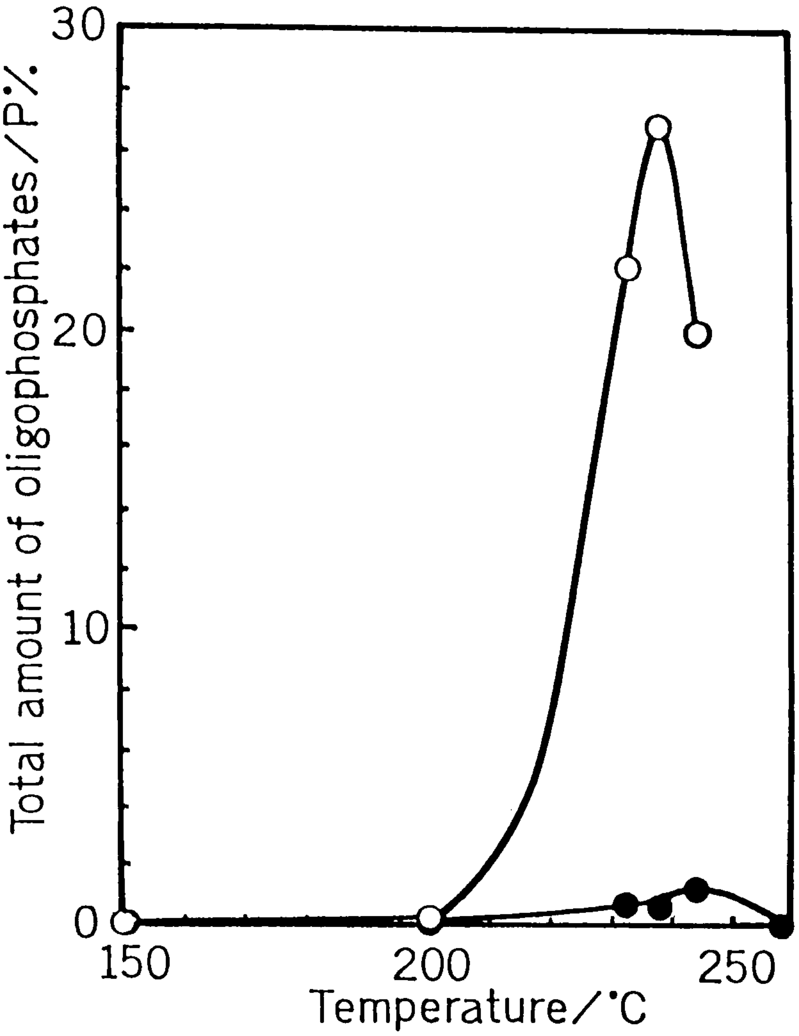


Fig. 4·6. Total amounts of oligophosphates (chain length = 1-5) in the products obtained by heating of $(NH_4)_4P_4O_{12}$ at 2.5 K min^{-1}. ○ : In a stream of humid air at 50 cm^3 min^{-1}, ● : in a stream of dry air at 50 cm^3 min^{-1}.

ammonia (Fig. 4·5), the release of ammonia from P_{4m} must be a "trigger" reaction for cleavage of P_{4m}.

X-Ray diffraction data for the thermal products of P_{6m} and P_{4m} are listed in Table 4·2. The diffraction lines of the respective products are similar to each other, except for those of starting materials. They also agree closely with the diffraction lines of ammonium polyphosphates reported by Shen et al.(16) and Frazier et al.(17) In addition, there was always a water-insoluble material, which must be ammonium polyphosphate, in the products of P_{4m} heated above 233°C.

4-4 Conclusion

A new ammonium cyclo-hexaphosphate, $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$, was prepared. The $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$ [P_{6m}] and anhydrous ammonium cyclo-tetraphosphate $(NH_4)_4P_4O_{12}$ [P_{4m}] were heated at 2.5 K min^{-1} to the temperatures where changes in their TG and DTA curves took place. The thermal reactions were carried out by controlling of the vapor pressure of water or ammonia present in atmosphere.

P_{6m} and P_{4m} were converted thermally to ammonium polyphosphates. The formation of the polyphosphates was considered to result from the polymerization of oligophosphate radicals, which were derived from the rings of P_{6m} or P_{4m}. The release of ammonia from P_{6m} and P_{4m} was thought to be a trigger reaction for the cleavage of their

Table 4·2. X-Ray Diffraction Data for Ammonium Polyphosphates Formed from Ammonium cyclo-Hexaphosphate $(NH_4)_6P_6O_{18}\cdot1.5H_2O$ and Ammonium cyclo-Tetraphosphate $(NH_4)_4P_4O_{12}$

From $(NH_4)_6P_6O_{18}\cdot1.5H_2O$		From $(NH_4)_4P_4O_{12}$	
d(A)	Intensity[a]	d(A)	Intensity[a]
6.86	W	6.92	W
		6.56	W
		6.24	W
5.99	VS	5.98	VS
		5.68	M
5.54	M	5.54	M
5.37	S	5.37	S
		5.16	W
		3.99	W
3.80	S	3.79	S
3.71	W	3.74	W
3.56	M	3.55	M
3.48	S	3.48	S
3.40	M	3.40	M
3.22	S	3.22	S
		3.12	W
3.09	W	3.07	M
3.02	VW	2.99	W
2.92	VW	2.91	M
2.88	M	2.88	VW
2.81	M	2.81	W
2.78	W	2.78	VW
2.74	W	2.74	W
2.70	W		

a) VS: Very strong, S: strong, M: medium, W: weak, VW: very weak.

rings. The radicals incorporated water molecules, which gave less formation of polyphosphates and exhibited a TG-gain. Corresponding to the TG-gain, the DTA curve of P_{4m} showed a remarkable exothermic peak.

4-5 References

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Chapter 5 Thermal Decomposition and Polymerization of Ammonium Strontium cyclo-Hexaphosphate $Sr_2(NH_4)_2P_6O_{18} \cdot 7H_2O$, Ammonium Copper(II) cyclo-Hexaphosphate $Cu_2(NH_4)_2P_6O_{18} \cdot 8.5H_2O$, Ammonium Calcium cyclo-Hexaphosphate $Ca_2(NH_4)_2P_6O_{18} \cdot 7H_2O$, Ammonium Strontium cyclo-Tetraphosphate $Sr(NH_4)_2P_4O_{12}$, and Ammonium Strontium cyclo-Triphosphate $Sr(NH_4)P_3O_9 \cdot 3H_2O$

5-1 Introduction

In general, the formation and the structure of condensed phosphates depend on the temperature and the time of heating, the cooling rate of the melts, and the pressure of water vapor in the atmosphere.[1-8] And the nature of the constituent cation is also a factor responsible for the structures of condensed phosphates.[2, 9]

As shown in Chapter 4, ammonium cyclo-tetra- and cyclo-hexaphosphates were decomposed to produce ammonium polyphosphates through the polymerization of oligophosphate radicals.[10] If the radical decomposition-polymerization has some relation to the elimination of ammonia, it must be observed in the thermal reaction of other ammonium cyclo-phosphates which partially include metal ions.

Ammonium bivalent-metal cyclo-phosphates have been studied in regard to several properties.[11-23] Since ammonium strontium cyclo-hexaphosphate

$Sr_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ [SrP_{6m}], ammonium copper (II) cyclo-hexaphosphate $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$ [CuP_{6m}], ammonium calcium cyclo-hexaphosphate $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ [CaP_{6m}], ammonium strontium cyclo-tetraphosphate $Sr(NH_4)_2P_4O_{12}$ [SrP_{4m}], and ammonium strontium cyclo-triphosphates $Sr(NH_4)P_3O_9\cdot 3H_2O$ [SrP_{3m}] were prepared by wet methods, their thermal decomposition and polymerization were studied by controlling of the partial pressure of water vapor present in atmosphere. Since their thermal behavior was accompanied by deammoniation, it was also checked by means of a neutralization titrimetry.

5-2 Experimental

Unless otherwise stated, the procedures were carried out as described in the preceding chapters.

5-2-1 Determination of Strontium, Calcium, Copper, Phosphorus, and the Water of Crystallization

Strontium and calcium were determined by a chelate replacement-titration method.[24] Copper(II) was also determined by a chelate back-titrimetry.[24]

Strontium ions were removed as strontium oxalate[25] or by the use of a cation-exchange resin Amberlite IR-120B.[26] Calcium and copper (II) ions were also removed by the cation-exchanger.[26] After the phosphates in the resultant solutions were hydrolyzed with a diluted hydrochloric acid, phosphorus was determined colorimetrically (see Chapter 3).

A sample was mixed with zinc oxide. The mixture was heated to a constant weight at 650°C.27) The amount of the water of crystallization could be determined by subtracting the weight loss due to the evolution of ammonia and the water arising from the NH_4^+ ions, calculated from the nitrogen content, from the total weight loss of the mixture.

5-2-2 IR Spectrophotometry

IR spectra were recorded on a JASCO IR spectrophotometer, IR-700, by the use of a Nujol-mull method.

5-2-3 Thermal Analysis

See Chapter 3.

5-2-4 HPLC-Flow Injection Analysis (HPLC-FIA)

The HPLC-FIA system and other procedures, unless stated particularly, were the same as those described in Chapter 3.

An appropriate amount of SrP_{6m}, CaP_{6m}, SrP_{4m}, or SrP_{3m} was dissolved in a 0.1 mol dm^{-3} aqueous Na_2H_2edta (disodium dihydrogen ethlenediaminetetraacetate) solution. After dilution with distilled water, the solution was injected into the HPLC-FIA system.

The CaP_{6m} and its thermal products were dissolved completely in the Na_2H_2edta solution, while the thermal products of SrP_{6m}, SrP_{4m}, and SrP_{3m} heated to above ca. 400°C were occasionally dissolved incompletely.

The HPLC-FIA analyses then did not give the accurate composition of them. By X-ray diffractometry, the corresponding products necessarily included long-chain β-$Sr(PO_3)_2$.[28] The undissolved component was regarded only as β-$Sr(PO_3)_2$, and the accurate percentage of phosphates of the samples was determined as described in 4-2-3.

CuP_{6m} and its thermal products were dissolved in a 1% (w/w) of sodium sulfide aqueous solution.[9] Copper(II) sulfide formed was filtered to be removed. The filtrate was diluted with distilled water, and injected into the HPLC-FIA system.

5-2-5 Preparation of Ammonium Strontium cyclo-Hexaphosphate $Sr_2(NH_4)_2P_6O_{18} \cdot 7H_2O$, Ammonium Copper (II) cyclo-Hexaphosphate $Cu_2(NH_4)_2P_6O_{18} \cdot 8.5H_2O$, Ammonium Calcium cyclo-Hexaphosphate $Ca_2(NH_4)_2P_6O_{18} \cdot 7H_2O$, Ammonium Strontium cyclo-Tetraphosphate $Sr(NH_4)_2P_4O_{12}$, and Ammonium Strontium cyclo-Triphosphate $Sr(NH_4)P_3O_9 \cdot 3H_2O$

Five mmols (3.045g) of ammonium cyclo-hexaphosphate, $(NH_4)_6P_6O_{18} \cdot 1.5H_2O$,[10] were dissolved in 30 cm^3 of water. Then the solution was mixed with 20 cm^3 (10 mmol) of a 0.5 mol dm^{-3} bivalent-metal chloride aqueous solution. The mixture was stirred for 30 min. The precipitate was then filtered off, washed with cold water, 50%(V/V) ethanol-water, and then methanol. The product was air-dried. Analytical data for ammonium strontium cyclo-hexaphosphate $Sr_2(NH_4)_2P_6O_{18} \cdot 7H_2O$ [SrP_{6m}], ammonium copper(II) cyclo-hexaphosphate $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$ [CuP_{6m}], and ammonium calcium cyclo-hexaphosphate $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ [CaP_{6m}] are summarized in Table 5·1. The X-ray diffraction data for SrP_{6m}, CuP_{6m}, and CaP_{6m} are listed in Tables 5·2, 5·3, and 5·4, respectively.

Fifteen mmols (5.82g) of anhydrous $(NH_4)_4P_4O_{12}$,[29] obtained from $Na_4P_4O_{12}\cdot 4H_2O$,[30] were dissolved in 60 cm^3 of water. Fifteen-cm^3 (7.5 mmol) of a 0.5 mol dm^{-3} strontium chloride aqueous solution was then added, and the mixture was stirred. After 1 h, the precipitate was filtered off, washed, and air-dried as described above. Analytical data for $Sr(NH_4)_2P_4O_{12}$ [SrP_{4m}] are listed in Table 5·5. The X-ray diffraction pattern was in agreement with that of $Sr(NH_4)_2P_4O_{12}$, reported by Durif et al.[11]

Sodium dihydrogenphosphate dihydrate, $NaH_2PO_4\cdot 2H_2O$, was heated in a platinum crucible. Crude sodium cyclo-triphosphate, $Na_3P_3O_9$, was obtained by keeping of the product at 520°C for ca. 5 h.[31] About 25 g of it was dissolved in 400 cm^3 of distilled water and the insoluble material was filtered off. About 400-700 cm^3 of methanol was then added to the filtrate. The precipitate was filtered off, washed with methanol and acetone, and air-dried. It was sodium cyclo-triphosphate monohydrate, $Na_3P_3O_9\cdot H_2O$, by X-ray diffractometry.[32] About 20 g of

Table 5·1. Analyses of Ammonium Bivalent Metal cyclo-Hexaphosphates

	Found/ %					Calcd for $Sr_2(NH_4)_2P_6O_{18}\cdot 7H_2O$/ %			
Ammonium Strontium cyclo-Hexaphosphate	Sr	P	N	H_2O	P present as $P_6O_{18}{}^{6-}$	Sr	P	N	H_2O
	21.87	23.03	3.32	15.57	≧ 97.0	21.61	22.91	3.45	15.53
	Found/ %					Calcd for $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$/ %			
Ammonium Copper(Ⅱ) cyclo-Hexaphosphate	Cu	P	N	H_2O	P present as $P_6O_{18}{}^{6-}$	Cu	P	N	H_2O
	15.82	23.90	3.36	19.69	100.0	16.25	23.76	3.58	19.58
	Found/ %					Calcd for $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$/ %			
Ammonium Calcium cyclo-Hexaphosphate	Ca	P	N	H_2O	P present as $P_6O_{18}{}^{6-}$	Ca	P	N	H_2O
	11.00	26.23	3.63	16.93	≧ 99.9	11.19	25.95	3.91	17.59

Table 5·2. X-Ray Diffraction Data for Ammonium Strontium cyclo-Hexaphosphate $Sr_2(NH_4)_2P_6O_{18}\cdot 7H_2O$

d(A)	Intensity[a]	d(A)	Intensity
8.66	S	3.18	W
7.08	W	3.14	VW
6.23	S	3.12	W
6.10	VS	3.01	S
5.79	M	2.94	M
5.53	S	2.89	M
5.43	M	2.84	VW
4.92	W	2.80	VW
4.67	W	2.76	M
4.33	W	2.71	M
4.02	W	2.68	M
3.91	M	2.65	M
3.83	M	2.63	M
3.67	M	2.62	M
3.52	VS	2.56	W
3.40	S	2.51	W
3.34	VW	2.46	S
3.22	S	2.34	M

a) VS: Very strong, S: strong, M: medium, W: weak, VW: very weak.

Table 5·3. X-Ray Diffraction Data for Ammonium Copper(II) cyclo-Hexaphosphate $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$

d(A)	Intensity[a]	d(A)	Intensity
8.42	VS	3.57	M
7.82	W	3.40	M
7.08	M	3.32	W
6.37	M	3.28	M
6.06	W	3.23	S
5.47	M	3.17	M
5.37	VS	3.09	M
4.69	M	3.04	M
4.62	M	3.02	M
4.57	VW	2.96	M
4.53	W	2.92	M
4.31	M	2.86	VW
4.19	VW	2.79	M
4.13	W	2.76	W
3.90	W	2.63	W
3.74	W	2.55	VW
3.64	M	2.47	W

a) VS: Very strong, S: strong, M: medium, W: weak, VW: very weak.

Table 5·4. X-Ray Diffraction Data for Ammonium Calcium cyclo-Hexaphosphate $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$

d(A)	Intensity[a]	d(A)	Intensity
9.02	VS	3.21	W
7.08	VS	3.16	M
6.28	M	3.14	S
6.19	S	3.11	M-S
5.75	S	3.07	M
5.64	W	3.05	M
5.53	M	2.99	M
4.48	W	2.92	M
4.39	M	2.86	M
4.06	M	2.84	M
3.98	M	2.77	M
3.78	M	2.75	S
3.66	W	2.71	M
3.59	M	2.69	W
3.50	M	2.66	M
3.46	W	2.61	W
3.39	M	2.55	VW
3.28	S	2.49	VW

a) VS: Very strong, S: strong, M: medium, W: weak, VW: very weak.

