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

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Ammonium *cyclo*-hexaphosphate 1.5-hydrate $(NH_4)_6P_6O_{18}\cdot 1.5H_2O$ was prepared. Under conditions similar to those in the thermal analysis (TG-DTA), the hydrate was heated in an electric furnace. The atmospheres used then were streams of humid air, dried air and dry ammonia gas. The products were characterized by the X-ray diffraction method and by HPLC-flow injection analysis (HPLC-FIA). The thermal decomposition of anhydrous ammonium *cyclo*-tetraphosphate $(NH_4)_4P_4O_{12}$ was also investigated. From each ammonium *cyclo*-phosphate, very analogous ammonium polyphosphate was produced. Its formation was considered to result from the polymerization of some lower-condenced phosphate radicals, which were generated on the cleavage of the ring anions of the *cyclo*-phosphates. The radicals incorporated water molecules in the atmosphere, which causes less formation of the ammonium polyphosphate and exhibited a TG gain and an exothermal DTA break. The exotherm could be attributed theoretically to the incorporation in case of the *cyclo*-tetraphosphate. Moreover, the release of ammonia from the starting material was supposed to be a trigger for the cleavage of the ring anions.

The ammonium *cyclo*-tri- and *cyclo*-tetraphosphates have been studied in regard to several properties by many authors.[1-10] Especially Coates and Woodard summarized the preparations, stability, and X-ray diffraction data of ammonium lower-condenced phosphates containing ammonium *cyclo*-tetraphosphate, but the thermal stability of the *cyclo*-tetraphosphate was mentioned a little.[10] As with the *cyclo*-tetraphosphate, the thermal stability of the ammonium salt of *cyclo*-hexaphosphate with a twelve-membered ring anion has not been reported. Therefore, it seemed that it would be of interest to obtain detailed informations on the thermal stability of the ammonium salt of these *cyclo*-phosphates.

The purpose of the present work was to study the thermal decomposition of ammonium *cyclo*-hexaphosphate, mainly in connection with the effect of humidity in the atmosphere; its preparation was established. In addition, by comparison with that of the *cyclo*-hexaphosphate, the pyrolysis of ammonium *cyclo*-tetraphosphate was investigated more closely.

Experimental

Chemicals, and Analyses of Phosphorus and Nitrogen. Chemicals: Unless otherwise stated, guaranteed-grade reagents were used without further purification.

Analyses of Phosphorus and Nitrogen: With a HPLC-flow injection system, the total phosphorus was determined colorimetrically. The nitrogen content was obtained by means of an ammonia-distillation method.

X-Ray Diffraction Analysis. The X-ray powder diffraction patterns were measured with a Rigaku Denki diffractometer, using nickel-filtered Cu $K\alpha$ radiation.

Thermal Analysis. The thermal analyses (TG-DTA) were carried out at the rate of 2.5° min^{-1} by means of a Rigaku 8002 SD Thermal Analyser. The measurements were performed in stationary air or in a stream of dry N_2 gas at a rate of 100 cm^3 min^{-1}, which did not influence the temperatures assigned to DTA breaks. If required, an atmosphere of stationary N_2 gas was also used. It was attained by the evacuation of the furnace of the TG-DTA device, followed by the introduction of dry N_2 gas. This procedure was repeated three times.

HPLC-Flow Injection Analysis (HPLC-FIA). A JASCO TRIROTER V Liquid Chromatograph was used. The system was equipped with two injection ports called "loop-valve sampler." One loop-valve sampler, placed ahead of a column, is used for the separation and determination of phosphates. The other, for the total phosphorus analysis, is situated after the column. A polystyrene-based anion exchanger (TSK gel SAX, d_p=10 μm, Toyo Soda) was packed in the column.

