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Synthesis and thermal behaviour of sodium monoimidocyclotriphosphate

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Trisodium monoimidocyclotriphosphate dihydrate, $Na_3P_3O_8NH \cdot 2H_2O$, was made by hydrolysing triimidocyclotriphosphate in an aqueous acetic acid solution at 70 °C. The monoimidocyclotriphosphate was converted to cyclotriphosphate by heating in air according to the reaction

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

1. Introduction

There are a number of condensed phosphates which contain imino groups; these compounds can be used as flame-proof materials, chemical fertilizers, precursors of phosphate glass containing nitrogen, biochemical materials, etc. The present authors have studied the synthesis and thermal property of imidodi-, diimidotri-, triimidocyclotri- and diimidocyclotriphosphates [1–4]. An imino group contained in the compounds was gradually substituted for bridging oxygen by heating in air and these imidophosphates were converted to their corresponding condensed phosphates. Coordination chemistry of some imidooligophosphates has also been studied using a nuclear magnetic resonance approach. Bridging oxygen of condensed phosphates does not coordinate to a metal ion, while nitrogen of an imino group of some small-ring imidooligophosphates acted as a coordination atom to a metal ion [5, 6]. This paper describes the synthesis and thermal behaviour of monoimidocyclotriphosphate.

2. Experimental procedure

2.1. Preparation

To prepare monoimidocyclotriphosphate hydrolytic substitution of the imino groups of triimidocyclotriphosphate for bridging oxygen was used. Fig. 1 shows the dependence of phosphate composition on the concentration of acetic acid for the hydrolytic process of triimidocyclotriphosphate in an aqueous acetic acid solution. At a higher concentration of acetic acid the substitution rate of imino groups for bridging oxygens was too fast to obtain a high yield of monoimidocyclotriphosphate, and at a lower concentration the substitution rate was too low. Fig. 2 shows the dependence of phosphate composition on reaction time for the hydrolytic process of triimidocyclotriphosphate in an aqueous acetic acid solution of water (50 cm^3)–acetic acid (20 cm^3). According to the results, the hydrolytic reaction condition of triimidocyclotriphosphate as written below was employed. Trisodium triimidocyclotriphosphate tetrahydrate (5 g) was dissolved in water (50 cm^3) and acetic acid (20 cm^3) was added to the solution. The mixed solution was heated to 70 °C and reacted for 8 h. After hydrolytic substitution ethanol (90 cm^3) was added to the resulting solution and a white precipitate, which was a mixture of triimidocyclotri-, diimidocyclotri- and monoimidocyclotri phosphates, was filtered off. The white precipitate (2 g) was dissolved in water (50 cm^3) and the solution was passed through a column packed with anion-exchange resin to isolate monoimidocyclotriphosphate by using

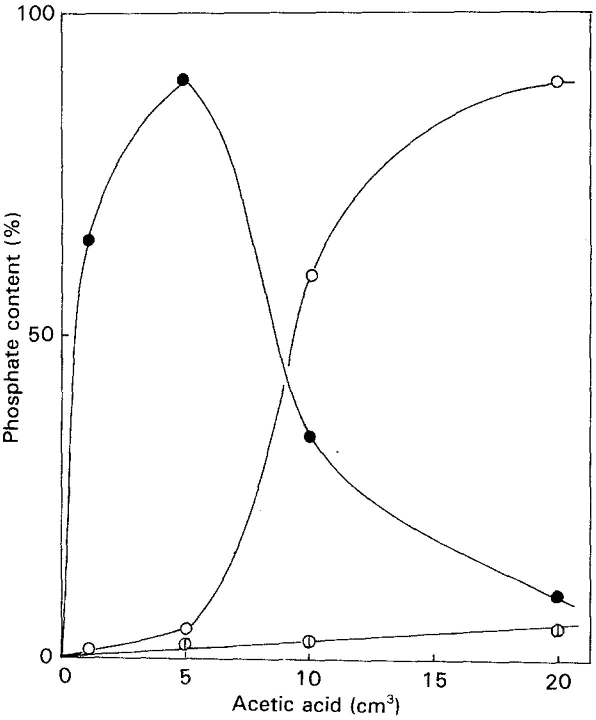

Figure 1 Dependence of phosphate composition on the concentration of acetic acid for the hydrolytic substitution of imino groups of triimidocyclotriphosphate in 50 cm^3 of water at 70 °C for 8 h. ●, Diimidocyclotriphosphate; ○, monoimidocyclotriphosphate; ⦶, cyclotriphosphate.