Table 5·5. Analyses of Ammonium Strontium cyclo-Tri- and cyclo-Tetraphosphates

Ammonium Strontium cyclo-Triphosphate	Found/ %					Calcd for $Sr(NH_4)P_3O_9 \cdot 3H_2O$/ %			
	Sr	P	N	H_2O	P present as $P_3O_9^{3-}$	Sr	P	N	H_2O
	21.88	23.95	3.33	14.28	$\geqq$ 93.0	22.10	23.43	3.53	13.62

Ammonium Strontium cyclo-Tetraphosphate	Found/ %				Calcd for $Sr(NH_4)_2P_4O_{12}$/ %		
	Sr	P	N	P present as $P_4O_{12}^{4-}$	Sr	P	N
	19.74	26.26	5.85	$\geqq$ 92.0	19.93	28.18	6.37

$Na_3P_3O_9 \cdot H_2O$ was dissolved in 150 cm^3 of distilled water. The solution was flowed through a column packed with ca. 500 cm^3 of the NH_4^+-type cation exchanger. Five dm^3 of methanol was gradually added to about 700 cm^3 of the effluent and then the solution was stirred for 30 min. The precipitate was filtered off, washed with methanol and acetone, and air-dried. It was identified to be anhydrous ammonium cyclo-triphosphate, $(NH_4)_3P_3O_9$, by X-ray diffractometry.[29] Twenty mmol (5.8188 g) of $(NH_4)_3P_3O_9$ were dissolved in 80 cm^3 of water. This solution was then mixed with 40 cm^3 (20 mmol) of a 0.5 mol dm^{-3} strontium chloride aqueous solution, and the mixture was stirred for 30 min. The precipitate was filtered off, washed, and air-dried. as above-mentioned. Analytical data and X-ray diffraction data for $Sr(NH_4)P_3O_9 \cdot 3H_2O$ [SrP_{3m}] are listed in Tables 5·5 and 5·6, respectively.

5-2-6 Thermal Reaction

See 3-2-5.

5-3 Results and Discussion

5-3-1 Thermal Decomposition and Polymerization of Ammonium Strontium cyclo-Hexaphosphate $Sr_2(NH_4)_2P_6O_{18} \cdot 7H_2O$, Ammonium Copper (II) cyclo-Hexaphosphate $Cu_2(NH_4)_2P_6O_{18} \cdot 8.5H_2O$, and Ammonium Calcium cyclo-Hexaphosphate $Ca_2(NH_4)_2P_6O_{18} \cdot 7H_2O$

Figure 5·1 shows TG and DTA curves of $Sr_2(NH_4)_2P_6O_{18} \cdot 7H_2O$ [SrP_{6m}] measured in static air and in a

Table 5·6. X-Ray Diffraction Data for Ammonium Strontium cyclo-Triphosphate $Sr(NH_4)P_3O_9 \cdot 3H_2O$

d(A)	Intensity[a]	d(A)	Intensity
7.69	M	2.86	M
7.25	VS	2.83	W
5.90	M	2.81	M
5.68	S	2.79	M
4.77	M	2.76	M
4.46	M	2.74	M
4.39	M	2.66	M
4.35	S	2.62	W
4.09	M	2.58	VW
3.93	M	2.55	VW
3.83	M	2.49	M
3.62	VS	2.47	VW
3.54	S	2.43	VW
3.41	M	2.35	W
3.39	VW	2.34	W
3.14	M	2.32	S
3.05	M	2.28	W
3.00	M	2.24	M

a) VS: Very strong, S: strong, M: medium, W: weak, VW: very weak.

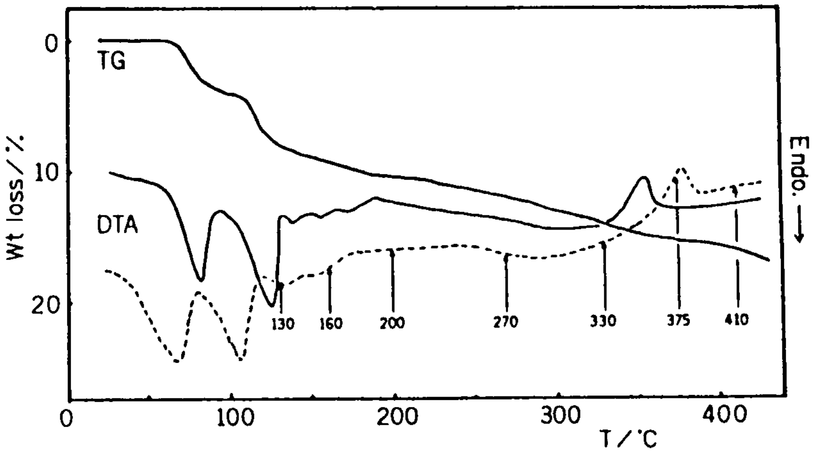

Fig. 5·1. Thermal analyses (TG-DTA) of $Sr_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ measured at 2.5 K min^{-1}. Solid line (——): TG and DTA measured in static air, dashed line (---): DTA measured in a stream of dry nitrogen at 50 cm^3 min^{-1}.

stream of dry nitrogen at 50 cm^3 min^{-1}. Figure 5·2 represents the percentage of phosphorus atoms present as cyclo-hexa-, oligo-(chain length n=1-6), and polyphosphates($n \geqq 7$) in the products obtained by heating of SrP_{6m} to the temperatures indicated by arrows on the DTA curve of Fig. 5·1. cyclo-Tri- and cyclo-tetraphosphates occasionally existed in the products heated to above 270°C. Since the percentage of phosphorus atoms present as the respective cyclo-phosphates in the products was less than ca. 5 %, the percentage is not plotted in Fig. 5·2. Ammonia was liberated from SrP_{6m}, as shown in Fig. 5·3.

Since ammonia was not generated to 200°C in the dry atmosphere, the hydrolysis, caused by the water of crystallization, of SrP_{6m} was thought to give the oligophosphates(n=1-6). Subsequently, the oligophosphates probably condensed to polyphosphates($n \geqq 7$).

Figure 5·4 illustrates IR spectra of SrP_{6m} and its products heated to 130 and 200°C in the dry atmosphere. The absorption at 3560 cm^{-1} was attributable to the "interstitial " water molecules, loosely held in the crystal structure.[33] The sharp and strong band at 1640 cm^{-1} of SrP_{6m} was also assigned to these water molecules.[33] The appearance of the absorption at 2360 cm^{-1}, assigned to P-OH stretching,[33, 34] demonstrated the formation of the oligophosphates.

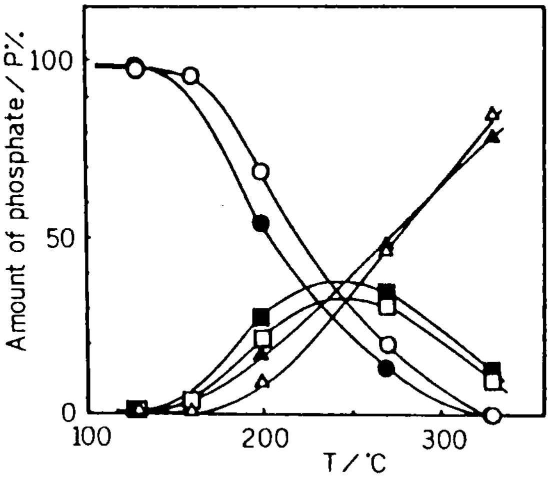

Fig. 5·2. Amounts of phosphates in the products obtained by heating of $Sr_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ at 2.5 K min^{-1} to the temperatures indicated by arrows on the DTA curve of Fig. 5·1. ○ and ● : cyclo-Hexaphosphates in the products heated in streams of dry nitrogen and humid air, respectively; □ and ■ : oligophosphates (chain length: n=1-6) in the products heated in streams of dry nitrogen and humid air, respectively; △ and ▲ : polyphosphates(n≧ 7) in the products heated in streams of dry nitrogen and humid air, respectively.

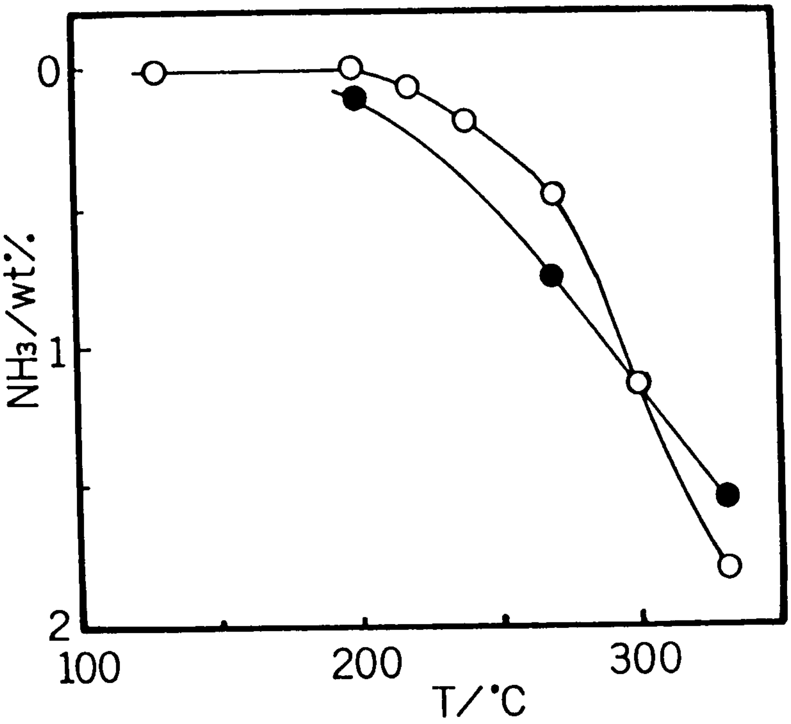

Fig. 5·3. Amounts of ammonia evolved by heating of $Sr_2(NH_4)_2P_6O_{18}\cdot7H_2O$ at 2.5 K min^{-1} to the temperatures indicated by arrows on the DTA curve of Fig. 5·1. ○ : Measured in a stream of dry nitrogen at 50 cm^3 min^{-1}, ● : measured in a stream of humid air at 50 cm^3 min^{-1}.

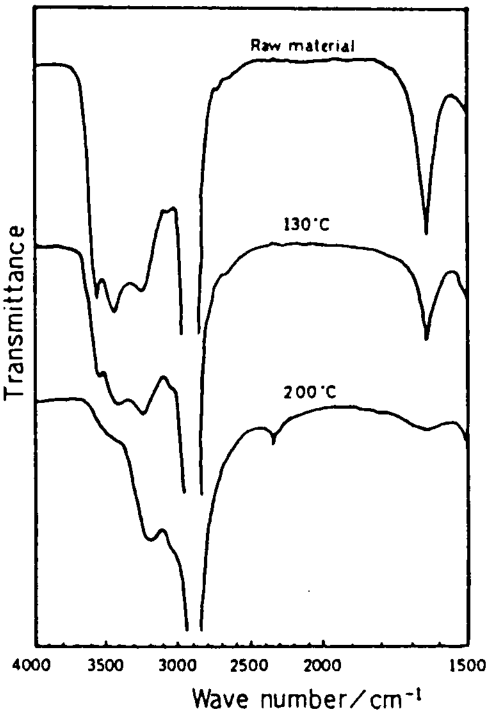

Fig. 5·4. IR spectra of $Sr_2(NH_4)_2P_8O_{18}\cdot7H_2O$ and its products heated in a stream of dry nitrogen to 130 and 200°C.

Figure 5·5 shows TG and DTA curves of $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$ [CuP_{6m}] measured in static air and in a stream of dry nitrogen at 50 cm^3 min^{-1}. Figure 5·6 shows the percentage of phosphorus atoms existing as cyclo-hexa-, oligo-(n=1-6), and polyphosphates($n\geqq 7$) in the products obtained by heating of CuP_{6m} to the temperatures indicated by arrows in Fig. 5·5. Although cyclo-tri- and cyclo-tetraphosphates were occasionally present in the products heated to above 430°C, their amounts are not plotted in Fig. 5·6. Ammonia was eliminated from CuP_{6m}, as indicated in Fig. 5·7.

Ammonia did not evolve up to 280°C. Therefore, since oligophosphates(n=1-6) were observed in the products heated to 150°C in a stream of dry nitrogen, the rings of CuP_{6m} were probably hydrolyzed by its water of crystallization. A part of the oligophosphates were thought to be subsequently condensed to the polyphosphates ($n\geqq 7$).

Figure 5·8 shows TG and DTA curves of $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ [CaP_{6m}] measured at 2.5 K min^{-1} in static air and in a stream of dry nitrogen at 50 cm^3 min^{-1}. Figure 5·9 shows the percentage of phosphorus atoms present as cyclo-hexa-, oligo-(n=1-6), and polyphosphates ($n \geqq 7$) in the products obtained by heating of CaP_{6m} to the temperatures illustrated by arrows in Fig. 5·8. When CaP_{6m} heated to above 345°C, the products contained small amounts of cyclo-tri- and cyclo-tetraphosphates. Since the main

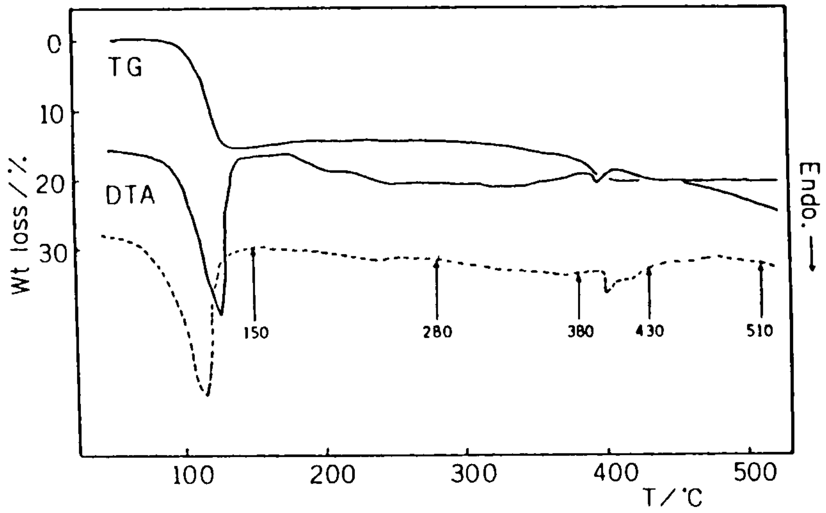

Fig. 5·5. Thermal analyses(TG-DTA) of $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$ measured at 2.5 K min^{-1}. Solid line (———): TG and DTA measured in static air, dashed line (---): DTA measured in a stream of dry nitrogen at 50 cm^3 min^{-1}.

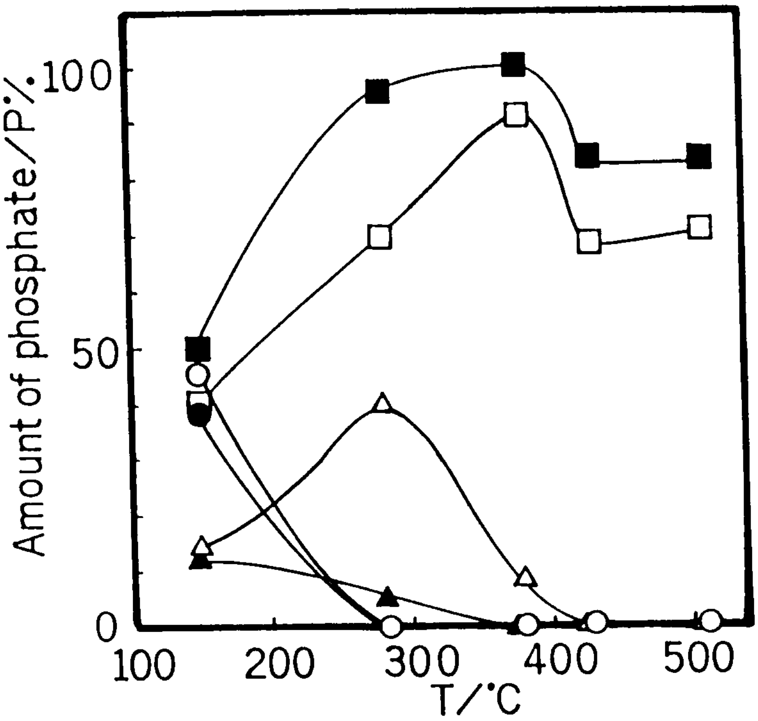

Fig. 5·6. Amounts of phosphates in the products obtained by heating of $Cu_2(NH_4)_2P_6O_{18}\cdot8.5H_2O$ at 2.5 K min^{-1} to the temperatures indicated by arrows on the DTA curve of Fig. 5·5. ○ and ● : cyclo-Hexaphosphates in the products heated in streams of dry nitrogen and humid air, respectively; □ and ■ : oligophosphates (chain length: n=1-6) in the products heated in streams of dry nitrogen and humid air, respectively; △ and ▲ : polyphosphates(n≧ 7) in the products heated in streams of dry nitrogen and humid air, respectively.