The eluent was flowed through at 1.0 cm^3 min^{-1}. It was prepared from appropriate concentrations of an aq. potassium chloride soln. and an aq. 0.1% (w/v) EDTA-4Na soln. The Mo(V)-Mo(VI) reagent for the colorimetric analysis was the 10-fold-diluted aq. solution of the reagent prepared by Lucena-Conde and Prat.[11] At a flow rate of 0.8 cm^3 min^{-1} it was introduced continuously into the stream of the effluent. Then the mixed solution was heated up to 140 °C by passing it through 10 m of 2.0×0.5 mm (O.D.×I.D.) PTFE tubing in an oil bath. The heteropoly blue thus formed was measured at 830 nm in a flow cell.

Thirty-mg portions of a sample were dissolved in water and diluted to 25 cm^3. When they were dissolved inadequately or not, 1—4 cm^3 of 10% (w/w) sodium chloride aq. soln. was then added. A two-cm^3 portion of this solution was transferred into a 50-cm^3 volumetric flask to be diluted. One hundred-μl portions of it were then analyzed.

When this solution contained many polyphosphates and/or their chain length became longer, the above-mentioned technique of analyzing the solution was not enough to produce the heteropoly blue completely. Consequently, the amount of the polyphosphates was estimated at less than the true value. To prevent this, a 2-cm^3 portion of 2-mol dm^{-3} hydrochloric acid was added to a 10-cm^3 portion of the preceding HPLC-FIA sample solution, and they were mixed well. It was allowed to stand at 70 °C for 1 h, cooled to room temperature, and then neutralized with ca. 2 cm^3 of

2-mol dm^{-3} sodium hydroxide aq. soln. This solution was subsequently diluted 5-fold and then injected into the loop-valve sampler located after the column in order to determine its total phosphorus content. The amount of the polyphosphates was calculated by subtracting the amount of phosphorus of all the phosphates (except for the polyphosphates) from the total phosphorus content.

Preparation of Ammonium *cyclo*-Hexa- and Ammonium *cyclo*-Tetraphosphates. Ammonium *cyclo*-Hexaphosphate $(NH_4)_6P_6O_{18} \cdot 1.5H_2O$: Ammonium *cyclo*-hexaphosphate could be prepared from sodium *cyclo*-hexaphosphate $Na_6P_6O_{18} \cdot 6H_2O$ by means of a cation exchanger. $Na_6P_6O_{18} \cdot 6H_2O$ was obtained in a way similar to the method reported by Griffith and Buxton.[12] A cation-exchange procedure was performed in accordance with the work by Coates and Woodard.[10]

The *cyclo*-hexaphosphate anion was contained at least 98.5% as phosphorus in the product. The impurities were mainly highly-condensed phosphates. The X-ray powder diffraction pattern did not agree with that of ammonium *cyclo*-hexaphosphate monohydrate prepared by Vol'fkovich et al.[13] (Table 1). Analyses of phosphorus and nitrogen: P, 30.55; N, 13.87%. The water content could be calculated based on the phosphorus value, as the molar ratio of phosphorus to nitrogen was 1.00 : 1.00. The formula was $(NH_4)_6P_6O_{18} \cdot 1.5H_2O$. Yield: about 11 g for 15 g of $Na_6P_6O_{18} \cdot 6H_2O$.

Ammonium *cyclo*-Tetraphosphate $(NH_4)_4P_4O_{12}$: Anhydrous ammonium *cyclo*-tetraphosphate was prepared by means of a cation-exchange method similar to that used for the *cyclo*-hexaphosphate. Sodium *cyclo*-tetraphosphate tetrahydrate[14] was used as the starting material. The ammonium *cyclo*-tetraphosphate was identified X-ray diffractometrically.[10]

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

Present work		Vol'fkovich et al.	
d(A)[a]	Intensity[b]	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) Cu $K\alpha$ radiation. b) VS: Very strong, S: strong, M: medium, W: weak, VW: very weak.

