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The Thermal Decomposition of Ammonium Strontium *cyclo*-Tri-, *cyclo*-Tetra-, and *cyclo*-Hexaphosphate

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Ammonium strontium *cyclo*-triphosphate $Sr(NH_4)P_3O_9\cdot 3H_2O$ [P_{3m}], *cyclo*-tetraphosphate $Sr(NH_4)_2P_4O_{12}$ [P_{4m}], and *cyclo*-hexaphosphate $Sr_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ [P_{6m}] were prepared by a wet method. The thermal decomposition of the *cyclo*-phosphates was investigated by means of TG-DTA, HPLC-FIA, X-ray analysis, and IR spectrometry. Streams of humid air and dry nitrogen gas were used to clarify the effect of humidity on the pyrolysis. The decomposition of the ring structure of P_{3m} and P_{4m} was accompanied by the elimination of ammonia. Although P_{6m} lost some of the waters of crystallization without any change in the structure, the ring was cleaved by the release of the other waters of crystallization. Regardless of the *cyclo*-phosphates, the final crystalline product was β-$Sr(PO_3)_2$, with a long-chain anion. The formation of β-$Sr(PO_3)_2$ was facilitated by water vapor in the cases of P_{3m} and P_{6m}. Unlike the pyrolysis of $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$ and $(NH_4)_4P_4O_{12}$, it was unlikely that P_{3m}, P_{4m}, and P_{6m} were decomposed to produce oligophosphate radicals. They were probably hydrolyzed to oligophosphates; then, polyphosphates were formed by the condensation of the oligophosphates.

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.[1–7] Moreover, it is known that the valence and the radius of the constituent metal ion also affect the structures of condensed phosphates.[8]

We reported in a previous paper[9] that ammonium *cyclo*-tetra- and *cyclo*-hexaphosphates decomposed to produce ammonium polyphosphate through some lower-condensed phosphate radicals. If such a mechanism as a radical decomposition-polymerization depends on the radius of the constituent cation, it is of interest to study the thermal decomposition of ammonium metal(II) *cyclo*-phosphate, prepared by replacing the ammonium ion of the ammonium *cyclo*-phosphates with a bivalent metal ion having a radius close to that of the ammonium ion.

Though the strontium ion has a radius somewhat less than that of the ammonium ion,[10] an attempt to produce ammonium strontium *cyclo*-hexaphosphate (P_{6m}) in solution was successful. However, we could not prepare ammonium barium (which has a radius[10] close to that of the ammonium ion) *cyclo*-hexaphosphate by a wet method. Therefore, we chose strontium as the metal ion to substitute for the ammonium ion.

Durif et al. prepared ammonium strontium *cyclo*-tetraphosphate by a solid-state reaction, and then investigated it crystallographically.[11] Ammonium strontium *cyclo*-triphosphate, synthesized through a solid-state reaction, was studied by means of IR spectroscopy by Serazetdinov et al.[12] However, ammonium strontium *cyclo*-hexaphosphate has not yet been reported. The purpose of this work is to study the thermal decomposition of P_{6m}, in connection with the effect of humidity in the atmosphere, as well as the thermal decompositions of ammonium strontium *cyclo*-tri- (P_{3m}) and *cyclo*-tetraphosphate (P_{4m}), both prepared by the wet method.

Experimental

Chemicals. Guaranteed-grade reagents were used unless otherwise stated.

Determination of Strontium, Nitrogen, Phosphorus, and the Water of Crystallization. The strontium was determined by means of a replacement titration technique, in which Mg-EDTA and Eriochrome Black T(EBT) were employed.[13] The nitrogen content was obtained by means of an ammonia-distillation method.[14]

The strontium ions were precipitated as strontium oxalate[15] or removed by the use of a cation-exchange resin, Amberlite IR-120B.[16] Then, phosphates were hydrolyzed with diluted hydrochloric acid.[17] The resultant phosphates were determined colorimetrically.[18]

A sample was mixed with zinc oxide. The mixture was heated to a constant weight at 650 °C.[19] 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.