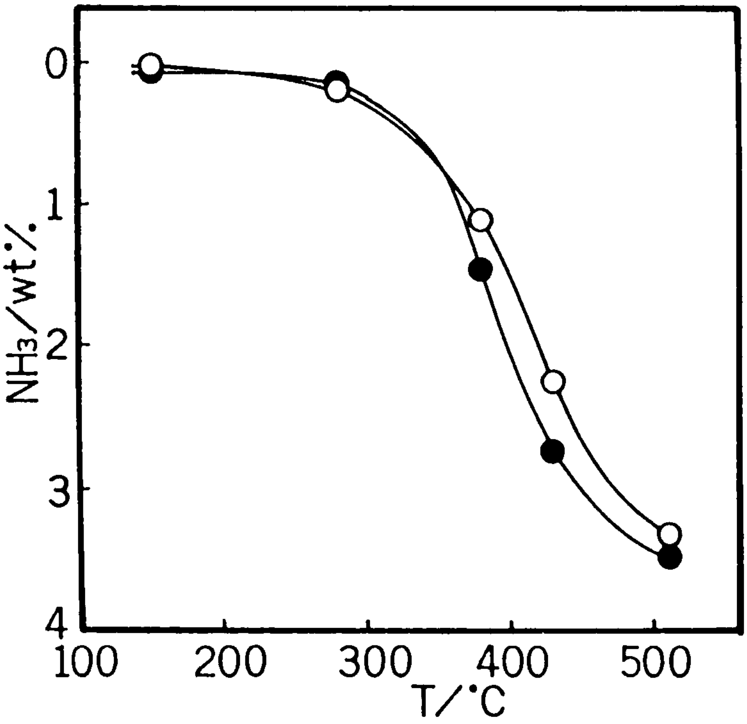

Fig. 5·7. Amounts of ammonia evolved by heating of $Cu_2(NH_4)_2P_6O_{18}\cdot8.5H_2O$ at 2.5 K min^{-1} to the temperatures indicated by arrows on the DTA curve of Fig. 5·5. ○ : Measured in a stream of dry nitrogen at 50 cm^3 min^{-1}, ● : measured in a stream of humid air at 50 cm^3 min^{-1}.

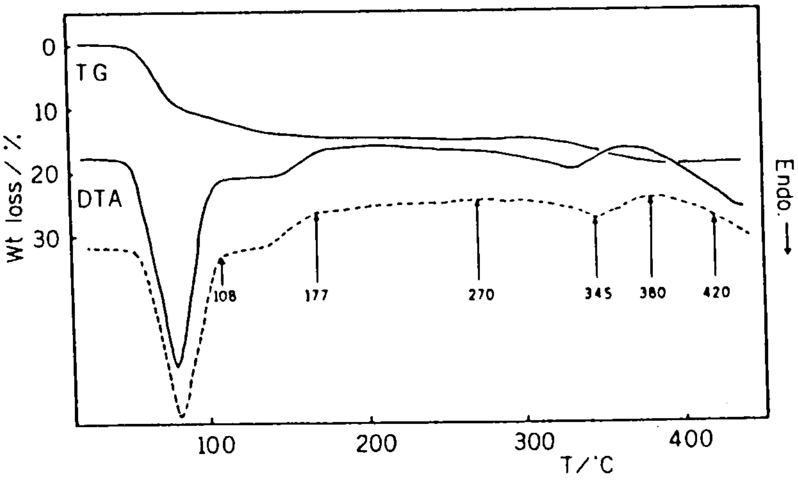

Fig. 5·8. Thermal analyses (TG-DTA) of $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ measured at 2.5 K min^{-1}. Solid line (——): TG and DTA measured in static air, dashed line (---): DTA measured in a stream of dry nitrogen at 50 cm^3 min^{-1}.

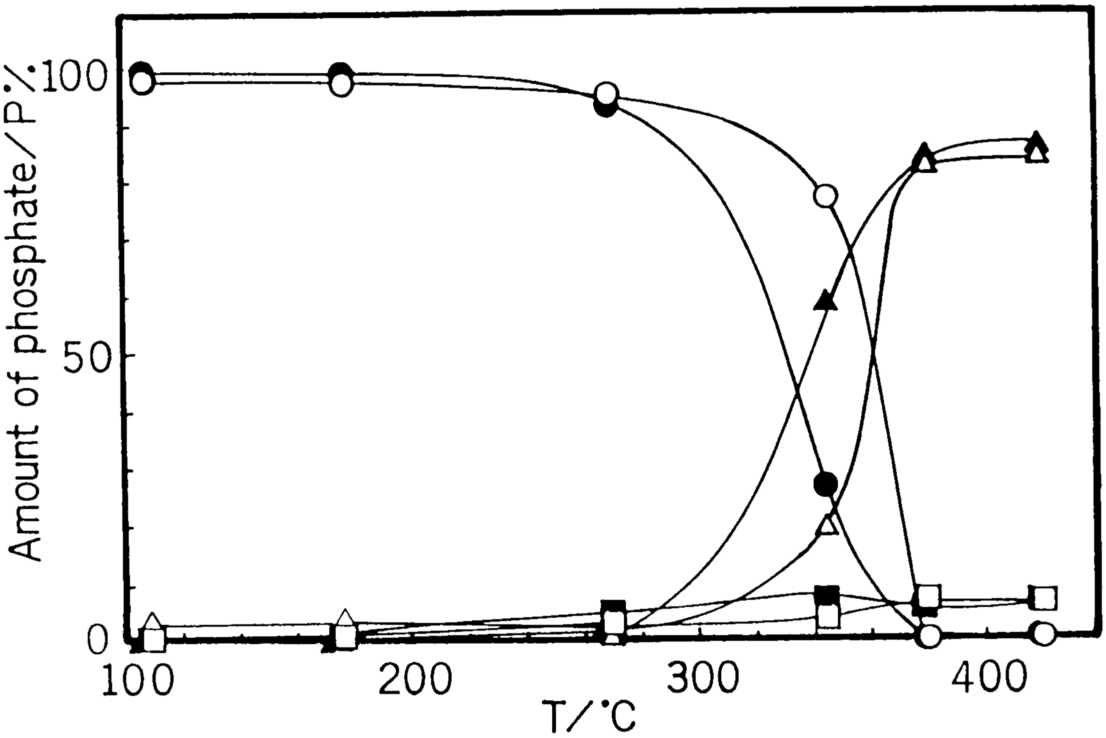

Fig. 5·9. Amounts of phosphates in the products obtained by heating of $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ at 2.5 K min^{-1} to the temperatures indicated by arrows on the DTA curve of Fig. 5·8. ○ and ● : cyclo-Hexaphosphates in the products heated in streams of dry nitrogen and humid air, respectively; □ and ■ : oligophosphates (chain length: n=1-6) in the products heated in streams of dry nitrogen and humid air, respectively; △ and ▲ : polyphosphates($n\geqq 7$) in the products heated in streams of dry nitrogen and humid air, respectively.

products were the oligo- and the polyphosphates, their amounts are not plotted in Fig. 5·9. Ammonia evolved as shown in Fig. 5·10. Even up to 270°C, the cyclo-hexaphosphate ions were not cleaved and ammonia was hardly liberated. There was little change in weight from 177 to 270°C. Therefore, a weight loss up to 170°C corresponds to the dehydration of the water of crystallization of CaP_{6m}, which causes a broad endothermic peak below 177°C, as expressed by the following equation:

$$Ca_2(NH_4)_2P_6O_{18} \cdot 7H_2O \longrightarrow Ca_2(NH_4)_2P_6O_{18} + 7H_2O \quad (5\cdot 1)$$

Figure 5·9 shows that polyphosphates ($n \geqq 7$) were produced at lower temperatures under humid conditions than under dry conditions, in proportion to the disappearance of cyclo-hexaphosphate. Although oligophosphates($n=1-6$) are the primitive hydrolytic products of CaP_{6m}, there were only small amounts of the oligophosphates even under humid conditions.

The TG-curve shows a plateau around 420°C (Fig. 5·8). A weight loss of ca. 3.7% from 270 to 420°C in a stream of dry nitrogen 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 unlikely as a thermal formation of the polyphosphates.

As mentioned in Chapter 4, ammonium cyclo-hexa- and

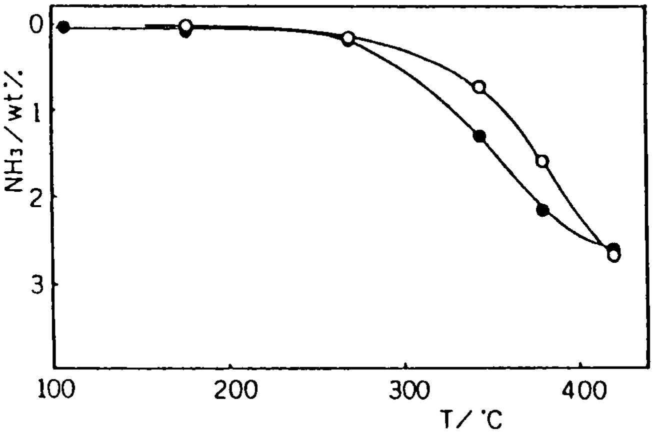

Fig. 5·10. Amounts of ammonia evolved by heating of $Ca_2(NH_4)_2P_8O_{18}\cdot 7H_2O$ at 2.5 K min^{-1} to the temperatures indicated by arrows on the DTA curve of Fig. 5·8. ○ : Measured in a stream of dry nitrogen at 50 cm^3 min^{-1}, ● : measured in a stream of humid air at 50 cm^3 min^{-1}.

cyclo-tetraphosphates are changed to ammonium polyphosphates through a radical polymerization.[10] Then, under dry conditions, ammonium oligophosphates are yielded a little or little. And it is the trigger reaction that a small amount of ammonia is liberated. $Ca_2(NH_4)_2P_6O_{18}$, formed according to Eq. 5·1, was converted to polyphosphates ($n \geqq 7$) at between 270 and 420°C. The conversion was accompanied by a liberation of ammonia (Fig. 5·10). The amounts of oligophosphates (n=1-6) were small as shown in Fig. 5·9. Although neither an increase in weight nor a corresponding exothermic peak is seen on the TG and DTA curves, unlike in the case of ammonium cyclo-tetraphosphate $(NH_4)_4P_4O_{12}$ (see Chapter 4),[10] it might be concluded that the polyphosphates were produced from CaP_{6m} through a polymerization of oligophosphate radicals.

5-3-2 Thermal Decomposition and Polymerization of Ammonium Strontium cyclo-Tetraphosphate $Sr(NH_4)_2P_4O_{12}$

Figure 5·11 shows TG and DTA curves of $Sr(NH_4)_2P_4O_{12}$ [SrP_{4m}] measured in static air and in a stream of dry nitrogen. Figure 5·12 shows the percentage of phosphorus atoms present as cyclo-tetra-, oligo- (chain length n=1-4), and polyphosphates ($n \geqq 5$) in the products obtained by heating of SrP_{4m} to the temperatures indicated by arrows on the DTA curve of Fig. 5·11. Since SrP_{4m} was decomposed above 360°C by a dynamic heatig method

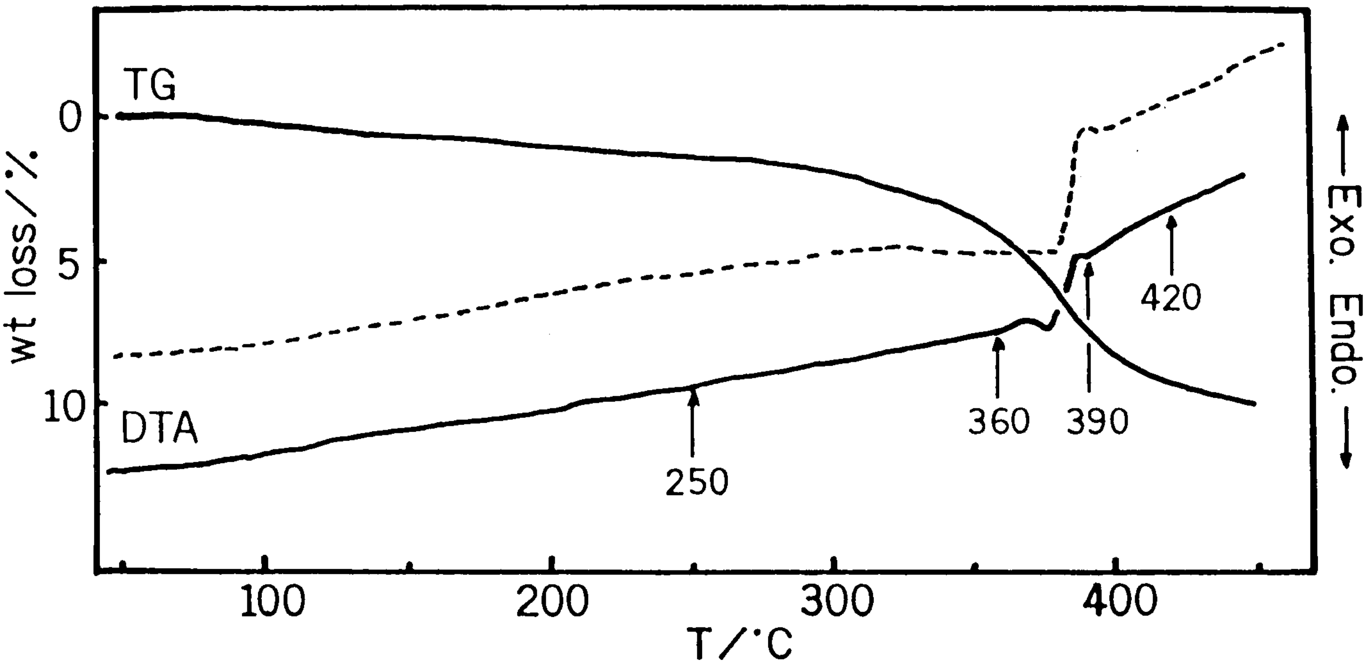

Fig. 5·11. Thermal analyses (TG-DTA) of $Sr(NH_4)_2P_4O_{12}$ measured at 2.5 K min^{-1}. Solid line (——): TG and DTA measured in static air, dashed line (---): DTA measured in a stream of dry nitrogen at 50 cm^3 min^{-1}.

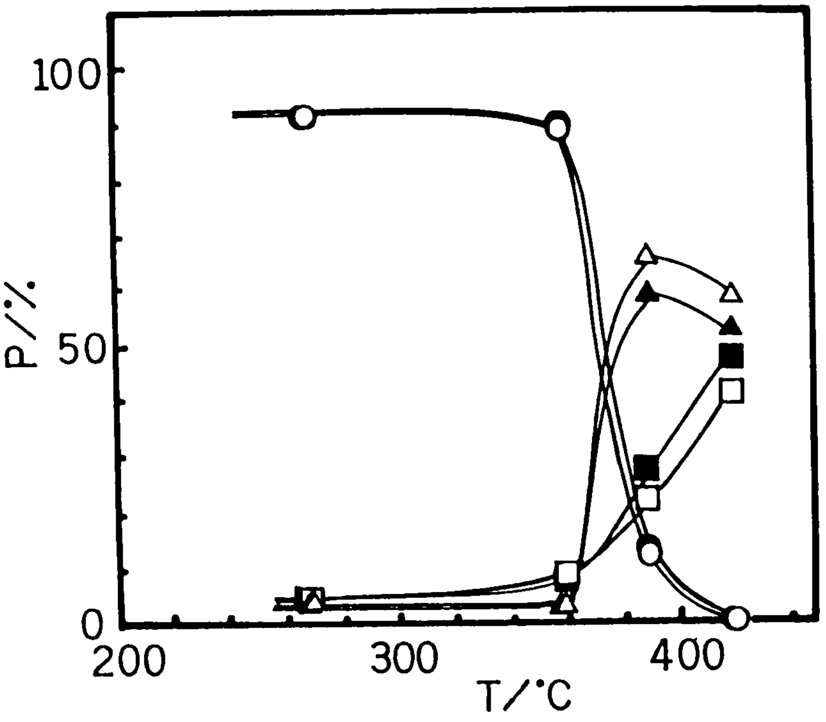

Fig. 5·12. Amounts of phosphates in the products obtained by heating of $Sr(NH_4)_2P_4O_{12}$ at 2.5 K min^{-1} to the temperatures indicated by arrows on the DTA curve of Fig. 5·11. ○ and ● : cyclo-Tetraphosphates in the products heated in streams of dry nitrogen and humid air, respectively; □ and ■ : oligophosphates (chain length: n=1-4) in the products heated in streams of dry nitrogen and humid air, respectively; △ and ▲ : polyphosphates($n \geq 5$) in the products heated in streams of dry nitrogen and humid air, respectively.

simultaneously to polyphosphates and oligophosphates (Fig. 5·12), the method did not reveal the mechanism of the formation of polyphosphates. Hence an isothermal heating was performed at lower temperatures and a short period (10 min).