Thermal-Decomposition Processes. The ammonium *cyclo*-phosphate (0.2 g) was spread on a porcelain boat in a layer less than 1 mm thick, so as to get the desired atmosphere instantly. The boat was placed in a quartz tube, which had been set in a cylindrical electric furnace (I.D.XL: 35X350 mm) beforehand. The sample was heated at the same rate (2.5° min^{-1}) as in the TG-DTA measurements. As soon as it reached at the required temperature, it was taken out and cooled to room temperature in a desiccator.

The humidity of the air entering at 50 cm^3 min^{-1} into the quartz tube was controlled by means of a Heatless Air Drier HF 200-9-30 (Nippon Pure Gas Co., Ltd.) or an Ace Constant-humidity Generator Model AHC-1 (Ace Scientific Laboratory Co., Ltd.). The amounts of water vapor in the quartz tube were nearly 0 and 1.04 mg per minute respectively. These two atmospheres should be considered to show the effect of humidity on the thermal decomposition more obviously than in the corresponding TG-DTA measurements. In addition, a stream of NH_3 gas (purity: 99.9%) was also used by introducing it directly from the cylinder at 50 cm^3 min^{-1}.

Results and Discussion

Thermal Decomposition of Ammonium *cyclo*-Hexaphosphate 1.5-Hydrate $(NH_4)_6P_6O_{18} \cdot 1.5H_2O$. The results of the thermal analyses (TG-DTA) of ammonium *cyclo*-hexaphosphate 1.5-hydrate (P_{6m}) in stationary air and in a stream of dry N_2 gas are shown in Fig. 1, (a) and (b) respectively. Three endothermic breaks — at about 180, 195 and around 300 °C—are observed in both atmospheres. Exothermal breaks are shown at 205 °C. As P_{6m} has 1.5 moles of water of crystallization and is considered to bring humidity to the atmosphere on heating, it is supposed that hardly any difference in the DTA curves is recognized. The endothermic break at around 300 °C was apparently attributable to the melting of the product.

In the N_2 gas stream, no increase in weight is found in the temperature range measured, but in the stationary air there is an increase from 195 to 205 °C (Fig. 1, (b) and (a)).

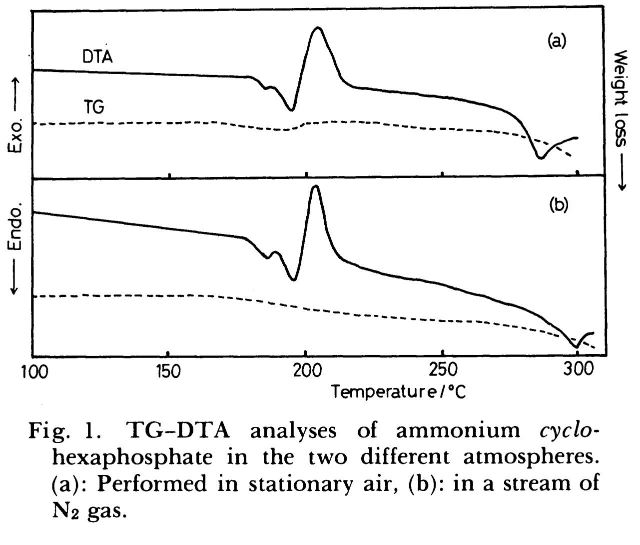


Fig. 1. TG-DTA analyses of ammonium *cyclo*-hexaphosphate in the two different atmospheres. (a): Performed in stationary air, (b): in a stream of N_2 gas.

In order to investigate the decomposition processes causing the DTA breaks in the range from 100 to 215 °C, many studies were carried out with a cylindrical electric furnace. The amount of P_{6m} and polyphosphates in the samples heated up to 100, 150, 180, 195, 205, and 215 °C are illustrated in Fig. 2.