X-Ray Diffractometry. The X-ray diffraction patterns were recorded on a Rigaku Denki Geigerflex X-ray diffractometer, RAD-IA, using nickel-filtered Cu $K\alpha$ radiation.

Thermal Analysis. About 20 mg of the sample was placed in a platinum pan. The thermal analyses (TG-DTA) were carried out at the heating rate of 2.5 °C min^{-1} on a Rigaku High-temperature-type Thermal Analyser, 8076 D1. The measurements were performed in stationary air or in a stream of dry N_2 gas at 50 cm^3 min^{-1}. The dry N_2 gas was introduced for 30 min before the measurements.

HPLC-Flow Injection Analysis (HPLC-FIA). The ratio of individual phosphates was determined according to the method in the literature.[9]

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

Thermal Decomposition. The thermal decomposition

Table 1. X-Ray Diffraction Data for Ammonium Strontium *cyclo*-Triphosphate, $Sr(NH_4)P_3O_9 \cdot 3H_2O$

d/Å	Intensity[a)]	d/Å	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.

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

d/Å	Intensity[a)]	d/Å	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.

was carried out in a way similar to that previously reported,[9)] although a stream of dry N_2 gas (50 cm^3 min^{-1}) was used instead of that of dry air.

The amount of ammonia evolved by the pyrolysis was determined as follows. The effluent gas (dry nitrogen or humid air) was introduced continuously into 30 cm^3 of a 0.01 mol dm^{-3} sulfuric acid at 50 cm^3 min^{-1}. When the furnace had reached the required temperature, the sample was taken out quickly and the gas (dry nitrogen or humid air) 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.

Preparation of Ammonium Strontium *cyclo*-Phosphates. Ammonium Strontium *cyclo*-Triphosphate Trihydrate $Sr(NH_4)P_3O_9 \cdot 3H_2O$: Twenty mmol (5.8188 g) of $(NH_4)_3P_3O_9$,[21)] prepared by means of the ammoniation of $Na_3P_3O_9 \cdot H_2O$,[22)] 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 and washed with cold water, 50% (v/v) ethanol–water, and then methanol. The product was air-dried. Found: Sr, 21.88; N, 3.33; P, 23.95; H_2O, 14.28%. Calcd for $Sr(NH_4)P_3O_9 \cdot 3H_2O$: Sr, 22.10; N, 3.53; P, 23.43; H_2O, 13.62%. The X-ray diffraction data are listed in Table 1. Ninety-three per cent of the P atoms were found by HPLC-FIA to be present as *cyclo*-$P_3O_9^{3-}$.

Ammonium Strontium *cyclo*-Tetraphosphate $Sr(NH_4)_2P_4O_{12}$: Fifteen mmol (5.82 g) of anhydrous $(NH_4)_4P_4O_{12}$,[21)] obtained from $Na_4P_4O_{12} \cdot 4H_2O$,[23)] were dissolved in 60 cm^3 of water. Fifteen-cm^3 (7.5 mmol) of the 0.5 mol dm^{-3} strontium chloride solution was then added, and the mixture was stirred. After 1 h, the precipitate was filtered off, washed, and dried as described above. At least 92% of the P atoms were in the form of *cyclo*-tetraphosphate. The X-ray diffraction pattern was in agreement with that of $Sr(NH_4)_2P_4O_{12}$, reported by Durif et al.[11)] The elemental analyses also suggested that the product was anhydrous $Sr(NH_4)_2P_4O_{12}$.