Table 5·7 lists the composition of phosphates of the isothermal products. Although, in the dry atmosphere, the fraction of the oligophosphates was hardly changed between 250 and 360°C, that of polyphosphates appreciably increased between 300 and 360°C. A part of the polyphosphates, therefore, might be produced directly from SrP_{4m}.
It might take place through a radical polymerization.
Since SrP_{4m} loses ammonia by heating, the products become acidic and hydrolysis takes place easily. Therefore, oligophosphates (n=1-4) were probably produced from hydrolysis of SrP_{4m} by a trace of water present in atmosphere.

5-3-3 Thermal Decomposition and Polymerization of Ammonium Strontium cyclo-Triphosphate $Sr(NH_4)P_3O_9 \cdot 3H_2O$

Figure 5·13 shows TG and DTA curves
of $Sr(NH_4)P_3O_9 \cdot 3H_2O$ [SrP_{3m}] measured in static air and in a stream of dry nitrogen at 50 cm^3 min^{-1}. Figure 5·14 shows the percentage of phosphorus atoms present as cyclo-tri-, oligo-(chain length n=1-3), and polyphosphates($n \geqq 4$) in the products obtained by heating of SrP_{3m} to the temperatures illustrated by arrows on the DTA curve of Fig. 5·13. Ammonia was then liberated from SrP_{3m},

Table 5·7. Amounts of Phosphates in the Isothermal Products Obtained by Heating of $Sr(NH_4)_2P_4O_{12}$ in a Stream of Dry Nitrogen or Humid Air

T/°C	Time/min	Atmosphere	Composition/ P %		
			Oligo-(n=1-4)	Poly-(n≧ 5)	cyclo-Tetra-
200	10	Dry nitrogen	9.3	–	90.7
		Humid air[a]	9.7	–	90.3
250	10	Dry nitrogen	13.9	0.3	85.8
		Humid air	14.2	1.3	84.6
300	10	Dry nitrogen	14.1	2.5	83.4
		Humid air	14.5	5.1	80.4
360	10	Dry nitrogen	13.0	22.4	64.6
		Humid air	23.4	32.0	44.6

a) Relative humidity 90 % at 25°C.

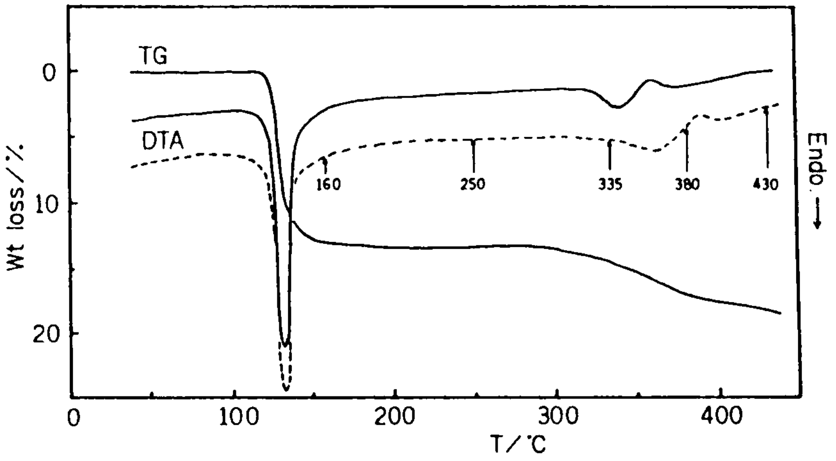

Fig. 5·13. Thermal analyses (TG-DTA) of $Sr(NH_4)P_3O_9 \cdot 3H_2O$ measured at 2.5 K min^{-1}. Solid line (——): TG and DTA measured in static air, dashed line (---): DTA measured in a stream of dry nitrogen at 50 cm^3 min^{-1}.

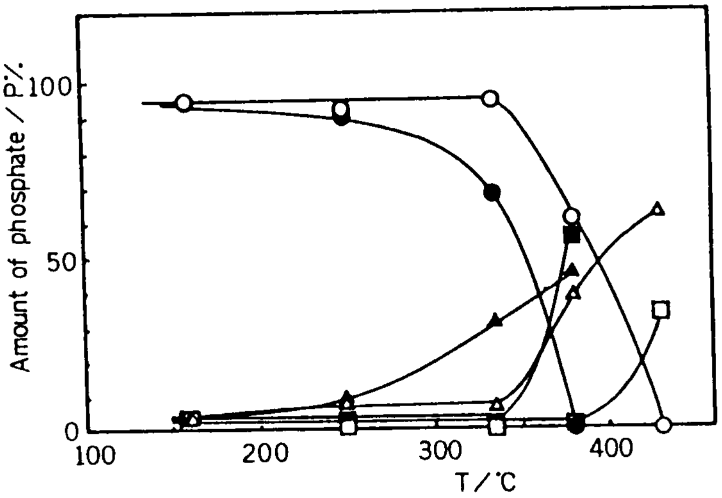

Fig. 5·14. Amounts of phosphates in the products obtained by heating of $Sr(NH_4)P_3O_9 \cdot 3H_2O$ at 2.5 K min^{-1} to the temperatures indicated by arrows on the DTA curve of Fig. 5·13. ○ and ● : cyclo-Triphosphates in the products heated in streams of dry nitrogen and humid air, respectively; □ and ■ : oligophosphates (chain length: n=1-3) in the products heated in streams of dry nitrogen and humid air, respectively; △ and ▲ : polyphosphates(n≧ 4) in the products heated in streams of dry nitrogen and humid air, respectively.

as shown in Fig. 5·15.

Since ammonia was not or was hardly evolved even up to 250°C, a sharp and strong endothermic peak at 130°C could be caused by the elimination of the water of crystallization of SrP_{3m}. The corresponding TG-loss(13.1%) was close to the calculated value(13.62%) given by the following equation:

$$Sr(NH_4)P_3O_9 \cdot 3H_2O \longrightarrow Sr(NH_4)P_3O_9 + 3H_2O. \qquad (5\cdot 2)$$

Polyphosphates were formed from anhydrous $Sr(NH_4)P_3O_9$ with elimination of ammonia. The elimination was accelerated by humidity. Especially, from 250 to 335°C, the relation between the formation of polyphosphates and the elimination of ammonia is clearly seen. Either an increase in weight or a corresponding exothermic peak, suggesting a radical polymerization,[10] is not detected in the thermal analytical curves of SrP_{3m}. Between ca. 300°C and ca. 400°C, a loss in weight, suggesting a dehydration-condensation, is seen on the TG curve. However, from 250 to 335°C in the humid atmosphere, oligophosphates(n=1-3) to be the primitive hydrolytic products of $Sr(NH_4)P_3O_9$ were hardly present in the products. Therefore, some part of the formation of polyphosphates must proceed through a radical polymerization, like in the thermal change of CaP_{6m} to polyphosphates.

X-Ray diffraction patterns suggested that the crystallization of β-$Sr(PO_3)_2$ with long-chain anion[28]

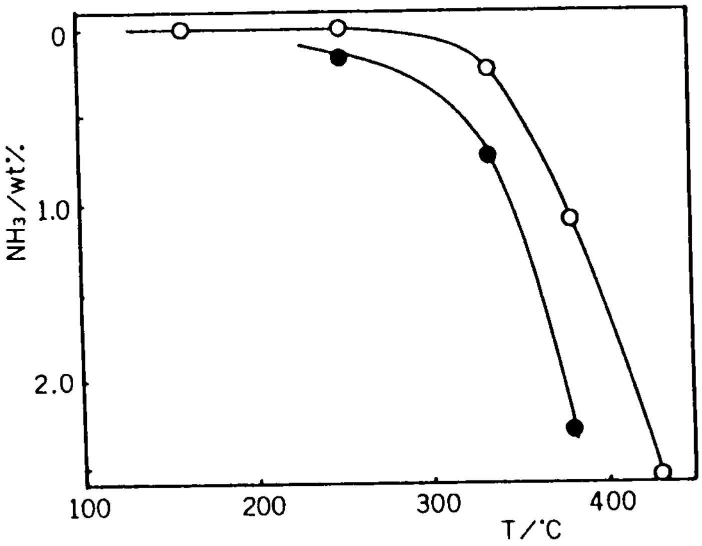

Fig. 5·15. Amounts of ammonia evolved by heating of $Sr(NH_4)P_3O_9 \cdot 3H_2O$ at 2.5 K min^{-1} to the temperatures indicated by arrows on the DTA curve of Fig. 5·13. ○ : Measured in a stream of dry nitrogen at 50 cm^3 min^{-1}, ● : measured in a stream of humid air at 50 cm^3 min^{-1}.

was responsible for the exothermic peaks at 355 and 390°C observed in the humid and dry atmospheres, respectively.

5-4 Conclusion

Ammonium strontium cyclo-hexaphosphate $Sr_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ [SrP_{6m}], ammonium copper (II) cyclo-hexaphosphate $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$ [CuP_{6m}], ammonium calcium cyclo-hexaphosphate $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ [CaP_{6m}], and ammonium strontium cyclo-triphosphates $Sr(NH_4)P_3O_9\cdot 3H_2O$ [SrP_{3m}] were prepared by wet methods. Ammonium strontium cyclo-tetraphosphate $Sr(NH_4)_2P_4O_{12}$ [SrP_{4m}] was also prepared. Thermal behavior of these ammonium bivalent-metal cyclo-phosphates was investigated by controlling of the partial pressure of water vapor present in atmosphere. Deammoniation accompanied by their thermal change was checked by a neutralization titrimetry. SrP_{6m}, CuP_{6m}, CaP_{6m}, SrP_{4m}, and SrP_{3m} were heated at 2.5 K min^{-1} to the temperatures where changes in their TG and DTA curves took place.

Rings of SrP_{6m} and CuP_{6m} were hydrolyzed by the water of crystallization. Therefore, the formation of polyphosphates (chain length: $n \geqq 7$) from SrP_{6m} and CuP_{6m} was considered to proceed through the condensation of oligophosphates ($n=1-6$).

Since CaP_{6m} or SrP_{3m} yielded polyphosphates ($n \geqq 7$ or 4, respectively) with little formation of the primitive hydrolytic products, i. e., oligophosphates (n=1-6 or 1-3, respectively), the polyphosphates were considered to be produced through a radical polymerization.

Since SrP_{4m} was decomposed simultaneously to oligophosphates (n=1-4) and polyphosphates($n \geqq 5$) by a dynamic heating method, the mechanism of the formation of polyphosphates could not be determined. However, an isothermal heating method indicated that a part of the polyphosphates was considered to be produced directly from SrP_{4m}. The change of SrP_{4m} to the polyphosphates might take place through a radical polymerization.

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Chapter 6 Thermal Condensation of Ammonium Amidotriphosphate $(NH_4)_4P_3O_9NH_2 \cdot H_2O$

6-1 Introduction

As mentioned in the preceding chapters, some polymerization mechanisms have been proposed for the thermal change of several inorganic phosphates including ammonium ions.(1-5) Well, nitrogen in the inorganic phosphates can also exist as phosphorus-nitrogen bonds, e. g., amino groups.

Inorganic phosphates with phosphorus-nitrogen bonds are potential candidates as a new class of fertilizer. They attracted our attention also as flame-proofing materials,(6) and probably in view of this several reports have been published regarding with their thermal decomposition.(7-19) Especially, amidophosphates have been studied by many workers.(9-19)

Amidotriphosphate ion has such a structure that the terminal oxygen atom of triphosphate ion is replaced with an amino group. It is well-known that amidotriphosphates are prepared by ammonolyses of cyclo-triphosphates in aqueous solutions.(20-22)

This chapter shows the thermal condensation of ammonium amidotriphosphate ($(NH_4)_4P_3O_9NH_2 \cdot H_2O$). An atmosphere of hydrogen chloride as an acidic deammoniation agent(23) was also used other than that of dry air, humid air (relative humidity 90 % at 25°C), and ammonia.

6-2 Experimental

Unless otherwise stated, the procedures were carried out as indicated in the preceding chapters.

6-2-1 Determination of Phosphorus and Nitrogen Present as Ammonium Ions, $N(NH_4^+)$, and as Amino and Imino Groups, $N(NH_2^-)$

Total phosphorus was determined colorimetrically with an HPLC-FIA system (see Chapter 4). Total nitrogen, N, was determined by the Kjeldahl method.[24] Nitrogen present as ammonium ions, $N(NH_4^+)$, was determined by an ammonia-distillation method without decomposition by use of concentrated sulfuric acid.[9, 21] Nitrogen present as amino and imino groups, $N(NH_2^-)$, was calculated by subtracting the $N(NH_4^+)$ from the total nitrogen, N.[9, 21]

6-2-2 IR Spectrophotometry

IR spectra were recorded on a JASCO IR spectrophotometer IR-700 by a KBr disc method.

6-2-3 Thermal Analysis (TG-DTA)

A sample was placed in a platinum pan. The thermal analyses (TG-DTA) were carried out in static air at a heating rate of 5 K min^{-1}, using a Rigaku Thermal Analyzer 8076 D1.

6-2-4 HPLC-Flow Injection Analysis (HPLC-FIA)

A sample was dissolved in a 0.1 mol dm^{-3} sodium hydroxide aqueous solution to prevent the cyclization of amidotriphosphate ions to cyclo-triphosphate ions, that readily occurs in acidic solutions.[20-22] The solution was diluted with distilled water, and was injected into an HPLC-FIA system which was the same as that described in Chapter 2.

The eluent was an aqueous KCl solution including 0.1 % (w/v) tetrasodium ethylenediaminetetraacetate tetrahydrate.[25] Table 6·1 shows the changes in concentration of the eluent with time. Polyphosphates with long-chain ions were eluted with a 1.0 mol dm^{-3} KCl aq. solution.

Table 6·1. Concentration of an Aqueous Potassium Chloride Solution Used in the Gradient Method

Period/ min	Initial Concenration/ mol dm^{-3}	Final Concentration/ mol dm^{-3}
0 - 25.0	0.180	0.200
25.0 - 37.8	0.200	0.293
37.8 - 50.6	0.293	0.345
50.6 - 63.4	0.345	0.378
63.4 - 76.2	0.378	0.398
76.2 - 89.0	0.398	0.415
89.0 - 101.8	0.415	0.425
101.8 - 114.6	0.425	0.433
114.6 - 127.4	0.433	0.443
127.4 - 140.2	0.443	0.448

Figure 6·1 shows an HPLC-FIA chromatogram of an inorganic-phosphates mixture including amidotriphosphate.

If the chain length of polyphosphates exsisting in the

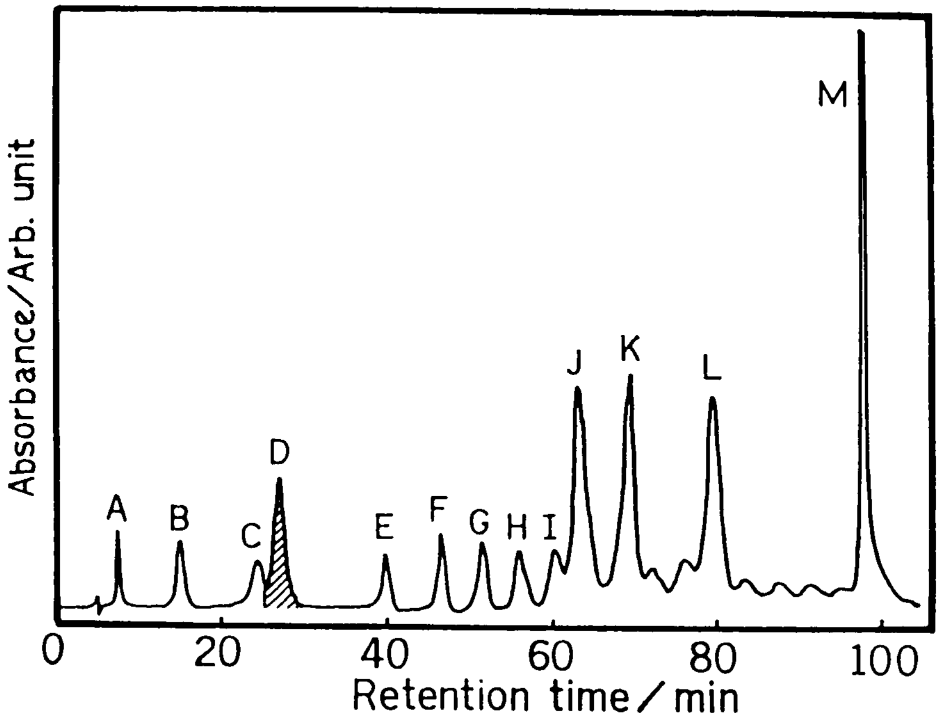


Fig. 6·1. HPLC-FIA chromatogram of an inorganic-phosphates mixture including amidotriphosphate. A: Mono-, B: di-, C: tri-, D: amidotri-, E: tetra-, F: penta-, G: hexa-, H: hepta-, I: octa-, J: cyclo-hexa-, K: cyclo-tetra-, L: cyclo-tri-, M: polyphosphates.

sample solution becomes longer, the HPLC-FIA technique for analyzing the solution is not enough to form the heteropoly blue complex completely. Consequently, the accurate composition of phosphates was determined in the same way as that described in Chapter 4.