Thilo and Grunze reported that the tetra- and octaphosphates were formed selectively in the course of the thermal decomposition of lithium *cyclo*-tetraphosphate tetrahydrate. They supposed that their formation was attributable to the polymerization of the "radicals," which had been produced thermally.[1] The same paper described that the radicals incorporated water molecules from the atmosphere. As the decomposition of P_{6m} is scarcely affected by the humidity (Fig. 2), the P_{6m} rings do not disappear upon hydrolysis, but decompose to "radicals." The TG-increase from 195 to 205 °C is probably due to the incorporation of water molecules. The polyphosphates form less in the presence of water vapor than in its absence (Fig. 2). Figure 3 shows that the total amount of oligophosphates is larger under the humid condition than under the dried condition. Thus, the incorporation of water molecules inhibits the polymerization of the radicals.

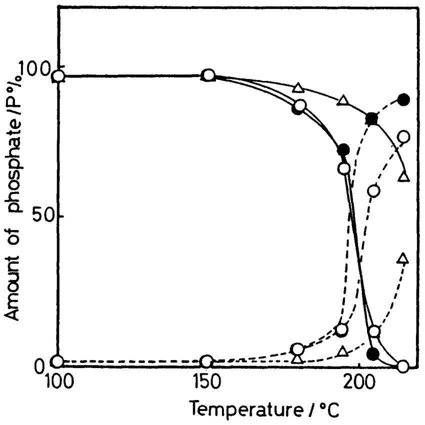


Fig. 2. Amounts of the *cyclo*-hexaphosphate and the polyphosphates in the products heated up to the required temperatures in the three different atmospheres. ——: *cyclo*-Hexaphosphate, ----: polyphosphates, O: in a stream of humid air, ●: in a stream of dried air, Δ: in a stream of NH_3 gas.

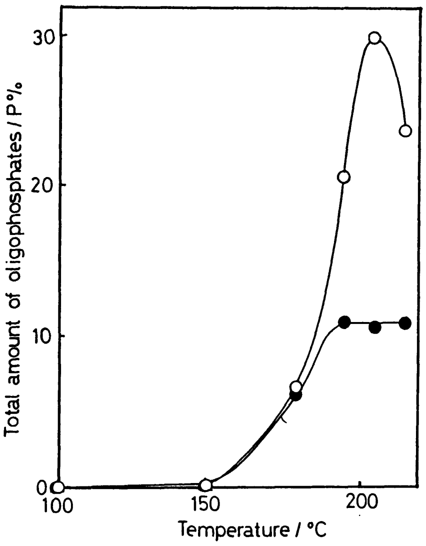


Fig. 3. Total amounts of oligophosphates in the humid and the dried atmospheres. O: In a stream of humid air, ●: in a stream of dried air.

Among the oligophosphates contained in the samples, di-(P_2) and monophosphate(P_1) were more abundant than the others. This shows that the P_{6m} ring decomposed into three or six parts to produce the P_2 or the P_1 radicals.

At any rate, the endothermic break at 195 °C, regardless of humidity, probably corresponds to the cleavage of the P_{6m} rings. The following exothermal break at 205 °C must be caused by the bonding of the water molecules with the radicals (see the next subsection, for an analogous exothermal reaction is explained there thermodynamically).

In a stream of NH_3 gas, P_{6m} remained more abundantly than in the humid and dried atmospheres (Fig. 2). The departure of ammonia molecules from P_{6m} is thought to be the trigger for the cleavage of P_{6m} to the P_1 and the P_2 radicals.

Thermal Decomposition of Ammonium *cyclo*-Tetraphosphate $(NH_4)_4P_4O_{12}$. Since the ammonium *cyclo*-tetraphosphate (P_{4m}) used was an anhydrous salt, it was expected that the humidity effect on the thermal decomposition would be more obvious than in the case of *cyclo*-hexaphosphate(P_{6m}), which has 1.5 moles of water of crystallization.