Ammonium Strontium *cyclo*-Hexaphosphate Heptahydrate $Sr_2(NH_4)_2P_6O_{18} \cdot 7H_2O$: Five mmol (3.045 g) of $(NH_4)_6P_6O_{18} \cdot 1.5H_2O$ were dissolved in 30 cm^3 of water.[9)] Then the solution was mixed with 20 cm^3 (10 mmol) of the 0.5 mol dm^{-3} strontium chloride solution. The mixture was stirred for 30 min. The precipitate was then filtered off, washed, and dried as above. Found: Sr, 21.87; N, 3.32; P, 23.03; H_2O, 15.57%. Calcd for $Sr_2(NH_4)_2P_6O_{18} \cdot 7H_2O$: Sr, 21.61; N, 3.45; P, 22.91; H_2O, 15.53%. At least 97% of the P atoms were found as *cyclo*-$P_6O_{18}^{6-}$ ions. The X-ray diffraction data are shown in Table 2.

Results and Discussion

Thermal Decomposition of Ammonium Strontium *cyclo*-Triphosphate $Sr(NH_4)P_3O_9 \cdot 3H_2O$. Figure 1 shows the thermal analyses (TG-DTA) in stationary air and in a stream of N_2 gas. Strong endothermic peaks with a weight loss appeared at 130 °C in both atmospheres. In stationary air (humid atmosphere), there was an endothermic peak at about 340 °C and an exothermic peak at about 355 °C. These peaks shifted to 360 and 390 °C respectively in a stream of dry N_2 gas (dry atmosphere).

The amount of the individual phosphate in the products obtained by heating up to the temperature indicated by arrows in Fig. 1, changed as is shown in Fig. 2. The *cyclo*-triphosphate anion of P_{3m} was not decomposed, at least not until 250 °C. Figure 3 represents the amount of ammonia evolved by heating P_{3m}, as a function of the temperature. Since ammonia

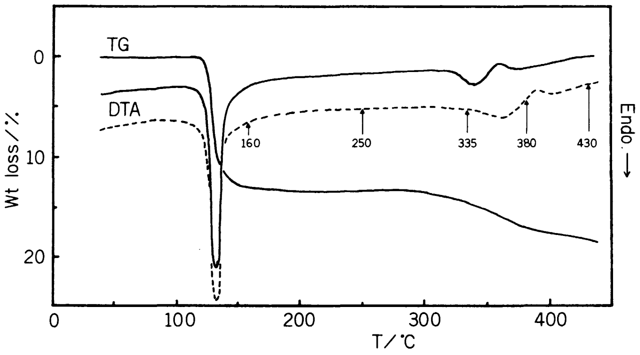

Fig. 1. Thermal analyses of $Sr(NH_4)P_3O_9 \cdot 3H_2O$ in the two different atmospheres. Solid line (—): TG and DTA measured in stationary air, dotted line (---): DTA in a stream of dry N_2 gas.

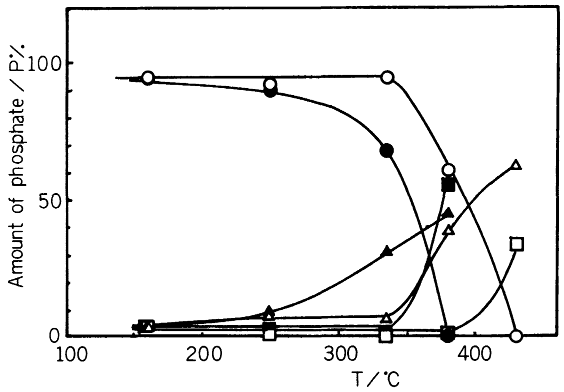

Fig. 2. Amounts of phosphates in the decomposition products of $Sr(NH_4)P_3O_9 \cdot 3H_2O$. ○ and ●: *cyclo*-Triphosphate observed in the dry and the humid atmospheres, respectively; □ and ■: oligophosphates with the chain length less than three, observed in the dry and the humid atmospheres respectively; △ and ▲: polyphosphates with the chain length more than four, in the dry and the humid atmospheres respectively.

was not evolved up to 250 °C in the dry atmosphere, the endothermic peak at 130 °C was attributed to the elimination of the water of crystallization. The corresponding TG-loss (13.1%) was close to the calculated value (13.62%).

