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Synthesis and thermal property of sodium triimidocyclotriphosphate

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Sodium triimidocyclotriphosphate tetrahydrate was made by reacting phosphorus pentachloride with ammonium chloride and then hydrolysing the resulting product in an aqueous sodium acetate solution. When the cyclotriphosphate was heated in air, it was directly converted to sodium cyclotriphosphate according to the reaction

$$(NaPO_2NH)_3 + 3H_2O \rightarrow (NaPO_3)_3 + 3NH_3$$

1. Introduction

Among many phosphorus–nitrogen compounds, phosphazenes are those best known and most intensively studied. They have a number of unusual characteristic properties of inorganic polymer, and the most important utility of the phosphazene polymers is the ease with which the properties can be modified by the introduction of different substituent groups [1]. There is a series of phosphorus–nitrogen polymers which have imino groups in their chain and ring skeletons. The compounds can be used as flame retardants, chemical fertilizers, biomaterials, chemical manufacture, etc. Inspite of the usage of the compounds, there has been no comparable study of the imidopolyphosphates with that on phosphazenes. We are trying to obtain basic physical and chemical information about imidopolyphosphates, and have previously reported the synthesis and hydrolytic properties of imidodiphosphate in solid and aqueous solution [2]. It has been found that the imidodiphosphate was directly converted to diphosphate by heating above 200 °C in air and was hydrolysed to phosphoramidate and orthophosphate in an aqueous solution. This paper describes the synthesis and thermal properties of triimidocyclotriphosphate.

2. Experimental procedure

2.1. Preparation

Hexachlorocyclotriphosphazene was made by reacting phosphorus pentachloride with ammonium chloride in 1,2-tetrachloroethane [3]. The phosphazene (50 g) was dissolved in dioxane in a three-necked round-bottom flask at 45–50 °C. Sodium acetate (250 g) was dissolved in 1 dm^3 water. The solution was heated at 45–50 °C and then added in the phosphazene solution. The resulting mixture was reacted at 45–50 °C for 3 h with stirring. The reaction product was allowed to stand overnight at room temperature (10–20 °C). The precipitate was filtered off and washed with 50 vol % aqueous ethanol and then ethanol. The product (50 g) was dissolved in 350 cm^3 water at 70 °C. Glycerol (350 cm^3), which was heated at 70 °C, was added to the product solution and this solution was heated at 70 °C for 1 h with stirring. The resulting hot solution was quickly filtered off. After sufficient cooling of the mother liquor, 150 cm^3 ethanol was added to the liquor. The white precipitate was filtered off and washed with 50 vol % aqueous ethanol, ethanol, and then diethyl ether.

2.2. Chemical analysis

The phosphorus, nitrogen and sodium in a sample were determined, respectively, by Molybdenum Blue colorimetric analysis, Kjeldahl technique, and atomic absorption spectrophotometric measurement.

2.3. High-performance liquid chromatography (HPLC)

The HPLC analysis, which was developed by Yoza *et al.* [4], was employed to separate and determine the phosphate species in a sample. A separation column (4 mm × 240 mm) with TSK-Gel(SAX-F0011), a Shimazu spectrophotometer (UV-110-02), and KCl eluents (0.18, 0.26, and 0.40 mol dm^{-3}) were used for the analysis. About 10 mg of a sample was dissolved in 10 cm^3 water and 200 mm^3 solution was injected into the column.

2.4. X-ray diffractometry

An X-ray diffraction (XRD) diagram of a powder sample was taken with nickel-filtered CuK_α radiation using Rigaku X-ray diffractometer, RAD-1B.

2.5. Infrared spectrophotometry

An infrared spectrum of a sample was recorded on a JASCO IR spectrophotometer, A-3, using the KBr disc method.

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2.6. ^{31}P nuclear magnetic resonance measurement

A sample was dissolved in water and the ^{31}P nuclear magnetic resonance (NMR) spectrum of the solution was taken using a JNM-GX 270 spectrograph. The chemical shifts are reported relative to external 85% orthophosphoric acid, with the positive shifts being downfield.

2.7. Thermogravimetry and differential thermal analysis

The thermogravimetry–differential thermal analysis (TG–DTA) measurement was used to study the thermal behaviour of the product using a Rigaku TG–DTA apparatus in air at a heating rate of 10 °C min^{-1}.