Thermal analyses of P_{4m} were carried out in three atmospheres: in stationary air, in a stream of dry N_2 gas, and in stationary dry N_2 gas. Contrary to the case

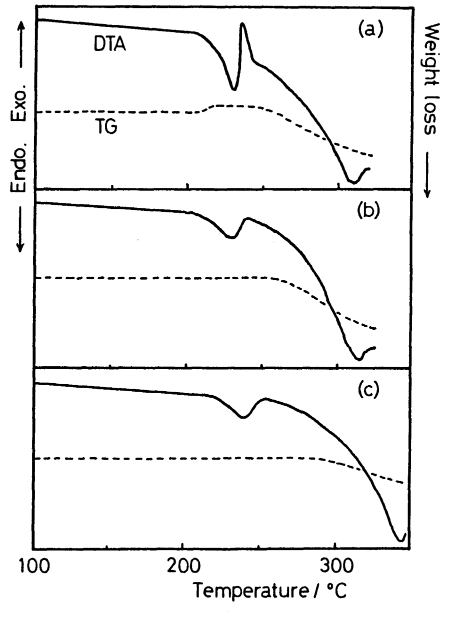


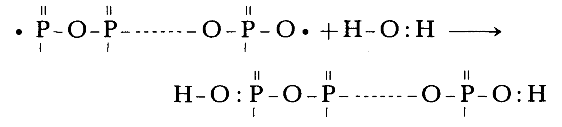
Fig. 4. TG–DTA analyses of ammonium *cyclo*-tetraphosphate in the three different atmospheres. (a): Performed in stationary air, (b): in a stream of N_2 gas, (c): in stationary N_2 gas.

of P_{6m}, the DTA curve in the humid atmosphere has an exothermal break at 238 °C (Fig. 4, (a)), while that in the dried atmosphere has no exotherm (Fig. 4, (b)). These DTA curves show endothermic processes at 233 and 230 °C respectively. On the DTA chart measured in the stationary dry N_2 gas, there is an endothermic break at the rather high temperature of 240 °C (Fig. 4, (c)).

P_{4m} was also heated up to 150, 200, 233, 238, and 244 °C (and sometimes 258 °C as well) in a cylindrical electric furnace. Figure 5 shows that the amount of P_{4m} in the products decreases rapidly between 200 and 238 °C in the humid and dried atmospheres. The decrease is independent of the humidity in the atmosphere. Therefore, the P_{4m} rings are not hydrolyzed.

If the polyphosphates are produced by the condensation of acidic ammonium oligophosphates, the thermogravimetric analysis will show a weight loss. However, in the dried atmosphere, the TG curve indicates no weight change (Fig. 4, (b)), and the amount of the polyphosphates increases rapidly in the range from 200 to 238 °C (Fig. 5). Consequently, the polyphosphates do not arise by the condensation, but are produced by the polymerization of the "radicals" which result from the cleavage of P_{4m}.

Only in the humid atmosphere is there an exothermal break, as is shown in Fig. 4, (a). Corresponding to this exotherm, a TG gain is observed. Therefore the exotherm at 238 °C may be attributed to the binding of the radicals with water molecules. The heat of the formation of the phosphate molecules brought about by the binding of the radicals with water molecules (ΔH; kJ mol^{-1}) can be calculated by means of the following scheme. In this scheme, ΔH should be



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

obtained by means of this equation; $\Delta H = (\text{O-H})_{\text{H}_2\text{O}} + [-\{(\text{O-H})+(\text{P-O})\}] \approx -(\text{P-O})$, where $(\text{O-H})_{\text{H}_2\text{O}}$ is the oxygen-hydrogen bond energy of water molecules, (O-H) is the oxygen-hydrogen bond energy of the phosphates produced, and (P-O) is the phosphorus-oxygen bond energy of the phosphates ca. 359.8 kJ mol^{-1}.[15] Consequently, the heat of the formation of the phosphates (ΔH) is the negative value of −359.8 kJ mol^{-1}. This value accounts for the exothermal reaction at 238 °C very well.