Figure 3 shows that the water vapor accelerated the evolution of ammonia. A similar "catalytic effect" of the water vapor was reported in the reaction of calcium oxide with ammonium chloride.[24]

The product obtained by heating up to 380 °C in the dry atmosphere contained many P_{3m} anions, and the evolution of ammonia was clearly observed above 335 °C. It was supposed that not the cleavage of the P_{3m} anions but the evolution of ammonia from P_{3m} caused the endothermic peak at 360 °C.

Since the decomposition of P_{3m} was influenced by the humidity, as is shown in Fig. 2, and since neither an increase in weight nor a corresponding exothermal

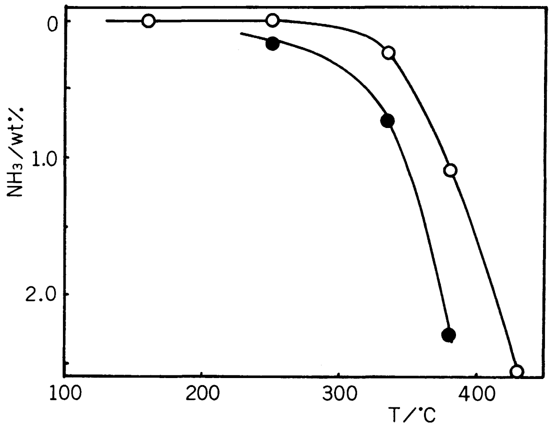

Fig. 3. Amount of ammonia evolved by heating $Sr(NH_4)P_3O_9 \cdot 3H_2O$. ○: Measured in the dry atmosphere, ●: in the humid atmosphere.

peak may be seen in Fig. 1, P_{3m} can not be thought to form oligophosphate radicals.[9] Therefore, polyphosphates with a chain length of more than four must be produced through the condensation of oligophosphates.

Considerable ammonia was lost at 380 and 430 °C in the humid and dry atmospheres respectively (Fig. 3). It is expected that the product became acidic and that a vigorous hydrolytic reaction took place at 380 and 430 °C. Obviously, the total quantities of the oligophosphates with a chain length of less than three, which were considered to be the initial hydrolytic products of P_{3m} (or perhaps the oligophosphates are produced from the polyphosphates), were greater at 380 and 430 °C (Fig. 2).

Although the products from 160 to 380 °C under dry conditions did not change X-ray diffractometrically, the sample heated up to 380 °C was somewhat amorphous. The X-ray diffraction pattern of the product obtained by heating up to 430 °C under the dry condition agreed with that of β-$Sr(PO_3)_2$ with a long-chain anion. Consequently, the exothermic peak at 390 °C (or 355 °C for the humid conditions) was attributable to the following reaction (1), although the temperature was lower than 430 °C, as has been observed by Ropp et al.:[20]

$$Sr(PO_3)_2\,[\text{amorphous}] \longrightarrow \beta\text{-}Sr(PO_3)_2\,[\text{crystalline}] \quad (1)$$

The thermal decomposition may be summarized as follows (the water of crystallization was lost at 130 °C):

$$Sr(NH_4)P_3O_9 \cdot 3H_2O \longrightarrow Sr(NH_4)P_3O_9 + 3H_2O \quad (2)$$

Above 335 °C (or 250 °C for the humid conditions), polyphosphates began to form, accompanied by the evolution of ammonia (Figs. 2 and 3). Therefore, the following reaction takes place above that temperature:

$$\mathrm{Sr(NH_4)P_3O_9} \longrightarrow \mathrm{Sr(PO_3)_2}\,[\text{amorphous}] + \mathrm{(NH_4)_{1-\mathit{n}}H_{\mathit{n}}(PO_3)}\,[\text{amorphous}] + n\mathrm{NH_3} \qquad (3)$$

where $Sr(PO_3)_2$ and $(NH_4)_{1-n}H_n(PO_3)$ are polyphosphates. They are formed through the condensation of oligophosphates. At a higher temperature (430 and 380 °C respectively), because of the loss of ammonia, the hydrolysis becomes vigorous enough to produce an appreciable amount of oligophosphates, as has been mentioned above.