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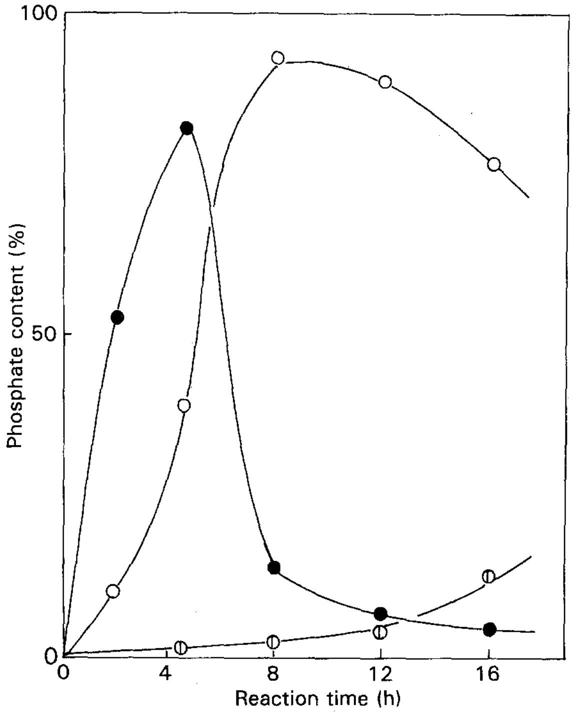


Figure 2 Dependence of phosphate composition on reaction time for the hydrolytic substitution of imino groups of triimidocyclotriphosphate in water (50 cm^3)–acetic acid (20 cm^3) solution at 70 °C. ●, Diimidocyclotriphosphate; ○, monoimidocyclotriphosphate; ⦶, cyclotriphosphate.

a 0.4 mol dm^{-3} sodium chloride solution as an eluent. Ethanol (100 cm^3) was added into an every-separation aliquot (75 g). A white precipitate was filtered off and washed with 50 and then 90 vol % aqueous ethanol.

2.2. Chemical analysis

The phosphorus, nitrogen and sodium in the samples were determined by Molybdenum Blue colorimetric analysis, the Kjeldahl technique and atomic absorption spectrophotometric measurement respectively. The amount of bound water was determined by heating loss.

2.3. High-performance liquid chromatography (HPLC)

The HPLC analysis, developed by Yoza *et al.* [7], was employed to separate and determine the phosphate species in a given sample. A separation column (4 × 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 sample was dissolved in 10 cm^3 water and 200 mm^3 of the solution was injected into the column.

2.4. ^{31}P nuclear magnetic resonance (NMR) measurement

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

2.5. X-ray diffractometry (XRD)

An XRD diagram of a powder sample was taken with nickel-filtered CuK$_\alpha$ radiation using a Rigaku X-ray diffractometer (RAD-1B).

2.6. Thermogravimetry–differential thermal analysis (TG–DTA)

The 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

3.1. Isolation of monoimidocyclotriphosphate

The result of HPLC analysis of the products, which were obtained by adding ethanol into an every column-separation aliquot, is shown in Fig. 3. Monoimidocyclotriphosphate was included in the separation aliquot of 450–825 g. The yield of the monoimidocyclotriphosphate was ca. 1.0–1.1 g.

3.2. Composition of the product

Quantitative analysis of the product showed that the contents of sodium, phosphorus and nitrogen were