6-2-5 Preparation of Ammonium Amidotriphosphate $(NH_4)_4P_3O_9NH_2 \cdot H_2O$

An ammonium cyclo-triphosphate, $(NH_4)_3P_3O_9$, prepared according to Ref. 26, had a new X-ray diffraction pattern. The X-ray diffraction data are listed in Table 6·2. After allowing the $(NH_4)_3P_3O_9$ to stand for about six months below room temperature, its X-ray diffraction lines changed to those reported in Ref. 26, while several of the original lines remained. After the ammonium cyclo-triphosphate thus formed was heated at 5 K min^{-1} to 300°C in a stream of ammonia, its X-ray diffraction lines agreed completely with those listed in Table 6·2. It indicates that the new phase of ammonium cyclo-triphosphate is a high-temperature phase. Found: P, 31.22; N, 14.15 %. Calcd for $(NH_4)_3P_3O_9$: P, 31.92; N, 14.44 %.

Ammonium amidotriphosphate monohydrate, $(NH_4)_4P_3O_9NH_2 \cdot H_2O$, was prepared by ammonolysis of $(NH_4)_3P_3O_9$.[21] HPLC-FIA data for several $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ samples prepared showed that more than 95.0 % of the phosphorus atoms exist as amidotriphosphate ions. Found: P, 26.93; N(NH_4^+), 16.02; N(NH_2^-), 3.89 %.

Table 6·2. X-Ray Diffraction Data for a New Phase of Ammonium cyclo-Triphosphate $(NH_4)_3P_3O_9$

d/A	Intensity[a)]	d/A	Intensity
8.66	M	3.11	S
6.37	W	3.05	VW
6.23	S	2.99	VW
5.94	M	2.90	M
5.75	VS	2.87	M
5.40	M	2.85	W
4.72	W	2.68	W
4.35	W	2.59	VW
4.15	W	2.50	VW
3.91	W	2.47	VW
3.86	W	2.43	VW
3.67	W	2.38	VW
3.64	W	2.35	VW
3.49	M	2.30	VW
3.40	M	2.27	W
3.25	W		

a) VS: very strong, S: strong, M: medium, W: weak, VW: very weak.

Calcd for $(NH_4)_4P_3O_9NH_2 \cdot H_2O$: P, 27.07; $N(NH_4^+)$, 16.33; $N(NH_2^-)$, 4.08 %. However, the ammonium amidotriphosphate sample used throughout thermal decomposition experiments was only pure.

6-2-6 Thermal Reaction

Thermal reaction was carried out, by means of dynamic heating methods (heating rate: 5 K min^{-1}) or isothermal methods. The isothermal heating began, when the sample was set in the furnace which had been kept at the required temperatures beforehand.

Streams of dry air and humid air (relative humidity 90 % at 25°C) at 50 cm^3 min^{-1} were obtained as mentioned in Chapter 2. Ammonia (purity: 99.9 %) was flowed directly from a cylinder. A stream of hydrogen chloride was prepared by adding concentrated sulfuric acid to ammonium chloride, then dried with concentrated sulfuric acid.

6-3 Results and Discussion

Figure 6·2 shows TG and DTA curves of $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ [AATP] measured at 5 K min^{-1} in static air. The endothermic peak at 300°C reflects the melting of the product.

Figure 6·3 depicts the percentage of phosphorus atoms existing as amidotri-, mono- to tri-, oligo- (chain length n= 4-11), poly-, and cyclo-triphosphates in the products obtained by heating of AATP in static air to the

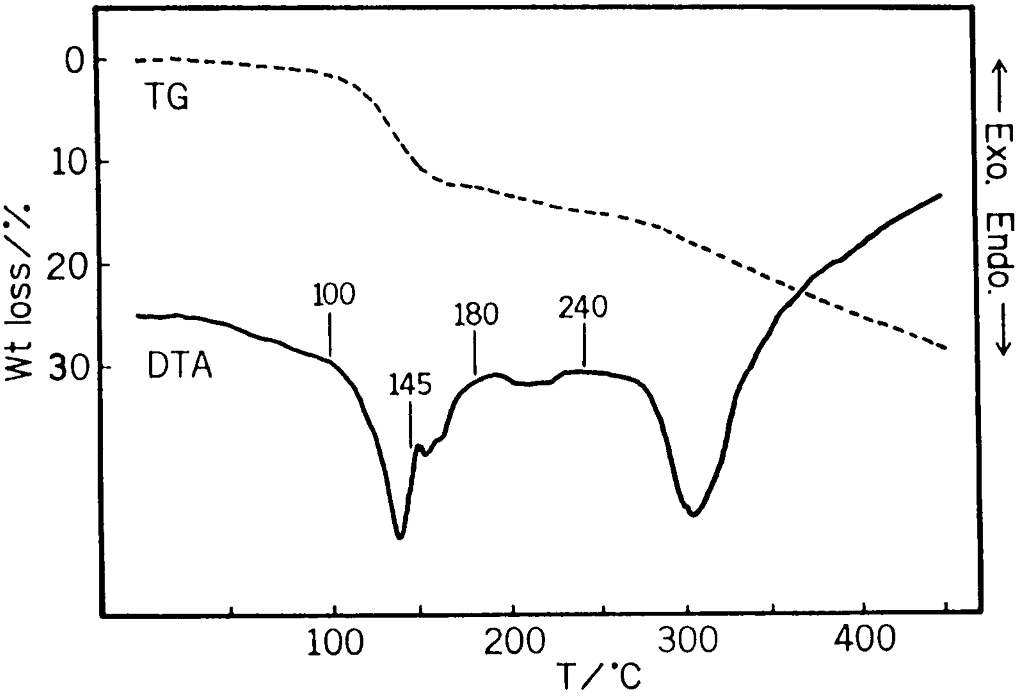


Fig. 6·2. TG and DTA curves of $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ measured at 5 K min^{-1} in static air.

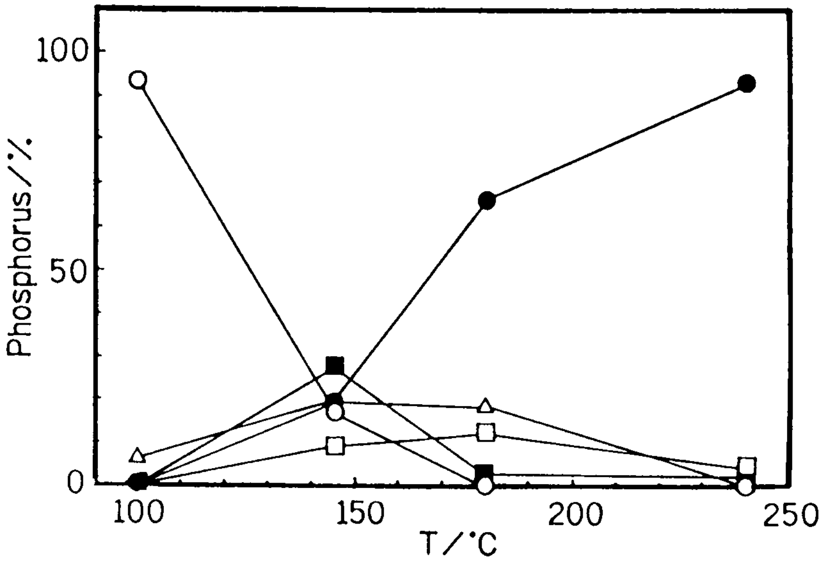


Fig. 6.3. Amounts of phosphates in the products heated in static air to the temperatures indicated on the DTA curve of Fig. 6·2. Heating rate: 5 K min^{-1}. ○ : Amidotri-, ● : poly-, □ : mono-, di-, and tri-, ■ : oligo- (chain length: n=4-11), △ : cyclo-triphosphates.

temperatures indicated on the DTA curve in Fig. 6·2. Peaks not assignable to these phosphate ions were occasionally detected on the HPLC-FIA chromatograms. In view of the short retention time, they are probably short-chain phosphate ions with one or several phosphorus-nitrogen bonds, and are denoted as "other" phosphates in Table 6·3. Since these amount to only less than ca. 4 % as phosphorus atoms, they are neglected in Fig. 6·3.

Release of the water of crystallization from $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ [AATP] would give 5.25 % of weight loss. The weight loss at 145 °C was significantly larger, ca. 12.1 %. Therefore, the endothermic peak at about 140°C may reflect elimination of ammonia as well as the water of crystallization.

The X-ray diffraction pattern of the sample heated to 180°C showed the lines for ammonium polyphosphate (I-form)[27] and those for ammonium cyclo-triphosphate given in Table 6·2 (Fig. 6·4). The lines at 15.4 and 28.8° (2θ) are attributable to the cyclo-triphosphate. The sample heated to 240°C was mostly ammonium polyphosphate as judged from Figs. 6·3 and 6·4. The weight loss in the TG curve at 240°C was ca. 15.4 %, which is close to that calculated according to the following equation (15.18 %):

$$(NH_4)_4P_3O_9NH_2 \cdot H_2O \longrightarrow 3(NH_4)PO_3 + 2NH_3 + H_2O \qquad (6\cdot 1)$$

Samples of AATP were heated at 5 K min^{-1} to 100, 145, 180, and 240°C, in streams of four different gases.

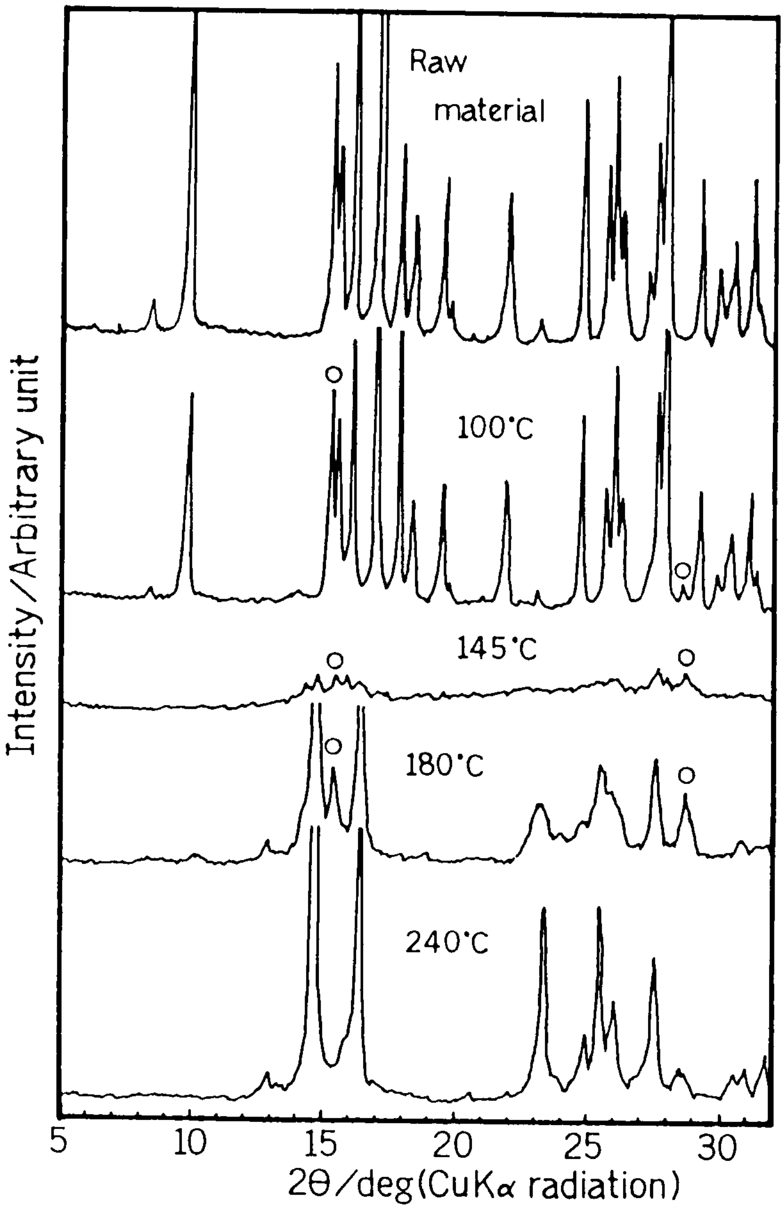
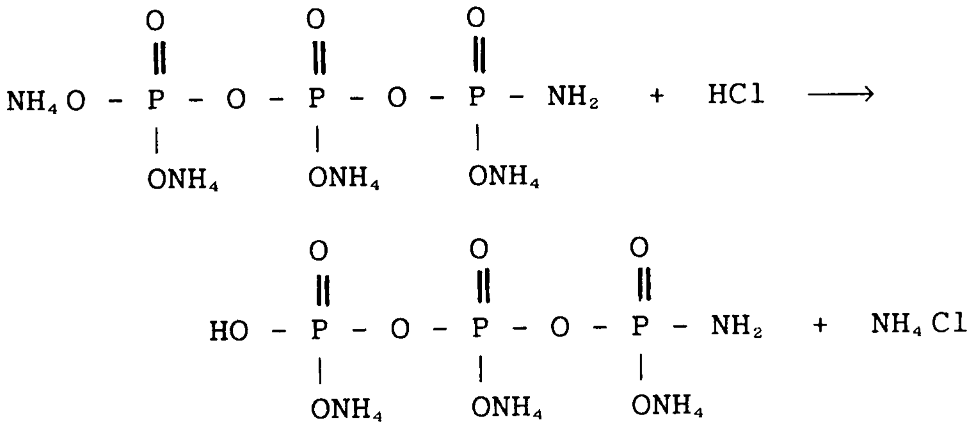


Fig. 6·4. X-Ray diffraction patterns of $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ and its products heated in static air to the temperatures indicated on the DTA curve of Fig. 6·2. Heating rate: 5 K min^{-1}. ○ : The lines were attributable to the ammonium cyclo-triphosphate indicated in Table 6·2.

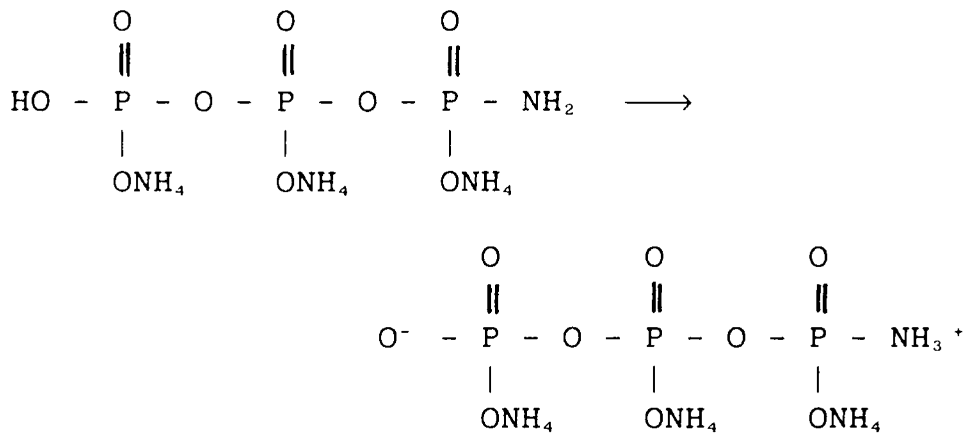
Table 6·3 shows the composition of phosphates of the products. It was reported that amidotriphosphate ions cyclized again to cyclo-triphosphate ions in acidic solutions.[20-22] As seen in Table 6·3, the products occasionally contained cyclo-triphosphates. Such samples exhibited necessarily two diffraction lines at 15.4 and 28.8° (2θ), which agreed with those listed in Table 6·2. Quimby and Flautt,[20] and Feldmann and Thilo[21] described that a zwitterion was formed as an intermediate in the cyclization of amidotriphosphate ion in solution.