Thermal Decomposition of Ammonium Strontium *cyclo*-Hexaphosphate $Sr_2(NH_4)_2P_6O_{18}\cdot 7H_2O$. Figure 4 shows the results of thermal analyses in the dry and humid atmospheres. The products, heated up to the temperatures indicated by the arrows in Fig. 4, were analyzed. Heating up to 200 °C, irrespective of the conditions, did not cause any ammonia-elimination. Consequently, the two large endothermic peaks below 130 °C and the set of endothermic peaks from 130 to 200 °C were considered to result from the elimination of the water of crystallization. The two large endothermic peaks were shifted to a higher temperature by an enhanced partial pressure of water vapor.

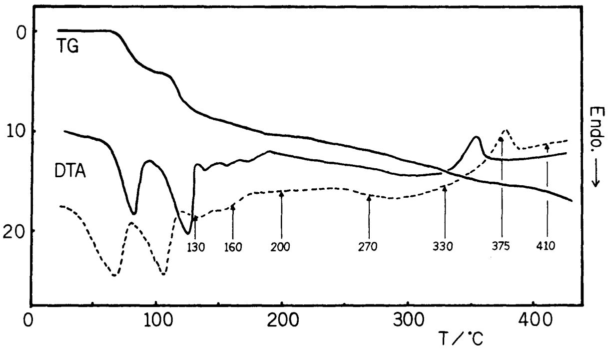

Fig. 4. TG-DTA analyses of $Sr_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ measured in the two different atmospheres. Solid line (—): TG and DTA in stationary air, dotted line (---): DTA in a stream of dry N_2 gas.

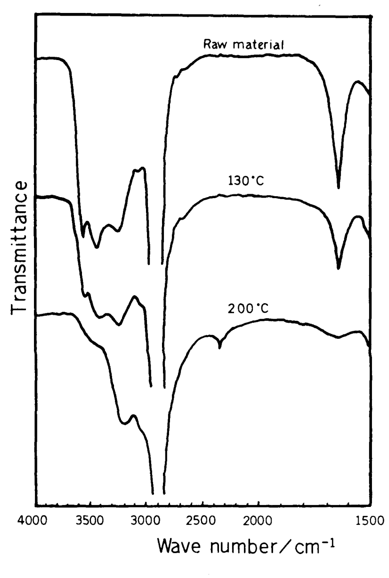

Fig. 5. IR spectra of the products at 130 and 200 °C of $Sr_2(NH_4)_2P_6O_{18}\cdot 7H_2O$ in dry atmosphere.

There were absorptions at 3560 cm^{-1} in the IR spectra of P_{6m} and the product heated up to 130 °C (Fig. 5). These absorptions (as high as 3580 cm^{-1}) were attributed to the "interstitial" water molecules, loosely held in the crystal lattice.[25] The sharp and strong band at 1640 cm^{-1} of P_{6m} was also assigned to these water molecules.[25] The "interstitial" water may be identical with the so-called "Zeolitic Water."[26,27] Since the *cyclo*-hexaphosphate anion was not cleaved (Fig. 6), and since the structure of the products did not change X-ray diffractometrically until 130 °C (though the diffraction lines became weak), the endothermic peaks below 130 °C can be regarded as being caused by the elimination of a part of the interstitial water molecules.

The decomposition of P_{6m} was found not to be dependent on the humidity, and neither an increase in weight nor the corresponding exothermic reaction was observed (Figs. 6 and 4). Thus, P_{6m} could not be presumed to produce oligophosphate radicals as in the pyrolysis of $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$.[9] Therefore, it was probably cleaved by hydrolysis. The absorptions at 1640, 3440, and 3560 cm^{-1} almost disappeared in the sample heated to 200 °C (Fig. 5). Consequently, P_{6m} was considered to lose the water of crystallization completely. The appearance of the peak at 2360 cm^{-1}, assigned to P–OH stretching,[25,28] certainly resulted from the hydrolysis.