3. Results and discussion

The elemental analysis for the product gave the following result: Na 18.1%; P 25.0%; N 11.7%. The calculated contents of the elements for $(NaPO_2NH)_3 \cdot 4H_2O$ were: Na 18.4%; P 24.8%; N 11.2%. The product gave only one ^{31}P NMR peak of triimidocyclotriphosphate at − 1.1 p.p.m. (at pH 10) and the XRD diagram of the product was almost the same as that described in the JCPDS card of $(NaPO_2NH)_3 \cdot 4H_2O$ (no. 16-932).

The TG–DTA curves of sodium triimidocyclotriphosphate tetrahydrate are shown in Fig. 1. The thermal products which are numbered in Fig. 1 were removed from a furnace and subjected to further analysis to study the thermal reactions. The result of the analysis is shown in Table I and the XRD diagrams of the thermal products are given in Fig. 2. The first large endothermic peak accompanying weight loss was caused by the removal of water of crystallization because the phosphate distribution in Table I showed that thermal product 1 contained only triimidocyclotriphosphate. The weight loss of the thermal product agreed with the dehydration

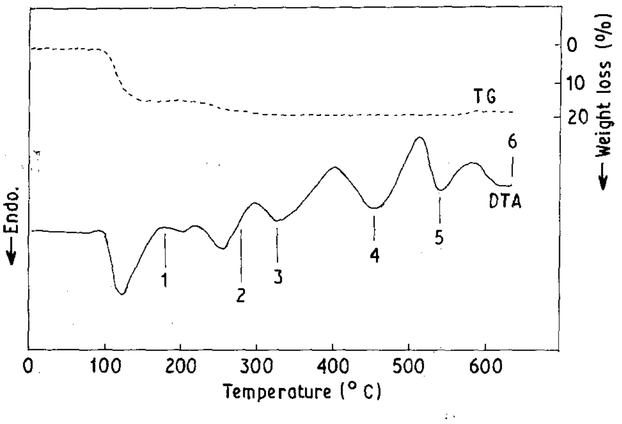

Figure 1 TG and DTA curves of $(NaPO_2NH)_3 \cdot 4H_2O$.

$$(NaPO_2NH)_3 \cdot 4H_2O \rightarrow (NaPO_2NH)_3 \cdot H_2O + 3H_2O \quad (1)$$

After the second endothermic peak with a gradual small weight loss, the thermal product contained small amounts of diimidocyclotri-, monoimidocyclotri-, and cyclotriphosphates other than triimidocyclotriphosphate. The following successive reactions or simultaneous reactions can be written for the thermal change.

Successive reactions

$$(NaPO_2NH)_3 + H_2O \rightarrow Na_3P_3O_7(NH)_2 + NH_3 \quad (2)$$

$$Na_3P_3O_7(NH)_2 + H_2O \rightarrow Na_3P_3O_8NH + NH_3 \quad (3)$$

$$Na_3P_3O_8NH + H_2O \rightarrow (NaPO_3)_3 + NH_3 \quad (4)$$

Simultaneous reactions

$$(NaPO_2NH)_3 + H_2O \rightarrow Na_3P_3O_7(NH)_2 + NH_3 \quad (2)$$

$$(NaPO_2NH)_3 + 2H_2O \rightarrow Na_3P_3O_8NH + 2NH_3 \quad (5)$$

$$(NaPO_2NH)_3 + 3H_2O \rightarrow (NaPO_3)_3 + 3NH_3 \quad (6)$$

It is difficult to determine which reaction is reasonable for the step. Because all these reactions cause a gain in weight of the thermal product, the weight loss at this step may be due to removal of the rest of the water of crystallization. Thermal product 2 showed only very weak XRD peaks of sodium cyclotriphosphate. The main component of thermal product 2 was triimidocyclotriphosphate. Thus, the dehydrated triimidocyclotriphosphate must be amorphous. The weight loss of thermal product 3 was very near to that

TABLE I Weight loss and composition of thermal products of $(NaPO_2NH)_3 \cdot 4H_2O$

Thermal product	Weight loss (%)	Total nitrogen (%)	Insoluble part (%)	Phosphates (P%)			
				Triimido	Diimido	Monoimido	Cyclotri
1	14.7	13.7	–	100	–	–	–
2	17.9	11.4	–	89.3	2.5	1.4	6.8
3[a]	19.2	8.5	1–2	74.2	3.8	1.0	21.0
4[a]	19.6	3.8	30–40	–	2.2	18.4	79.4
5[a]	19.2	0.6	3–4	–	0.4	11.0	82.4
6	18.7	–	–	–	–	1.2	98.8

[a] The product contained insoluble part.