Table 6·3 shows that cyclo-triphosphate ions exist most abundantly in samples heated to 100°C in gaseous hydrogen chloride. This is probably due to the formation and subsequent cyclization of the zwitterion expressed by the following equations:

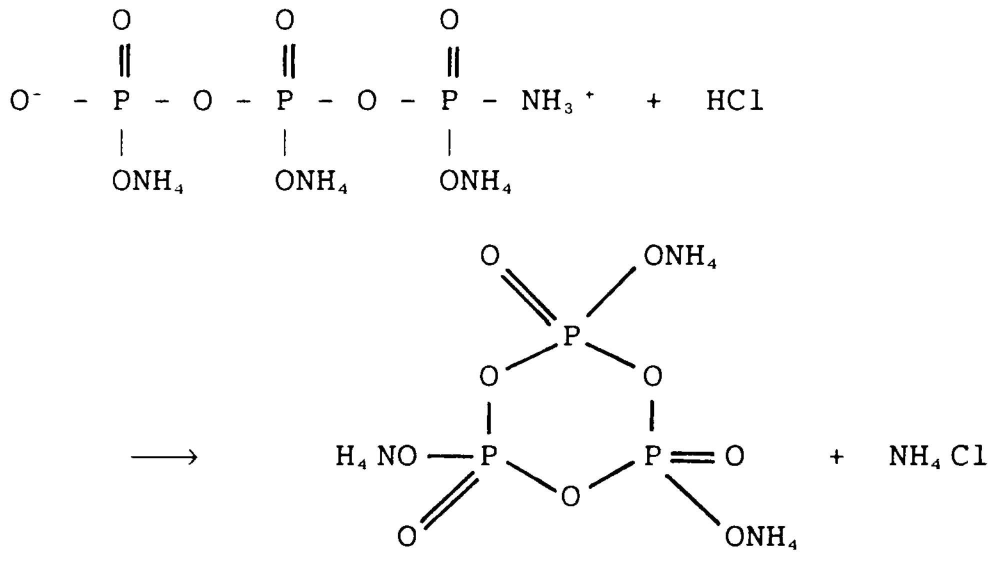


$$NH_4O-\underset{ONH_4}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-O-\underset{ONH_4}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-O-\underset{ONH_4}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-NH_2 + HCl \longrightarrow$$

$$HO-\underset{ONH_4}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-O-\underset{ONH_4}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-O-\underset{ONH_4}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-NH_2 + NH_4Cl \qquad (6\cdot 2)$$



$$\mathrm{HO-\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}-NH_2} \longrightarrow \mathrm{O^{-}-\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}-NH_3^{+}} \qquad (6\cdot 3)$$



(6·4)

Oligophosphates (n=4-12) were formed more in samples heated to 145 and 180°C in dry HCl than in the other atmospheres. Sato et al. reported that polyphosphates were produced by condensation of the zwitterions resulting from a reaction of amidophosphates with hydrogen chloride.[28,29] Therefore, the oligophosphates may also be formed by condensation of the zwitterions indicated on the right-hand side of Eq. 6·3.

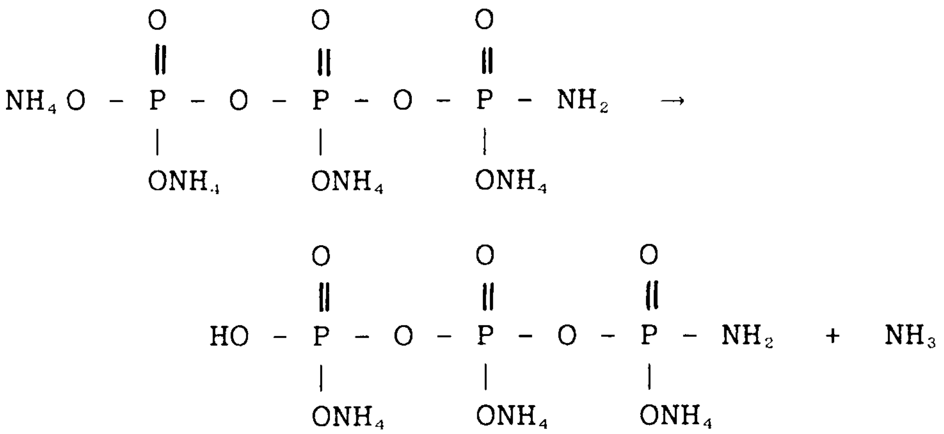
The zwitterions can be also produced by a direct deammoniation from AATP, according to the Eqs. 6·5 and 6·3.

Table 6·3. Amounts of Phosphates in the Products Obtained by Heating of $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ at 5 K min^{-1} in Streams of Four Different Gases to the Temperatures Indicated on the DTA Curve of Fig. 6·2

T/°C	Atmosphere	Composition/ P %					
		amidotri-	mono-,di-,and tri-	oligo-[a]	poly-	cyclo-tri-	other[b]
100	Dry air	88.9	–	0.7	1.6	8.8	–
	Humid air	95.6	–	–	–	4.4	–
	NH_3	100.0	–	–	–	–	–
	Dry HCl	51.3	5.4	7.5	3.3	32.6	–
145	Dry air	17.4	7.1	25.0	31.7	13.6	5.2
	Humid air	67.7	4.9	7.8	5.3	12.3	2.0
	NH_3	79.7	6.1	12.4	–	–	1.9
	Dry HCl	3.4	34.1	44.2	2.3	15.9	–
180	Dry air	3.0	8.3	3.2	63.1	21.8	0.6
	Humid air	–	20.6	4.7	52.6	22.2	–
	NH_3	70.7	8.3	5.9	15.2	–	–
	Dry HCl	–	36.9	60.6	2.5	–	–
240	Dry Air	–	2.9	0.8	96.4	–	–
	Humid air	–	12.8	5.1	82.2	–	–
	NH_3	–	4.8	–	95.2	–	–

a) Chain length from 4 to 12.

b) They are probably short-chain phosphates with one or several phosphorus-nitrogen bonds.



$$NH_4O-\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}-NH_2 \rightarrow HO-\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}-NH_2 + NH_3 \qquad (6\cdot 5)$$

(6·5)

Therefore, in static air and in streams of dry air and humid air, they probably also polymerized to ammonium oligo- and polyphosphates, or cyclized to ammonium cyclo-triphosphate (see Fig. 6·3 and Table 6·3).

The IR spectrum of $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ showed a large peak of ammonium ions at 1400-1500 cm^{-1},[30] and a small peak of amino groups at 1630 cm^{-1}.[31] The sample heated to 100°C in HCl showed a peak at 1400-1500 cm^{-1}, and a faint peak at 1670 cm^{-1}. Although Corbridge and Lowe reported that the zwitterions of amidophosphates all exhibited absorption at 1618-1615 cm^{-1} and at 1470-1468 cm^{-1},[30] it was unable to identify the zwitterions of the amidotriphosphates by the IR spectra.

The products heated to 240°C entirely consisted of polyphosphate ions, and showed an X-ray diffraction pattern of I-form of ammonium polyphosphate.[27] The sample heated to 240°C in dry air was analyzed: P, 31.17; $N(NH_4^+)$, 12.86; $N(NH_2^-)$, 0.69 %. The result reveals the presence of some phosphorus-nitrogen bonds in the ammonium polyphosphate.

Ammonium amidotriphosphate $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ [AATP] thermally produced a new phase of ammonium cyclo-triphosphate. The cyclo-triphosphate disappeared at higher temperatures. In order to investigate the process in more detail, isothermal runs were carried out in a stream of dry air. The essential features of the results obtained are displayed in Figs. 6·5 and 6·6. Mono- to triphosphates were hardly observed (less than 1 %) in samples heated at 100°C; thus, they are not plotted in Fig. 6·5. Tetra- and pentaphosphates were the only species among oligophosphates in samples heated at 180°C. However, since their total quantity was less than 1.6 %, they are neglected in Fig. 6·6. The chromatograms of samples heated at 100 and 180°C both showed no peaks of "other" phosphates.

At 100°C the amount of cyclo-triphosphate ions did not change with reaction time, and that of oligophosphates was also constant after 20 min (Fig. 6·5). These ions were probably formed via zwitterions. cyclo-Triphosphate ions were detected clearly at 10 min at 180°C (Fig. 6·6). They decreased with the passage of time to disappear completely in 30 min. X-Ray diffraction analyses gave the same results. Therefore, at higher temperatures, the cyclo-triphosphates were converted to ammonium polyphosphates (I-form).(27)

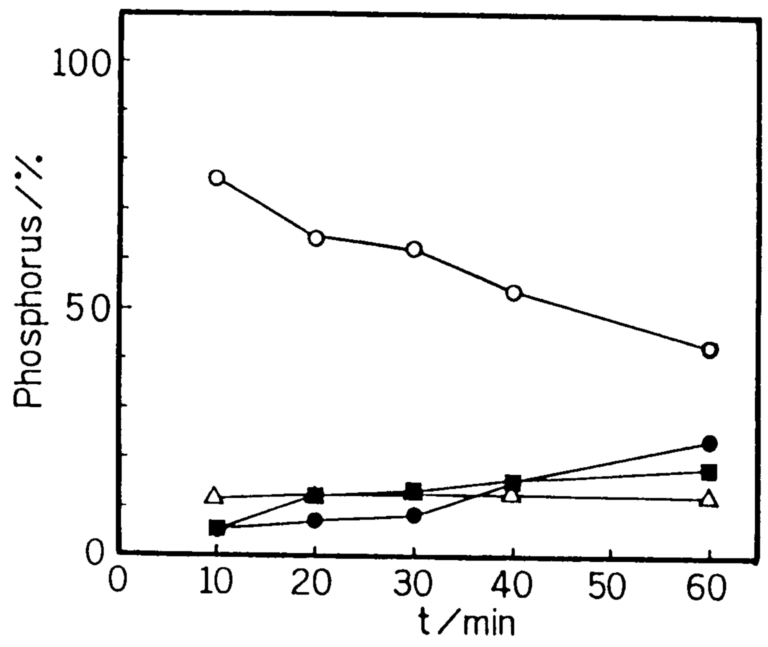


Fig. 6·5. Changes in amounts of phosphates in the products heated at 100°C in a stream of dry air at 50 cm^3 min^{-1}.

○ : Amidotri-, ● : poly-, ■ : oligo- (n= 4-12),

△ : cyclo-triphosphates.

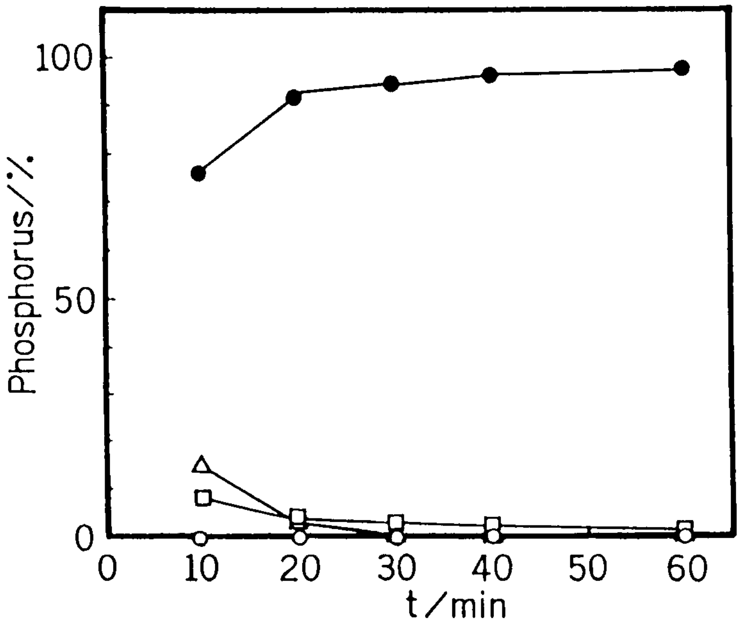


Fig. 6·6. Changes in amounts of phosphates in the products heated at 180°C in a stream of dry air at 50 cm^3 min^{-1}.

○ : Amidotri-, ● : poly-, □ : mono-, di-, and tri-,

△ : cyclo-triphosphates.

6-4 Conclusion

The thermal condensation of ammonium amidotriphosphate $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ [AATP] was investigated by changing of atmospheres. AATP was heated at 5 K min^{-1} up to 100, 145, 180, and 240°C in four different atmospheres: in a stream of dry air, humid air, ammonia, and dry hydrogen chloride. The products were analyzed by HPLC-FIA, X-ray diffractometry, and IR spectrophotometry.

A new phase of ammonium cyclo-triphosphate was observed at lower temperatures, except for in the ammonia atmosphere. cyclo-Tri-, oligo- (chain length = 4-12), and polyphosphates were most probably formed via zwitterions. By an action of gaseous hydrogen chloride as an acidic deammoniation agent, cyclo-triphosphates were most abundant in samples heated to 100°C in its atmosphere, while oligophosphates were more abundant in those heated to 145 and 180°C.

When AATP heated to 240°C in the atmospheres except for that of hydrogen chloride, it was changed to ammonium polyphosphates. Elemental analysis for the sample heated to 240°C in a stream of dry air showed that the ammonium polyphosphates formed contained some phosphorus-nitrogen bonds. Isothermal experiments at 180°C in a stream of dry air indicated that the new phase of ammonium cyclo-triphosphate was converted completely to ammonium polyphosphates.

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Chapter 7 Thermal Condensation of Silver Amidotriphosphate $Ag_4P_3O_9NH_2$ and Barium Amidotriphosphate $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$

7-1 Introduction

It is well-known that the thermal products of inorganic phosphates partially depend on the nature of the constituent cation.(1) As shown in Chapter 6, ammonium amidotriphosphate $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ [AATP] is thermally condensed to cyclo-tri-, oligo- and polyphosphates via zwitterions.(2) Therefore, it is also of interest whether amidotriphosphates other than AATP are condensed or not. Since silver amidotriphosphate $Ag_4P_3O_9NH_2$ [SATP] and barium amidotriphosphate $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$ [BATP] were obtained from AATP by wet methods, the thermal behavior of SATP and BATP was investigated.

7-2 Experimental

Unless otherwise stated, procedures were carried out according to those described in Chapter 6.

7-2-1 Determination of Barium and Silver

Barium was determined by a chelate replacement-titrimetry.(3) Silver was determined by atomic absorption spectrophotometry using a Shimadzu atomic absorption spectrophotometer Model AA-610.

7-2-2 IR Spectrophotometry

IR spectra were recorded with a JASCO IR spectrophotometer IR-700. For $Ag_4P_3O_9NH_2$ and its products, 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.

A KBr disc method was applied to the measurements of IR spectra of $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$ and its products.

7-2-3 Thermal Analysis (TG-DTA)

A sample was placed in a platinum pan. The thermal analyses (TG-DTA) were carried out at 5 K min^{-1} in static air and in a stream of dry air at 50 cm^3 min^{-1}, using a Rigaku Thermal Analyzer 8076 D1 or a MAC SCIENCE TG-DTA 2020.

7-2-4 HPLC-Flow Injection Analysis (HPLC-FIA)

For $Ag_4P_3O_9NH_2$ and its products, a sample was dissolved in a mixture of a 1.0 mol dm^{-3} NaCl aqueous solution and a 0.1 mol dm^{-3} NaOH aqueous solution. Silver chloride formed was filtered off. The filtrate was diluted with distilled water, and immediately injected into the HPLC-FIA system.

$Ba_2P_3O_9NH_2 \cdot 3.5H_2O$ or its products were dissolved in a 0.1 mol dm^{-3} aqueous tetrasodium ethylenediaminetetraacetate solution. It was diluted with distilled water, and analyzed as mentioned in Chapter 6.

7-2-5 Preparation of Silver Amidotriphosphate $Ag_4P_3O_9NH_2$ and Barium Amidotriphosphate $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$

Silver amidotriphosphate $Ag_4P_3O_9NH_2$ [SATP] was prepared from ammonium amidotriphosphate $(NH_4)_4P_3O_9NH_2 \cdot H_2O$.4)

Barium amidotriphosphate $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$ [BATP] was prepared as follows. Eight mmol (2.617 g) of ammonium amidotriphosphate ($(NH_4)_4P_3O_9NH_2 \cdot H_2O$)2, 4) 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 subsequently with water, acetone, and ether, and then air-dried. Analytical data for SATP and BATP are summarized in Table 7·1.