The radicals are considered to combine with water molecules in the atmosphere, so the water molecules can be expected to inhibit the radical polymerization. Practically, indeed, compared with the dried atmosphere, in the humid atmosphere the amount of the polyphosphates was poor, as is indicated in Fig. 5, while the total amount of the oligophosphates was rich.

Figure 6 represents the amount of the individual oligophosphate plotted against its chain length. Under the humid condition, mono-(P_1) and diphosphate (P_2) are present in larger quantities (Fig. 6, (a)). Only P_1 is detected in the dried atmosphere (Fig. 6, (b)). As a trace of water vapor may be found in the dried atmosphere, P_1 is thought to result from the P_1 radicals, trapping of the water molecules. Accordingly, it is concluded that the P_{4m} ring decomposes into four parts, thus producing the P_1 radicals, or perhaps into two parts, thus producing the P_2 radicals, as is revealed by the abundance of P_2 (Fig. 6, (a)). Moreover, the decomposition of the P_{4m} rings seems to cause the endothermic break at about 230 °C.

In a stream of ammonia gas, P_{4m} was very stable in the range from 150 to 244 °C (Fig. 5). The release of ammonia from the starting material of P_{4m}, must be a

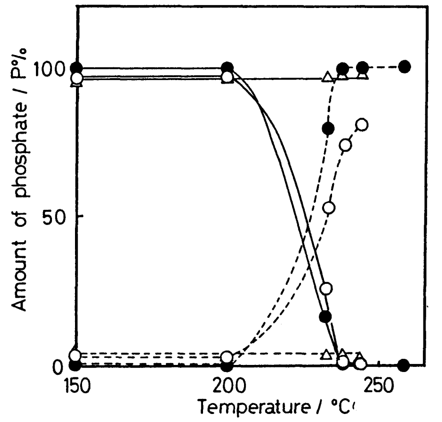


Fig. 5. Amounts of the *cyclo*-tetraphosphate and the polyphosphates in the products heated in the three different atmospheres. ——: *cyclo*-Tetraphosphate, ----: polyphosphates, ○: in a stream of humid air, ●: in a stream of dried air, △: in a stream of NH_3 gas.

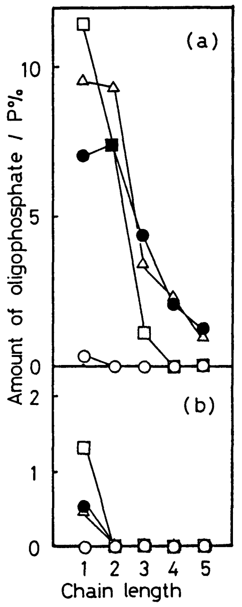


Fig. 6. Amount of the individual oligophosphate in the products. (a): In a stream of humid air, (b): in a stream of dried air, ○: 200 °C, ●: 233 °C, △: 238 °C, □: 244 °C.

Table 2. X-Ray Diffraction Data for Ammonium Polyphosphate 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)[a]	Intensity[b]	*d*(A)[a]	Intensity[b]
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	VM	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) Cu *Kα* radiation. b) VS: Very strong, S: strong, M: medium, W: very weak.

"trigger" for the cleavage of the P_{4m} anions, accompanied by the exotherm at about 230 °C. The shift of the exotherm to a higher temperature in the stationary N_2 gas (Fig. 5, (c)) is attributable to an enhanced partial pressure of ammonia by evacuation and may be thought to prove the "trigger reaction."

Characterization of the Polyphosphate. The X-ray diffraction data for the decomposition products of P_{6m} and P_{4m} are indicated in Table 2. The diffraction lines of the respective products are similar to each other, except for those of the 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, we observed that there was always a water-insoluble material, which must be ammonium polyphosphate,[16] in the product of P_{4m} heated above 233 °C.

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