Thermal Decomposition of Ammonium Amidotriphosphate $(NH_4)_4P_3O_9NH_2{\cdot}H_2O$

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Ammonium amidotriphosphate $(NH_4)_4P_3O_9NH_2{\cdot}H_2O$ 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. Oligophosphates (chain length=4—12) were more abundant in samples heated to 145 and 180 °C in hydrogen chloride. The *cyclo*-tri- and oligophosphates were most probably formed via a zwitterion form. When heated to 240 °C, the samples were changed to ammonium polyphosphates. Elemental analyses for the sample heated to 240 °C in dry air showed that the ammonium polyphosphates formed contained some phosphorus–nitrogen bonds. Isothermal experiments at 180 °C in dry air indicated that the new phase of ammonium *cyclo*-triphosphate was converted completely to ammonium polyphosphates.

Inorganic phosphates with phosphorus–nitrogen bonds are potential candidates as a new class of fertilizer. They attracted our attention also as flame-proofing materials, and probably in view of this several reports have been published regarding their thermal decomposition.[1–11] Especially, amidophosphates have been studied by many workers.[2–11]

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*-triphosphate in aqueous solutions.[12–14] Quimby and Flautt,[12] and Feldmann and Thilo[13] also reported that amidotriphophate ions cyclized again to *cyclo*-triphosphate ions in acidic solutions. We have been interested in whether the cyclization also takes place or not in solid state. Whether phosphorus–nitrogen phosphates are produced or not in such a solid-state reaction is also of interest.

In general, thermal decomposition of inorganic phosphates depends on temperature and time of heating, cooling of the melts, and atmosphere of heating.[15]

We studied the thermal decomposition of some inorganic phosphates with regard to the effect of atmosphere, especially of humidity.[16,17] As an extension thermal decomposition of ammonium amidotriphosphate $(NH_4)_4P_3O_9NH_2{\cdot}H_2O$ was studied in the present work in four different atmospheres: dry air, humid air (relative humidity 90% at 25 °C), ammonia, and dry HCl. The products were analyzed by HPLC-FIA, X-ray diffractometry, and IR spectrophotometry as in the preceding work.[16,17]

Experimental

Preparation of Ammonium Amidotriphosphate $(NH_4)_4P_3O_9NH_2{\cdot}H_2O$. Ammonium amidotriphosphate was prepared by ammonolysis of ammonium *cyclo*-triphosphate.[13] The latter was obtained according to Ref. 18, but the X-ray diffraction data were different from those in Ref. 18. The present data are listed in Table 1. Analyses of the new ammonium *cyclo*-triphosphate clarified that it was an anhydrous form and was pure. After allowing the sample to stand for about six months below room temperature, the X-ray diffraction lines changed to those reported in Ref. 18 while several of the original lines remained. The *cyclo*-triphosphate ions were not decomposed. The ammonium *cyclo*-triphosphate thus formed was heated again at 5 K min^{-1} to 300 °C in a stream of ammonia. Its *cyclo*-triphosphate ions were not decomposed and the X-ray diffraction data agreed completely with those of the new ammonium *cyclo*-triphosphate. These indicate that the new phase of ammonium *cyclo*-triphosphate, in line with the data in Table 1, is its high-temperature phase.

HPLC-FIA data for several $(NH_4)_4P_3O_9NH_2{\cdot}H_2O$ samples thus 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%. Calcd for $(NH_4)_4P_3O_9NH_2{\cdot}$

Table 1. X-Ray Diffraction Data for a New Phase of Ammonium *cyclo*-Triphosphate $(NH_4)_3P_3O_9$

d/Å	Intensity[a]	d/Å	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.