7-3 Results and Discussion

7-3-1 Thermal Condensation of Silver Amidotriphosphate $Ag_4P_3O_9NH_2$

Figure 7·1 shows TG and DTA curves of $Ag_4P_3O_9NH_2$ [SATP] measured at 5 K min^{-1} in static air and in a stream of dry air. The DTA curve of SATP measured in static air shows an exothermic peak at about 210°C. A TG-gain is observed corresponding to the exothermic peak. When the thermal analyses were performed in a stream

Table 7·1. Analyses of Silver Amidotriphosphate $Ag_4P_3O_9NH_2$ and Barium Amidotriphosphate $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$

Silver Amido-triphosphate	Found/ %					Calcd for $Ag_4P_3O_9NH_2$ / %		
	Ag	P	$N(NH_4^+)$	$N(NH_2^-)$	P present as $P_3O_9NH_2^{4-}$	Ag	P	$N(NH_2^-)$
	61.78	13.23	0.01	1.82	$\geqq 93.9$	63.04	13.57	2.05

Barium Amido-triphosphate	Found/ %					Calcd for $BaP_3O_9NH_2 \cdot 3.5H_2O$/ %		
	Ba	P	$N(NH_4^+)$	$N(NH_2^-)$	P present as $P_3O_9NH_2^{4-}$	Ba	P	$N(NH_2^-)$
	43.78	15.17	—	2.24	$\geqq 92.7$	46.50	15.73	2.37

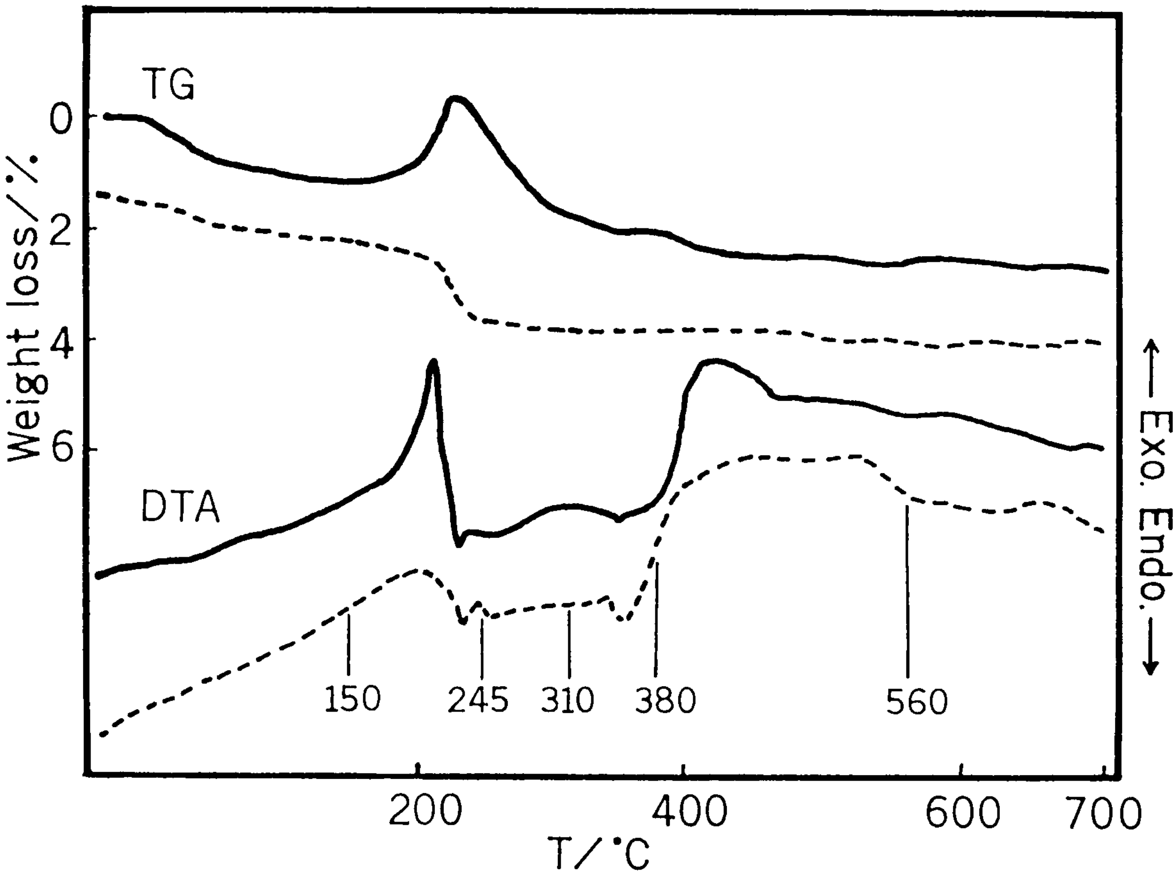

Fig. 7·1. TG and DTA curves of $Ag_4P_3O_9NH_2$ measured at 5 K min^{-1}. Solid line (——): in static air, dashed line (---): in a stream of dry air at 50 cm^3 min^{-1}.

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 7·2 shows the percentage of phosphorus atoms present as amidotri-, mono-, di-, and tri-, oligo- (chain length = 4-13), and polyphosphates in the products heated in static air to the temperatures indicated on the DTA curve of Fig. 7·1. 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 peaks are attributable to short-chain phosphates with one or several phosphorus(P)-nitrogen(N) bonds. Although ca. 2.8-% portion of phosphorus atoms was present as the P-N phosphates, it was not plotted in Fig. 7·2. When heated to 150°C, SATP remained mostly undecomposed, as was recognized by X-ray diffractometry (Fig. 7·3).

SATP was heated to the temperatures indicated in Fig. 7·1 in streams of dry air, humid air, and dry hydrogen chloride. The percentage of phosphorus atoms present as the various phosphates in the products is summarized in Table 7·2.

Some peaks other than those of amidotri-, mono-, di-,

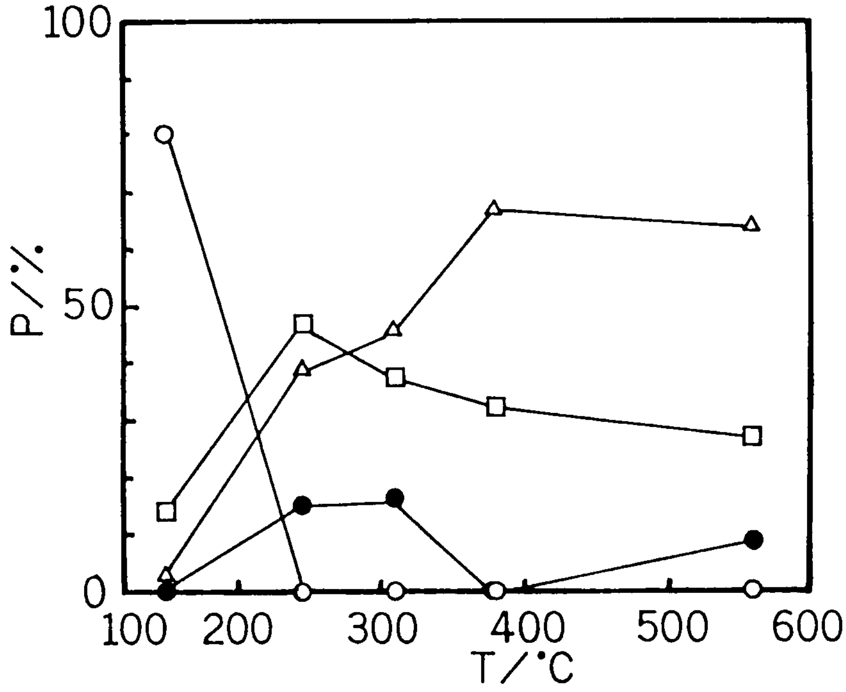

Fig. 7·2. Changes in the amounts of phosphates in the products obtained by heating of $Ag_4P_3O_9NH_2$ in static air to the temperatures indicated on the DTA curve of Fig. 7·1. Heating rate: 5 K min^{-1}. ○ : Amidotri-, ● : poly-, □ : mono-, di-, and tri-, △ : oligo- (chain length =4-13).

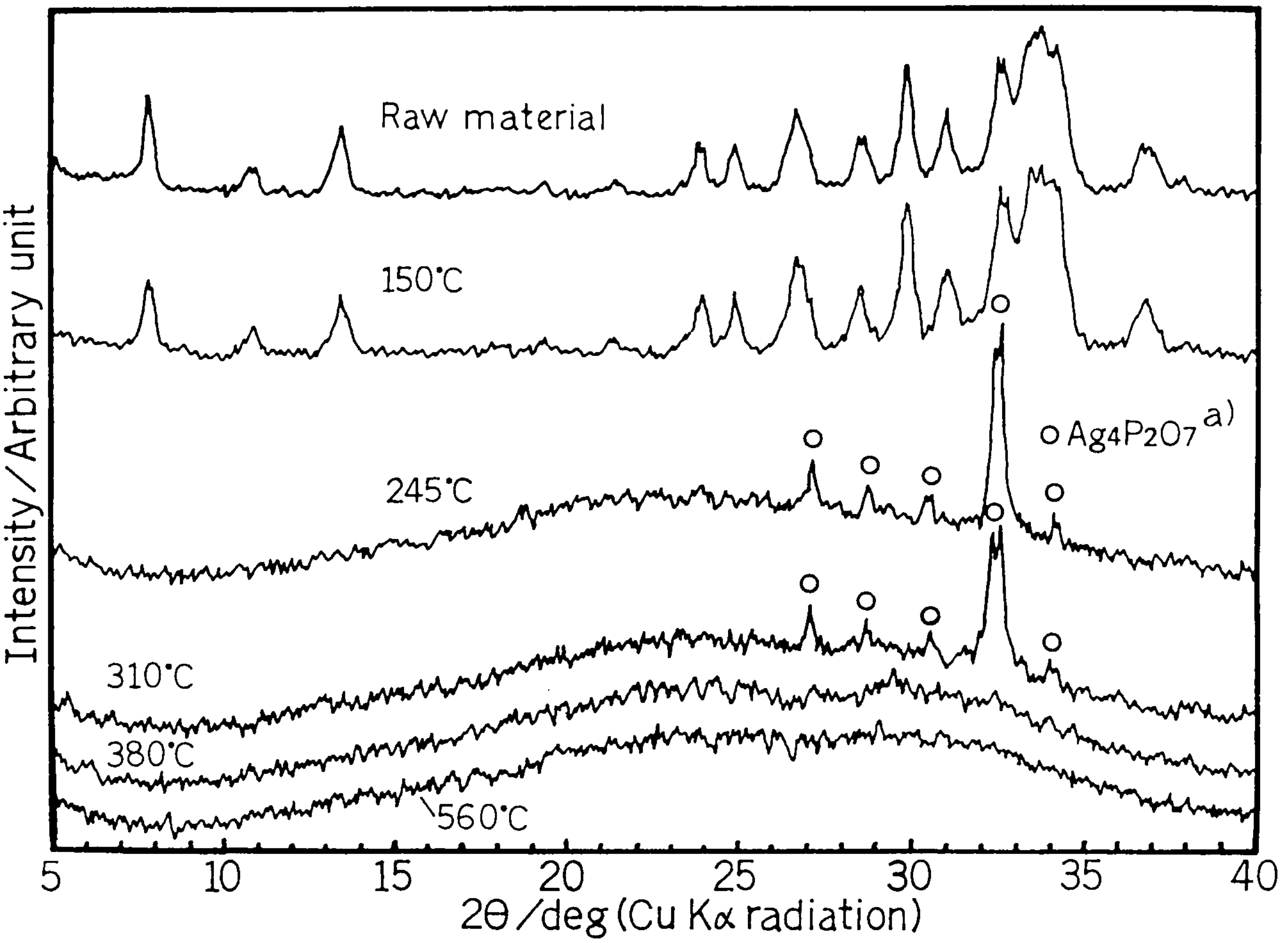

Fig. 7·3. X-Ray diffraction patterns of $Ag_4P_3O_9NH_2$ and its products heated in static air to the temperatures indicated on the DTA curve of Fig. 7·1. Heating rate: 5 K min^{-1}.

a) JCPDS Card No. 37-187.

Table 7·2. Amounts of Phosphates in the Products Obtained by Heating of $Ag_4P_3O_9NH_2$ at 5 K min^{-1} in Streams of Three Different Gases to the Temperatures Indicated on the DTA Curve of Fig. 7·1

T/°C	Atmosphere	Composition/ P %				
		Amidotri-	Mono-, di-, and tri-	Oligo-[a]	Poly-	Other[b]
150	Dry air	80.1	12.9	2.4	–	4.6
	Humid air	81.7	14.1	1.7	–	2.5
	Dry HCl	–	67.6	32.4	–	–
245	Dry air	2.8	19.8	13.9	63.5	–
	Humid air	–	63.9	36.1	–	–
	Dry HCl	–	74.8	25.2	–	–
310	Dry air	–	14.7	36.3	46.6	2.5
	Humid air	–	35.8	48.3	15.9	–
380	Dry air	–	11.5	44.3	43.3	1.0
	Humid air	–	26.0	72.2	1.9	–

a) The chain length was from four to thirteen.

b) These anions were thought to have short or middle chain structures with one or several phosphorus-nitrogen bonds.

and tri-, oligo- (chain length= 4-13), 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. They are denoted as "other " in Table 7·2.

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 7·2). Therefore the oligophosphates might have resulted from the condensation of zwitterions, as was the case for the condensation of $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ [AATP] by HCl.[2) If the condensation of oligophosphates by HCl took place through the zwitterions, SATP was expected to be condensed even at room temperature. In view of this, SATP was reacted with HCl for 1 or 3 h. Indeed, the fraction of phosphorus atoms existing then as oligophosphates was 31.9 and 26.5 % in the products, respectively. Hence the condensation of SATP to the oligophosphates by HCl must take place through the zwitterions.

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 $Ag_4P_3O_9NH_2$. The product heated to 245°C in a stream of dry air was analyzed to obtain P, 13.32; N(NH_4^+), 0.01; N(NH_2^-), 0.52 %. As shown in Table 7·2, 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. 7·4).⁶·⁷⁾ An absorption band at 1570 cm^{-1} may be assigned to the (P)-N-H deformation.⁶·⁷⁾ These absorptions are not seen in 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),⁶·⁸⁾ they are not clearly detectable in the spectrum of Fig. 7·4 B. Thus, IR spectra do not demonstrate the presence of P-N bonds in the product.

7-3-2 Thermal Condensation of Barium Amidotriphosphate $Ba_2P_3O_9NH_2\cdot 3.5H_2O$

Figure 7·5 shows TG and DTA curves of $Ba_2P_3O_9NH_2\cdot 3.5H_2O$ [BATP] measured at 5 K min^{-1}. Figure 7·6 shows 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 of

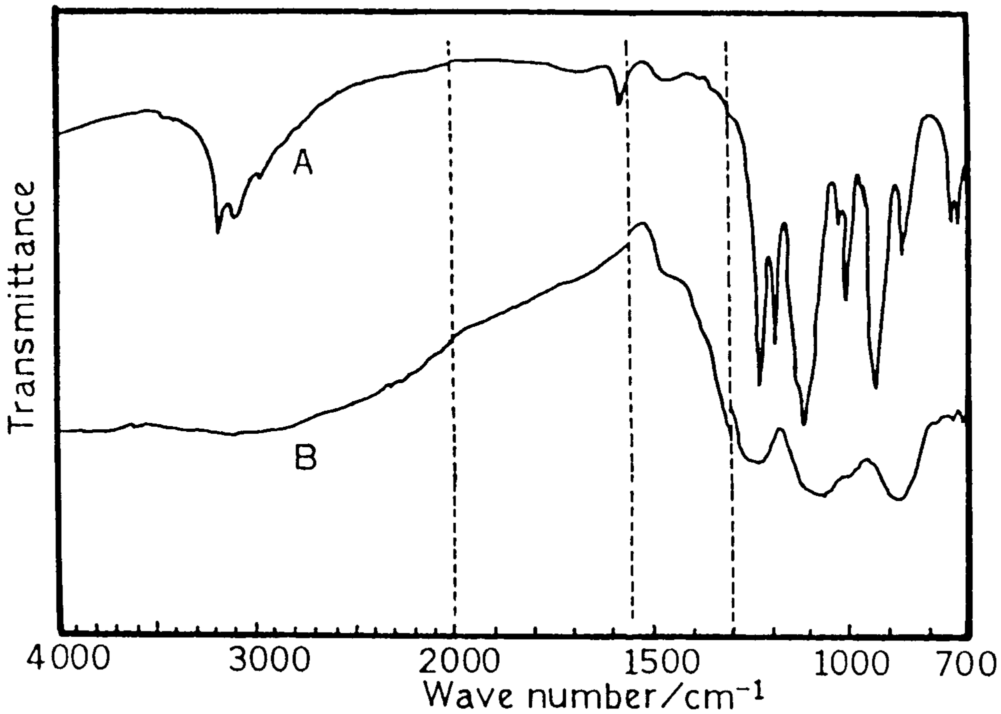

Fig. 7·4. IR spectra of $Ag_4P_3O_9NH_2$ and the product heated at 5 K min^{-1} to 245°C in a stream of dry air. The spectra for 4000-2000 cm^{-1} and for 1550-1300 cm^{-1} were obtained with mull methods by use of HCB (hexachlorobutadiene) as dispersant. The spectra for 2000-1550 cm^{-1} and for 1300-700 cm^{-1} were obtained by use of Nujol. A: $Ag_4P_3O_9NH_2$, B: product heated to 245°C.