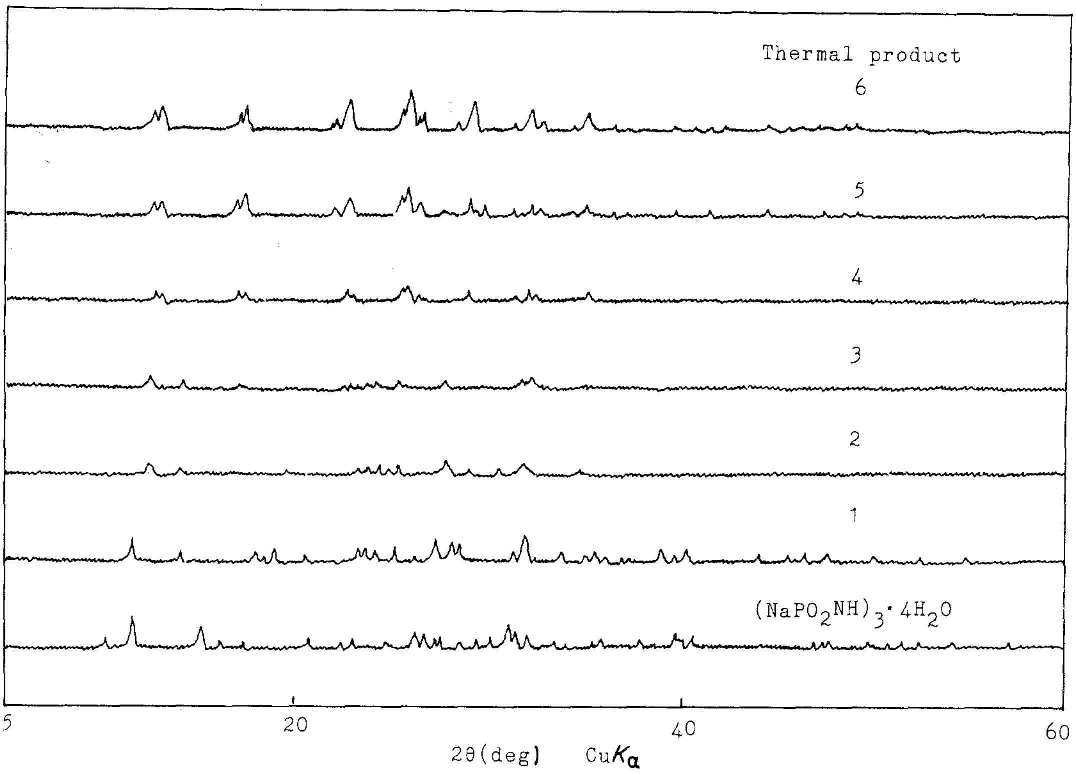

Figure 2 XRD diagrams of the thermal products of $(NaPO_2NH)_3 \cdot 4H_2O$.

of the reaction

$$(NaPO_2NH)_3 \cdot 4H_2O \rightarrow (NaPO_2NH)_3 + 4H_2O \quad (7)$$

but the thermal product contained a large amount of cyclotriphosphate and the nitrogen content was less than that of $(NaPO_2NH)_3$. The contents of diimidocyclotri- and monoimidocyclotriphosphates were very small at this step. It seems unreasonable that the very rapid successive Reactions 2–4 are preferred over the simultaneous Reactions 2, 5 and 6 because, as shown in Table I, the content of monoimidocyclotriphosphate in thermal products 4 and 5 was not small. Therefore, the simultaneous reactions can be preferential for the thermal substitution of iminogroups for oxygen, and Reactions 2 and 5 are slow and Reaction 6 is rapid. By the way, a small part of the thermal product 3 was insoluble in water and the insoluble product was considered to be long chain imidopolyphosphates according to the reaction

$$n(NaPO_2NH)_3 + mH_2O \rightarrow Na_{3n}P_{3n}O_{6n+m}(NH)_{3n-m} + mNH_3 \quad (3n > m) \quad (8)$$