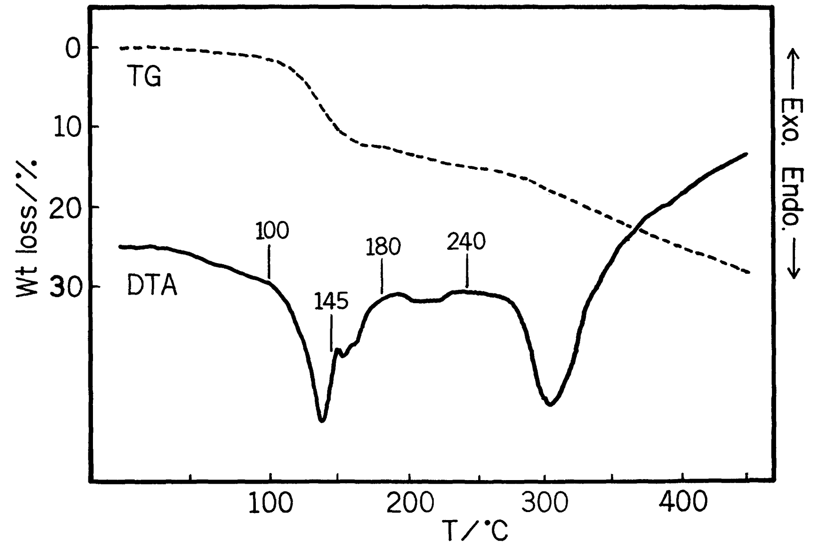


Fig. 1. Thermal analytical curve for $(NH_4)_4P_3O_9NH_2\cdot H_2O$ in stationary air. Heating rate: 5 K min^{-1}

H_2O: P, 27.07; N(NH_4^+), 16.33; N(NH_2^-), 4.08%. The ammonium amidotriphosphate sample used throughout thermal decomposition experiments was pure.

Thermal Decomposition. Thermal decomposition experiments were carried out in a cylindrical electric furnace, by means of dynamic heating methods (heating rate: 5 K min^{-1}) or isothermal methods. The effect of atmosphere on the decomposition was examined by the use of a stream of dry air (50 cm^3 min^{-1}) and humid air (50 cm^3 min^{-1}). The former was obtained by passing air through molecular sieves, and the latter with a humidity generator give 90% of relative humidity at 25 °C.[17] A stream of ammonia (purity: 99.9%) was also used by introducing it directly from a cylinder. Hydrogen chloride was prepared by adding concentrated sulfuric acid to ammonium chloride, then dried with concentrated sulfuric acid. Before heating, the cylindrical furnace was purged with these gases of about twice its volume.

Analyses. Total nitrogen was determined by the Kjeldahl method. Nitrogen present as ammonium ions, N(NH_4^+), was determined by an ammonia-distillation method without decomposition by use of concentrated sulfuric acid. Nitrogen present as amino or imino groups, N(NH_2^-), was calculated by subtracting the N(NH_4^+) from the total nitrogen.[13] Thermal analyses (TG-DTA) were carried out in stationary air at a heating rate of 5 K min^{-1}. The composition of phosphates was determined by an HPLC-FIA method. A 10 mg portion of a sample was dissolved in 2 cm^3 of 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.[12–14] The solution was diluted to 500 cm^3 with distilled water, and was immediately analyzed with an HPLC-FIA system. Total phosphorus was determined colorimetrically with the HPLC-FIA system.[16] IR spectra were recorded on a JASCO IR spectrophotometer IR-700 by a KBr disc method. Other procedures were essentially the same as those described previously.[16,17]

Results and Discussion

Thermal Decomposition in Stationary Air. Figure 1 shows a result of thermal analyses (TG-DTA) in stationary air. Four endothermic peaks are seen at about 140, 155, 210, and 300 °C. The peak at 300 °C reflects the melting of sample.

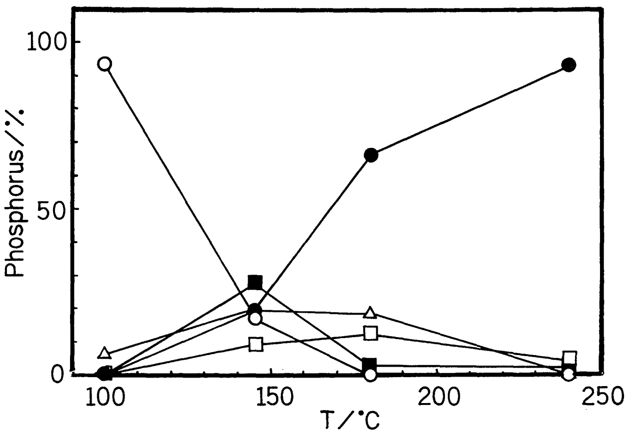


Fig. 2. Changes in amounts of phosphates in the products decomposed at 5 K min^{-1} in stationary air. ○: amidotri-, ●: poly-, □: mono-, di-, and tri-, ■: oligo- (chain length=4—11), △: *cyclo*-tri-.