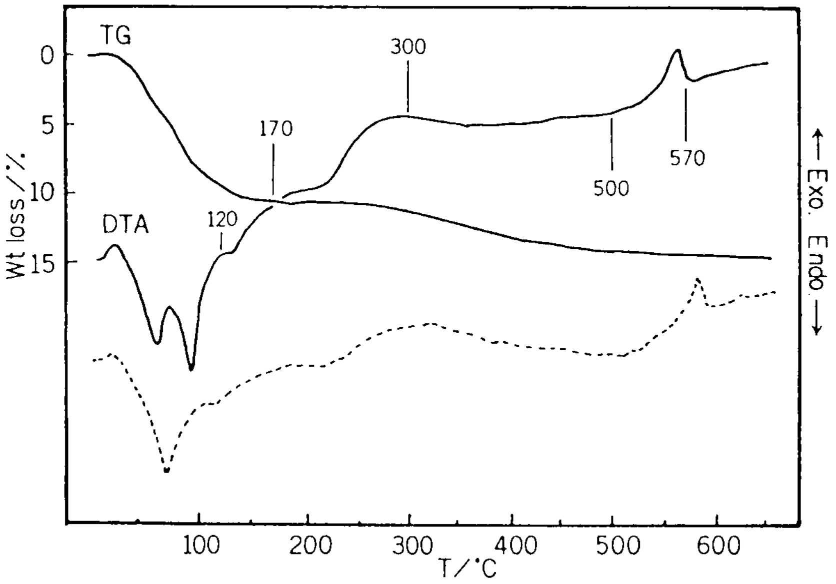

Fig. 7·5. TG and DTA curves of $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$ measured at 5 K min^{-1}. Solid line(———): TG and DTA measured in static air, dashed line (---): DTA measured in a stream of dry air at 50 cm^3 min^{-1}.

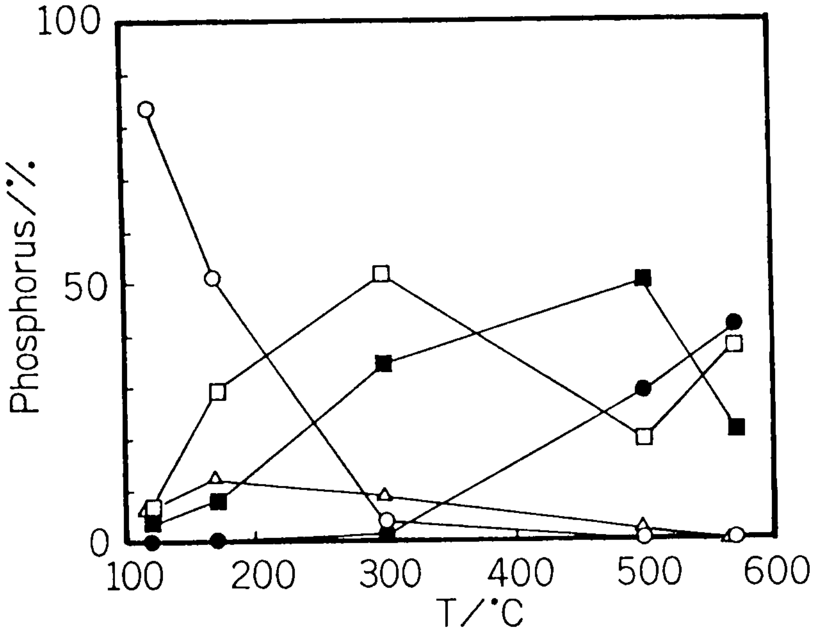

Fig. 7·6. Amounts of phosphates in the products obtained by heating of $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$ in static air to the temperatures indicated on the DTA curve of Fig. 7·5. Heating rate: 5 K min^{-1}. ○ : Amidotri-, ● : poly-, □ : mono-, di-, and tri-, ■ : oligo- (chain length =4-11), △ : other (these phosphates were thought to have short or middle chain length with one or several phosphorus-nitrogen bonds).

BATP in static air to the temperatures indicated on the DTA curve of Fig. 7·5. 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(P)-nitrogen(N) bonds. They are also plotted in a group in Fig. 7·6 and expressed as "other."

Figure 7·7 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 ions.8) Therefore, the product heated to 170°C contained ammonium ions, which must have been formed from amino groups. The spectrum of BATP shows a small absorption at 1602 cm^{-1}. The absorption probably arose from amino groups.6, 7, 9) It disappeared on the IR spectrum of the sample heated to 300°C, which agreed with the result that amidotriphosphate ions were almost cleaved below 300°C (see Fig. 7·6).

BATP was heated at 5 K min^{-1} to the temperatures indicated on the DTA curve of Fig. 7·5 in three different atmospheres. Table 7·3 shows the percentage of phosphorus atoms present as the respective phosphates in the thermal products. Below 170°C, a large portion of BATP was hydrolyzed by hydrogen chloride to mono-, di-, and

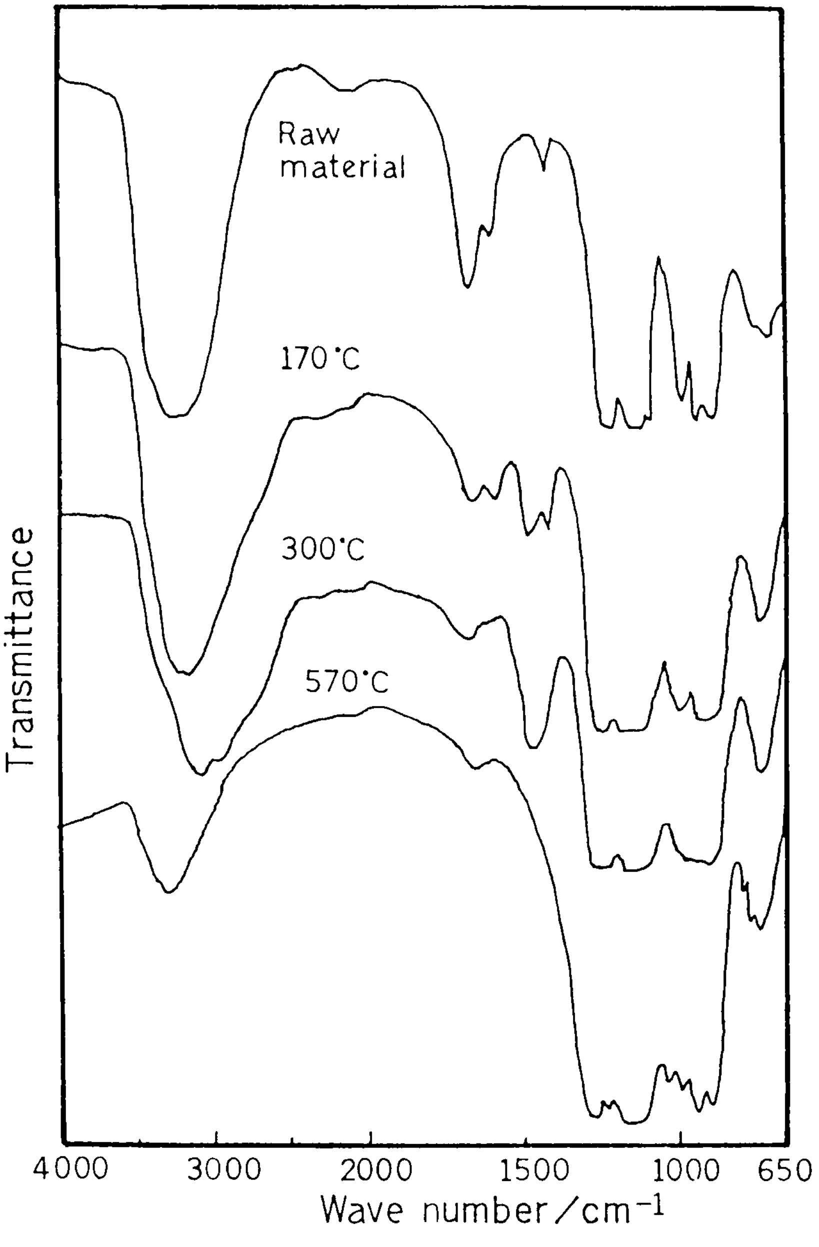

Fig. 7·7. IR spectra of $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$ and its products heated at 5 K min^{-1} to 170, 300, and 570°C in static air.

Table 7·3. Amounts of Phosphates in the Products Obtained by Heating of $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$ at 5 K min^{-1} in Three Different Gases to the Temperatures Indicated on the DTA Curve of Fig. 7·5

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

triphosphates. Although BATP did not seem to produce the zwitterions by an action of hydrogen chloride, perhaps, the zwitterions formed might immediately react with its water of crystallization.

7-4 Conclusion

Thermal decomposition and condensation of silver amidotriphosphate $Ag_4P_3O_9NH_2$ [SATP] and barium amidotriphosphate $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$ [BATP] were investigated. SATP and BATP were heated at 5 K min^{-1} mainly in streams of dry air, humid air, and dry hydrogen chloride.

SATP remained almost undecomposed up to 150°C in static air. It was partially condensed to oligophosphates (chain length =4-13) by hydrogen chloride even at room temperature, which was considered to proceed through zwitterions. When SATP heated to 245°C in a stream of dry air, the product was mainly composed of polyphosphates which contained some phosphorus-nitrogen bonds.

A large portion of BATP was hydrolyzed by hydrogen chloride below 170°C. Perhaps, the hydrolysis might indicate that the zwitterions formed reacted with the water of crystallization.

7-5 References

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2) A. Takenaka, J. Ooe, I. Motooka, and H. Nariai, Bull. Chem. Soc. Jpn., 64, 2700 (1991).

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7) K. Nakanishi, "Sekigai-sen-kyushu-spekutoru, Teisei To Enshu," Nankodo, Tokyo (1960), Chap. 3.

8) D. E. C. Corbridge and E. J. Lowe, J. Chem. Soc., 1954, 493.

9) E. Steger, Z. Elektrochem., 61, 1004 (1957).

Chapter 8 Summary

Some of the inorganic condensed phosphates can be dissolved with little decomposition in water or aqueous solutions. Therefore, they are expected to be an available example for studies on the formation of so-called "inorganic polymers." This thesis demonstrates the thermal behavior of several inorganic phosphates containing nitrogen as ammonium ions or amino groups. Changing of atmosphere was available for this work.

Chapter 1 shows, at first, the introduction to the classification, structures, and analyses of inorganic phosphates. The studies on the phosphates having ammonium ions are also introduced. And inorganic phosphates with phosphorus-nitrogen bonds are shown regarding with their classification, reaction, and so forth.

Chapters 2 - 7 show the thermal behavior of inorganic phosphates which contain nitrogen atoms as ammonium ions or amino groups. Condensation and polymerization of these phosphates can be classified to the following four types:

I Condensation

$NH_4H_2PO_4$ [MAP], $(NH_4)_2HPO_4$ [DAP], and $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$ [NZHP] were condensed to chain phosphates. $(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$ [NMHP] was at first condensed to chain phosphates, and finally changed to magnesium cyclo-tetraphosphate $Mg_2P_4O_{12}$. The condensation of MAP, DAP, NMHP was not appreciably affected by humidity, while that of NZHP was partially affected by humidity.

II Hydrolysis and subsequent condensation

Ammonium strontium cyclo-hexaphosphate $Sr_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ [SrP_{6m}] and ammonium copper(II) cyclo-hexaphosphate $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$ [CuP_{6m}] were hydrolyzed by the water of crystallization to oligophosphates (chain length $n = 1$-6). Therefore, polyphosphates ($n \geqq 7$) were probably formed through condensation of the oligophosphates.

III Radical polymerization

Ammonium cyclo-hexaphosphate $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$ [P_{6m}] and ammonium cyclo-tetraphosphate $(NH_4)_4P_4O_{12}$ [P_{4m}] were converted to long-chain ammonium polyphosphates.
The rings of P_{6m} and P_{4m} were cleaved independent of humidity exsisting in atomsphere. The polyphosphates were thought to be formed through a polymerization of oligophosphate radicals.

Ammonium calcium cyclo-hexaphosphate $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ [CaP_{6m}] and ammonium strontium cyclo-triphosphate $Sr(NH_4)P_3O_9\cdot 3H_2O$ [SrP_{3m}] lost the water of crystallization without the cleavage of their ring ions. CaP_{6m} and some of SrP_{3m} were changed to polyphosphates($n \geqq 7$ or 4, respectively), which was thought to take place through a radical polymerization. A part of ammonium cyclo-tetraphosphate $Sr(NH_4)_2P_4O_{12}$ [SrP_{4m}] was directly converted to polyphosphates ($n \geqq 5$). The conversion might take place through a radical polymerization.

Ⅳ Condensation through zwitterions

Ammonium amidotriphosphate $(NH_4)_4P_3O_9NH_2 \cdot H_2O$ [AATP] was condensed to cyclo-tri-, oligo- (n=4-12), and polyphosphates through a zwitterion. Except for in gaseous hydrogen chloride, AATP was finally changed to ammonium polyphosphate which contained some phosphorus-nitrogen bonds. At lower temperatures, the formation of the cyclo-tri-, oligo-, and polyphosphates was accelerated by hydrogen chloride.

Silver amidotriphosphate $Ag_4P_3O_9NH_2$ [SATP] was partially condensed to oligophosphates (n=4-13) by hydrogen chloride at room temperature. It was attributed to the formation of the zwitterions. A large portion of barium amidotriphosphate $Ba_2P_3O_9NH_2 \cdot 3.5H_2O$ [BATP] was hydrolyzed by hydrogen chloride at lower temperatures. Perhaps, it might indicate that the zwitterions formed immediately reacted with the water of crystallization.

Chapter 8 describes the summary.

The present author also expects that this thesis will be available for the development of new inorganic phosphate materials.

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I am deeply indepted to Dr. Makoto Hattori, President of Yonago National College of Technology, and to the members of the Department of Industrial Chemistry of that college for their encouragement and support during the course of this work. I also wish to express my thanks to the graduates of my laboratory of Yonago National College of Technology for their assistance in carrying out the experiments on this work.

LIST OF PUBLICATIONS

(1) The Thermal Decomposition of Ammonium cyclo-Hexaphosphate $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$ and Ammonium cyclo-Tetraphosphate $(NH_4)_4P_4O_{12}$; A. Takenaka, I. Motooka, and H. Nariai, Bull. Chem. Soc. Jpn., <u>60</u>, 4299 (1987).

(2) The Thermal Decomposition of Ammonium Strontium cyclo-Tri-, cyclo-Tetra-, and cyclo-Hexaphosphates; A. Takenaka, I. Motooka, and H. Nariai, Bull. Chem. Soc. Jpn., <u>62</u>, 2819 (1989).

(3) Thermal Decomposition of Ammonium Copper(II) cyclo-Hexaphosphate $Cu_2(NH_4)_2P_6O_{18}\cdot 8.5H_2O$ and Ammonium Calcium cyclo-Hexaphosphate $Ca_2(NH_4)_2P_6O_{18}\cdot 7H_2O$; A. Takenaka, H. Kobayashi, K. Tsuchie, I. Motooka, and H. Nariai, Bull. Chem. Soc. Jpn., <u>62</u>, 3808 (1989).

(4) The Thermal Decomposition of Ammonium Zinc Trihydrogenbis(phosphate) Monohydrate $(NH_4)ZnH_3(PO_4)_2\cdot H_2O$; A. Takenaka, T. Hieda, K. Kimura, I. Motooka, and H. Nariai, Bull. Chem. Soc. Jpn., <u>63</u>, 964 (1990).

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(8) Thermal Decomposition of Silver Amidotriphosphate $Ag_4P_3O_9NH_2$; A. Takenaka, I. Motooka, and H. Nariai, Bull. Chem. Soc. Jpn., 65, 1985 (1992).

(9) Thermal Condensation of Ammonium Dihydrogenphosphate $NH_4H_2PO_4$ and Diammonium Hydrogenphosphate $(NH_4)_2HPO_4$; Yonago Kogyo-koto-senmon-gakko Kenkyu-hokoku, in preparing.