The exothermic peak at around 375 °C in the dry atmosphere was shifted to a lower temperature (about 350 °C) in the humid atmosphere. The X-ray diffractogram showed that the phase transition from

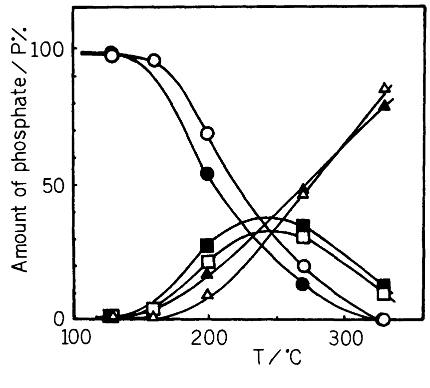

Fig. 6. Amounts of phosphates in the products of $Sr_2(NH_4)_2P_6O_{18}\cdot 7H_2O$. ○ and ●: *cyclo*-Hexaphosphate observed in the dry and the humid atmospheres, respectively; □ and ■: oligophosphates with the chain length less than six, observed in the dry and the humid atmospheres respectively; △ and ▲: polyphosphates with the chain length more than seven, in the dry and the humid atmospheres respectively.

amorphous $Sr(PO_3)_2$ to β-$Sr(PO_3)_2$ was exothermic. McGilvery and Scott reported that water vapor facilitated the crystallization of sodium triphosphate, and that water was considered to promote the diffusion of the sodium ions.5) In a similar way, the diffusion of the strontium ion in the amorphous phase, which was produced before the exothermic peak, might also be facilitated by water vapor, so that the crystallization of β-$Sr(PO_3)_2$ occurred under the humid conditions at a lower temperature.

Thermal Decomposition of Ammonium Strontium *cyclo*-Tetraphosphate $Sr(NH_4)_2P_4O_{12}$. The thermal analysis shows only the large endothermic peak at about 375 °C; this temperature was not influenced by the humidity. The endothermic peak corresponds to the elimination of ammonia from P_{4m}. The decomposition of P_{4m} was accompanied by the elimination of ammonia—analogously to the cleavage of P_{3m}.

The products above 375 °C always contained β-$Sr(PO_3)_2$. No exothermic peak caused by the transition of amorphous $Sr(PO_3)_2$ to β-$Sr(PO_3)_2$ was recognized; the endothermic peak may be supposed to conceal it.

Compared to the cases of $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$ (215 °C) and $(NH_4)_4P_4O_{12}$ (238 °C),9) the decomposition temperatures of P_{6m} (330 °C) and P_{4m} (420 °C) were heightened by the replacement of the NH_4^+ ion with the Sr^{2+} ion. The ring anions of all the ammonium strontium *cyclo*-phosphates studied (P_{3m}, P_{4m}, and P_{6m}) decomposed, accompanied by a weight loss. No corresponding exothermic peak attributable to the incorporation of water molecules, suggesting the radical formation,9) was observed in the respective thermal analysis. The decompositions of $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$ and $(NH_4)_4P_4O_{12}$ to the oligophosphate radicals were not influenced by the humidity,9) whereas the degradation of P_{3m} and P_{6m} depended on the water vapor (Figs. 2 and 6); thus, P_{3m} and P_{6m} were not supposed to bring about a radical decomposition-polymerization. On the other hand, P_{4m} decomposed irrespective of the humidity. However, its thermal analysis showed no increase in weight and no exothermic peak. Accordingly, P_{4m} also could not be proved to produce oligophosphate radicals thermally. In conclusion, the radical decomposition-polymerization of *cyclo*-phosphates probably has no definite relation to the radius of the constituent cation.

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