Figure 2 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 to the temperatures indicated on the DTA curve in Fig. 1. 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 2. Since these amount to only less than ca. 4% as phosphorus atoms, they are neglected in Fig. 2.

Release of the water of crystallization from $(NH_4)_4P_3O_9NH_2\cdot H_2O$ 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.

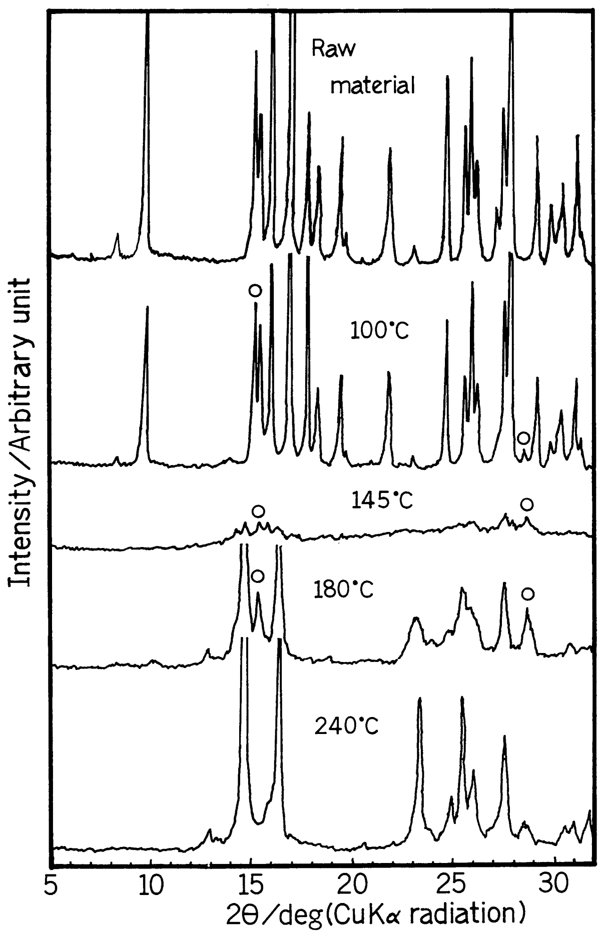


Fig. 3. X-Ray diffraction patterns of the samples decomposed in stationary air. Heating rate: 5 K min^{-1}. O: the lines were attributable to the ammonium *cyclo*-triphosphate indicated in Table 1.

The X-ray diffraction pattern of the sample heated to 180 °C showed the lines for ammonium polyphosphate (I-form)[19] and those for ammonium *cyclo*-triphosphate given in Table 1 (Fig. 3). 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. 2 and 3. The weight loss on the TG curve at 240 °C was ca. 15.4%, which is close to that calculated according to the following equation (15.18%):

$$(NH_4)_4P_3O_9NH_2\cdot H_2O \rightarrow 3(NH_4)PO_3+2NH_3+H_2O$$

The weight loss at temperatures above 240 °C might be due to the release of ammonia, water, or phosphorus pentoxide from the sample.

Effect of Atmosphere on the Thermal Decomposition. Samples of ammonium amidotriphosphate were heated at 5 K min^{-1} to 100, 145, 180, and 240 °C, in streams of four different gases. Table 2 shows the composition of phosphates of the products. At 100 and 145 °C in dry air, dehydration of $(NH_4)_4P_3O_9NH_2\cdot H_2O$ induced rapid decomposition of the amidotriphosphate ions. As water vapor suppresses the dehydration and consequently the decomposition of amidotriphosphate ions, the latter reaction is expected to proceed slowly in a humid atmosphere. Indeed at 100 and 145 °C, there remain markedly more amidotriphosphate ions undecomposed when heated in humid air than in dry air. Amidotriphosphate ions were stable up to 180 °C in a stream of ammonia; this implies that amidotriphosphates also were cleaved by elimination of ammonia.