The ^{31}P NMR spectrum of the water-soluble part of product 3 is shown in Fig. 3. The peaks at − 3.5 to − 8 p.p.m. are due to diimidocyclotri- and monoimidocylotriphosphates and the result agrees well with that of the HPLC analysis in Table I. After the next large exothermic peak, thermal product 4 showed an XRD pattern of sodium cyclotriphosphate and the content of the cyclotriphosphate in the water-soluble part was about 80 P%. This means that the substitution of imino groups for oxygen and the formation of cyclotriphosphate by Reaction 6 proceeded through the thermal process. The amount of water-insoluble part of the thermal product was 30%–40%. Accordingly, the reorganization of the triimidocyclotriphosphate to chain imidopolyphosphates by Reaction 8 also progressed at this step. The water-insoluble part of thermal product 5 was less than several per cent and the content of cyclotriphosphate in the thermal product was about 82 P%. The following thermal change could be considered for the process:

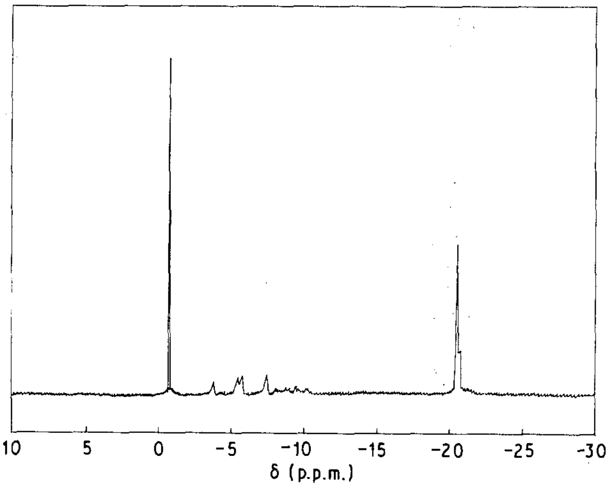

Figure 3 ^{31}P NMR spectrum of thermal product 3.

$$Na_{3n}P_{3n}O_{6n+m}(NH)_{3n-m} + (3n - m)H_2O \rightarrow n(NaPO_3)_3 + (3n - m)NH_3 \quad (3n > m) \quad (9)$$

As Fig. 2 shows, the phosphates other than sodium cyclotriphosphate were X-ray diffractometrically amorphous in thermal products 3–5. After the last

TABLE II Composition of thermal products of the insoluble product

Thermal product	Total nitrogen (%)	XRD	Phosphates (P%)		
			Tri	Cyclotri	Cyclotetra
SM[a]	6.8	Amorphous	–	–	–
7[b]	4.1	$(NaPO_3)_3$	19.2	78.4	2.4
8[b]	2.5	$(NaPO_3)_3$	13.3	85.2	1.5
9	0.7	$(NaPO_3)_3$	0.6	99.1	0.3

[a] SM, the water-insoluble thermal product of $(NaPO_2NH)_3 \cdot 4H_2O$.
[b] The sample contained an insoluble part.

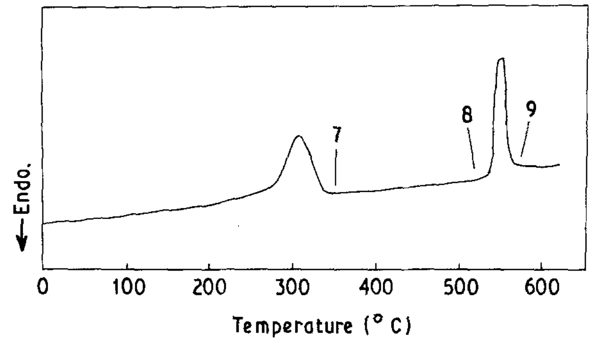

Figure 4 DTA curve of the insoluble thermal product.

exothermic peak at about 600 °C, the product contained about 99 P% sodium cyclotriphosphate. It can be concluded that Reaction 9 progressed during the heating.

The water-insoluble imidopolyphosphates were prepared by treating thermal product 4 with water and removing the water-soluble part from the product. The DTA curve of the water-insoluble phosphates is shown in Fig. 4. No measurable weight change of the sample was observed. The thermal products, as numbered in Fig. 4, were removed from the furnace and subjected to further analysis to study the thermal behaviour of the imidopolyphosphates. The analytical results are listed in Table II. Thermal product 7 showed an XRD pattern of sodium cyclotriphosphate. The exotherm at about 290 °C may be caused by thermal Reaction 9, but the substitution of imino groups for oxygen did not complete at this step because the nitrogen content of the product 7 was 4.1%. After the next exothermal change, the nitrogen content was very small. Accordingly, Reaction 9 seemed to be complete at this step. Imino groups in the imidopolyphosphates may be gradually substituted for oxygen to make sodium cyclotriphosphate in air at a temperature higher than 200 °C.

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