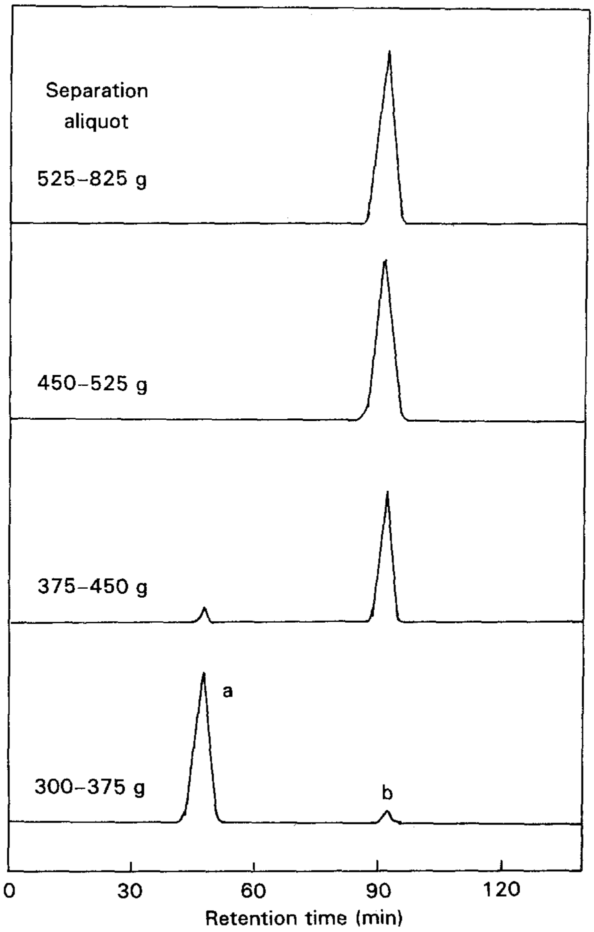
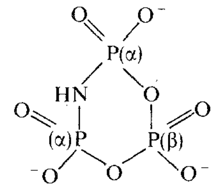


Figure 3 HPLC profiles of the hydrolysis product of triimidocyclotriphosphate. a, Diimidocyclotriphosphate; b, monoimidocyclotriphosphate.

19.6, 26.5 and 4.1% respectively. The calculated contents of the elements of trisodium monoimidocyclotriphosphate dihydrate, $Na_3P_3O_8NH \cdot 2H_2O$, were (%): Na, 20.2; P, 27.3; N, 4.1. The chemical structure of a monoimidocyclotriphospate ion can be written as follows



The ^{31}P-NMR peak of P(α) was expected to be a doublet and that of P(β) a triplet. The height of P(α) was expected to be twice that of P(α). The ^{31}P-NMR spectrum of the product is given in Fig. 4. The product gave peaks at about − 10 (doublet) and − 19 (triplet) p.p.m. The height of the peak at − 10 p.p.m. was about twice as high as that at − 19 p.p.m. These results were in agreement with the structural character of monoimidocyclotriphosphate. Accordingly, it was concluded that the product was trisodium monoimidocyclotriphosphate dihydrate, $Na_3P_3O_8NH \cdot 2H_2O$. The XRD data of the product is shown in Table I. The product was stable at room temperature (5–30 °C).

3.3. TG–DTA analysis

TG and DTA curves of sodium monoimidocyclotriphosphate dihydrate are shown in Fig. 5. The analytical result and XRD patterns of the thermal products are given in Table II and Fig. 6, respectively. The two endothermic peaks below 150 °C were accompanied by a rapid weight loss. Since thermal product 1 was composed only of monoimidocyclotriphosphate, the thermal processes were thought to be caused by removal of the water of crystallization. The XRD pattern of thermal product 1 could be due to anhydrous trisodium monoimidocyclotriphosphate. Thermal product 2 showed a similar XRD pattern, but the sample contained cyclotriphosphate. The cyclotriphosphate could be produced by the following substi-

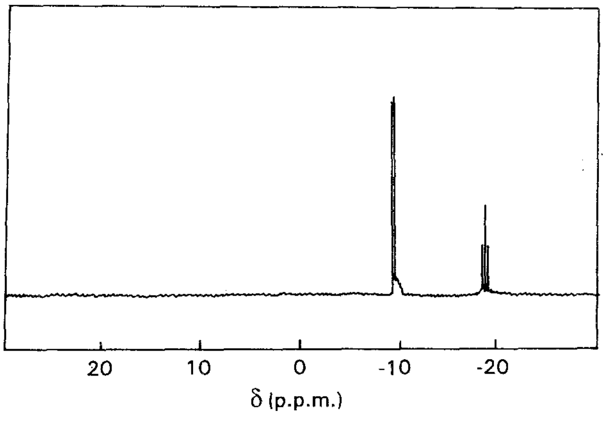


Figure 4 ^{31}P-NMR spectrum of the product.