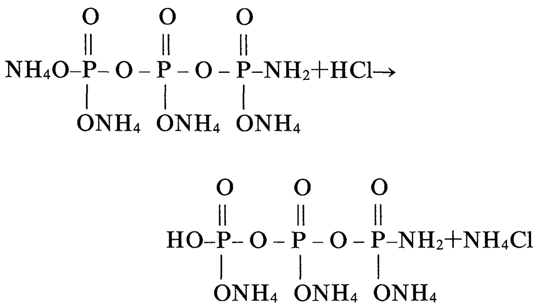
It was reported that amidotriphosphate ions cyclized again to *cyclo*-triphosphate ions in acidic solutions.[12–14] As seen in Table 2, the products occasionally contained *cyclo*-triphosphates. Such samples exhibited necessari-

Table 2. Effect of the Atmosphere on the Phosphates Composition in the Products Obtained by Heating of $(NH_4)_4P_3O_9NH_2\cdot H_2O$

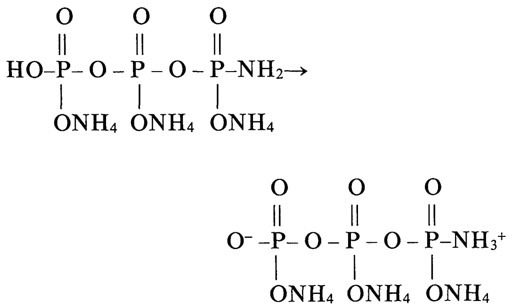
T/°C	Atmosphere	Composition/P%					
		Amidotri-	Mono-, di-, and tri-	Oligo-[a]	Poly-	*cyclo*-Tri-	Other[b]
100	Dry air	88.9	—	0.7	1.6	8.8	—
	Humid air	95.6	—	—	—	4.4	—
	NH_3	100.0	—	—	—	—	—
	Dry HCl	51.3	5.4	7.5	3.3	32.6	—
145	Dry air	17.4	7.1	25.0	31.7	13.6	5.2
	Humid air	67.7	4.9	7.8	5.3	12.3	2.0
	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) See text.

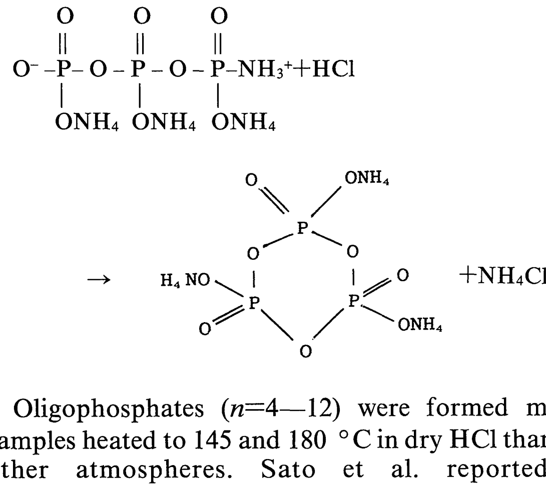
ly two diffraction lines at 15.4 and 28.8 ° (2θ), which agreed with those listed in Table 1. Quimby and Flautt,[12] and Feldmann and Thilo[13] described that a zwitterion was formed as an intermediate in the course of the cyclization of amidotriphosphate ion. Table 2 shows that *cyclo*-triphosphate ions exist most abundantly in samples heated to 100 °C in hydrogen chloride. This is probably due to the formation and subsequent cyclization of the zwitterion expressed by the following equations:



$$\mathrm{NH_4O\text{-}\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}O\text{-}\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}O\text{-}\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}NH_2+HCl\rightarrow HO\text{-}\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}O\text{-}\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}O\text{-}\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}NH_2+NH_4Cl} \quad (1)$$



$$\mathrm{HO\text{-}\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}O\text{-}\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}O\text{-}\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}NH_2\rightarrow O^-\text{-}\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}O\text{-}\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}O\text{-}\underset{\underset{ONH_4}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}NH_3^+} \quad (2)$$



(3)

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.[20,21] Therefore, the oligophosphates may also be formed by condensation of the zwitterions indicated on the right-hand side of Eq. 2. The zwitterions must be also resulted from a reaction of amidotriphosphate ions with water. Sato et al. suggested the occurrence of such a reaction.[20,21]

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} [22] and a small peak of amino groups at 1630 cm^{-1}.[23] The sample heated to 100 °C in HCl showed a peak at 1400—1500 cm^{-1}, and a faint peak at 1670 cm^{-1}. The shift from 1630 to 1670 cm^{-1} might be due to the formation of hydrogen bonds. Although Corbridge and Lowe reported that the zwitterions of amidophosphates all exhibited absorption at 1618—1615 cm^{-1} and at 1470—1468 cm^{-1},[22] we were unable to identify the zwitterions of the amidotriphosphates by the IR spectra.

Hydrogen chloride and water are expected to act as hydrolytic agents at higher temperatures. As a result of hydrolysis of the amidotriphosphates, mono- to triphosphates were indeed formed more in samples heated to 145 and 180 °C in HCl and in those heated to 180 and 240 °C in humid air (Table 2). Table 2 shows that there were no *cyclo*-triphosphates in samples heated in ammonia, which may indicate that the zwitterions are not formed in the presence of ammonia molecules.

The products heated to 240 °C entirely consisted of polyphosphate ions, and showed an X-ray diffraction pattern of I-form of ammonium polyphosphate.[19] 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.

Isothermal Decomposition in a Stream of Dry Air. Ammonium amidotriphosphate $(NH_4)_4P_3O_9NH_2\cdot H_2O$ 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. 4 and 5. Mono- to triphosphates were hardly observed (less than 1%) in

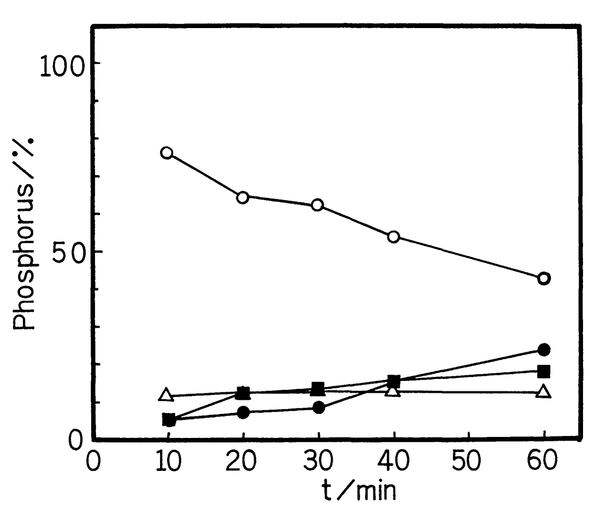


Fig. 4. Changes in the amounts of phosphates in products decomposed at 100°C in a stream of dry air. ○: amidotri-, ●: poly-, ■: oligo- (chain length= 4—12), △: *cyclo*-tri-.

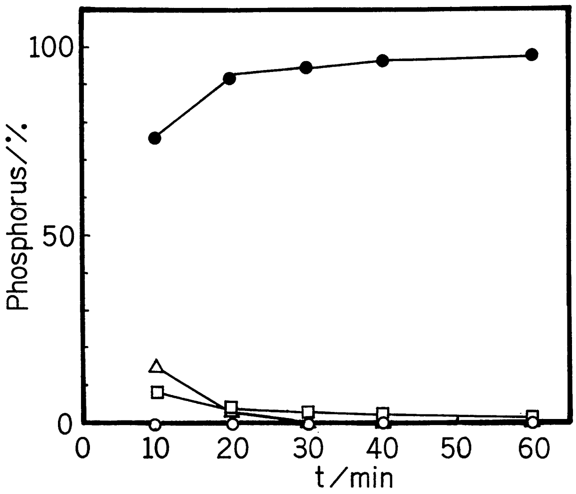


Fig. 5. Changes in the amounts of phosphates in products decomposed at 180°C in a stream of dry air. ○: amidotri-, ●: poly-, □: mono-, di-, and tri-, △: *cyclo*-tri-.

samples heated at 100 °C. 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. 5. 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. 4). These ions were probably formed via the zwitterions. *cyclo*-Triphosphate ions were detected clearly at 10 min at 180 °C (Fig. 5). 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).

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