TABLE I XRD data of $Na_3P_3O_8NH \cdot 2H_2O$

d(nm)	I/I_0	d(nm)	I/I_0
0.868	5	0.272	32
0.829	100	0.269	20
0.796	3	0.267	13
0.746	3	0.265	9
0.682	10	0.263	31
0.568	32	0.260	7
0.544	12	0.253	10
0.537	37	0.246	10
0.507	57	0.239	9
0.501	25	0.231	5
0.493	28	0.230	7
0.481	4	0.229	7
0.470	6	0.227	9
0.414	20	0.225	7
0.410	15	0.223	7
0.372	7	0.216	6
0.364	13	0.215	14
0.341	21	0.210	8
0.333	25	0.205	9
0.322	28	0.204	7
0.319	5	0.202	7
0.308	34	0.200	7
0.307	32	0.191	7
0.302	24	0.185	6
0.296	74	0.183	5
0.293	6	0.178	5
0.283	10	0.173	5
0.276	43	0.172	5
0.274	48	0.171	6

TABLE II Weight loss and composition of the thermal products of $Na_3P_3O_8NH \cdot 2H_2O$

Thermal product	Weight loss (%)	Total N (%)	Phosphates (P%) Monoimido-cyclotri	Phosphates (P%) Cyclotri
1	7.2	4.05	100	–
2	8.5	3.08	83.0	17.0
3	9.6	2.34	59.7	40.3
4	10.1	1.66	36.0	64.0
5	10.4	0.78	2.6	97.4
6	10.4	–	–	100

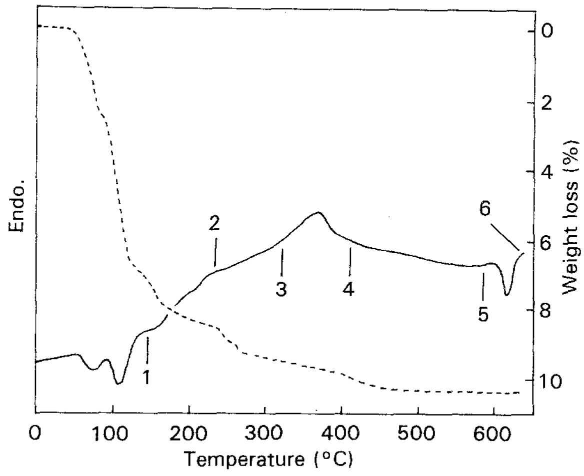


Figure 5 TG (– – –) and DTA (——) curves of $Na_3P_3O_8NH \cdot 2H_2O$.

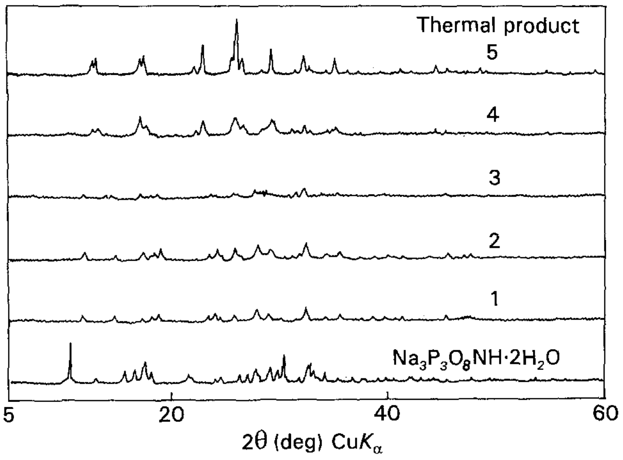


Figure 6 XRD diagrams of the thermal products of $Na_3P_3O_8NH \cdot 2H_2O$.

tution reaction

$$Na_3P_3O_8NH + H_2O \rightarrow (NaPO_3)_3 + NH_3 \qquad (1)$$

Thermal product 3 showed a similar weak XRD pattern to thermal products 1 and 2. Although thermal product 3 contained 40.3% P of cyclotriphosphate, the product did not exhibit any XRD peaks due to cyclotriphosphate. After the endothermic process at ca. 400 °C, thermal product 4 showed an XRD diagram of trisodium cyclotriphosphate. Therefore, the exothermic reaction was due to crystallization of amorphous trisodium cyclotriphosphate. The sample melted at ca. 650 °C and the last thermal product was trisodium cyclotriphosphate. Since the thermal products did not contain any phosphates other than monoimidocyclotri- and cyclotriphosphates, it was concluded that the hydrolytic cleavage of the P–NH–P and P–O–P linkages of the monoimidocyclotriphosphate did not occur. The overall thermal process of the monoimidocyclotriphosphate can be written as Equation 1.

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