Syntheses and Thermal Properties of Disodium and Diammonium Dihydrogentetra-μ-imido-cyclo-tetraphosphates

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Disodium dihydrogentetra-μ-imido-cyclo-tetraphosphate dihydrate has been made by adjusting pH of a solution of tetrascodium tetra-μ-imido-cyclo-tetraphosphate at 2.0 with hydrochloric acid. The compound was stable below 125°C and produced many kinds of imidopolyphosphates above 125°C.

Anhydrous diammonium dihydrogentetra-μ-imido-cyclo-tetraphosphate has been prepared by making the pH value of a solution of tetra-μ-imido-cyclo-tetraphosphoric acid above 10 with aqueous ammonia and then acidifying the solution to a pH value lower than 5.0 with hydrochloric acid. The product was stable up to 180°C. On heating at a higher temperature, it produced many kinds of condensed phosphates with imino groups.

Key words: Tetra-μ-imido-cyclo-tetraphosphate, Synthesis, Thermal property

1 Introduction

There are many kinds of phosphorus–nitrogen compounds. Among them, ammonium orthophosphates and condensed phosphates are used as flame-proof materials and phosphazenes are expected to be used as inorganic gums. Many papers about the compounds have been published. Being condensed phosphates of imino groups, imidopolyphosphates are useful for flame retardants, precursors of phosphate glass with nitrogen, biochemical materials, chemical fertilizers, etc. The present authors have published several papers on the syntheses, thermal behavior, complexation, and hydrolytic properties of several imidooligophosphates1)-9). This paper describes the syntheses and thermal properties of dihydrogentetra-μ-imido-cyclo-tetraphosphates.

2 Experimental

2·1 Preparation
Phosphorus pentachloride and ammonium chloride were reacted in 1,1,2,2-tetrachloroethane and the product was distilled under reduced pressure, then 2,2,4,4,6,6,8,8-octachloro-2,3,4,5,6,7,8,9-octachlorotetraphosphaza-3,6,7,8-tetraene was obtained10). The phosphazene (15 g) was dissolved in dioxane (200 cm³). Sodium acetate trihydrate (120 g) was dissolved in water (150 cm³). The solutions were warmed at 45 to 50°C and then mixed. The resulting mixture was stirred for 3 h at 45 to 50°C and a white precipitate was produced. The precipitate was filtered off and washed with 70 v% aqueous ethanol. The product was hydrated tetrasodium tetra-μ-imido-cyclo-tetraphosphate. A nearly saturated aqueous solution of the product was made.

2·1·1 Disodium dihydrogentetra-μ-imido-cyclo-tetraphosphate
The pH of the aqueous solution of tetrasodium tetra-μ-imido-cyclo-tetraphosphate was adjusted to 2.0 with hydrochloric acid and a white precipitate was produced. The precipitate was filtered off and washed with 70 v% aqueous ethanol and then acetone (product A).

2·1·2 Diammonium dihydrogentetra-μ-imido-cyclo-tetraphosphate
The pH of the aqueous solution of tetrasodium
tetra-\(\mu\)-imido-cyclo-tetraphosphate was prepared lower than 1.2 with hydrochloric acid and a precipitate was filtered off and washed with 70 v% aqueous ethanol. The product was tetra-\(\mu\)-imido-cyclo-tetraphosphoric acid dihydrate. The product was dissolved in water and the pH of the solution was made higher than 10 with aqueous ammonia, the pH of the resulting solution was then adjusted to lower than 5.0. A white precipitate was produced and washed with 70 v% aqueous ethanol and then acetone (product B).

2 · 2 Chemical analysis

The phosphorus, nitrogen, and sodium in a sample were determined, respectively, using Molybdenum Blue colorimetric analysis, Kjeldahl technique, and atomic absorption spectrophotometric measurement (Shimazu AA-680). Solubility was measured by placing 0.2 g of a sample in 50 cm\(^3\) of water and stirring the mixture for 1 h at room temperature (15–20°C).

2 · 3 High-performance liquid chromatography (HPLC)

The HPLC analysis with the gradient technique, which was developed by Baba et al.,\(^{11-13}\), was employed to separate and determine the phosphate species in a specimen. A separation column (4 × 240 mm) with TSK-gel (SAX-FF011) and KCl eluent (0.45 mol dm\(^{-1}\)) were used for the analysis. About 10 mg of each specimen was dissolved in 10 cm\(^3\) water and 200 mm\(^3\) of the solution was injected into the column.

2 · 4 X-Ray diffractometry (XRD)

An X-ray diffraction diagram of a sample was taken with nickel-filtered Cu K\(\alpha\) radiation using Rigaku X-ray diffractometer, RAD-1B.

2 · 5 \(31\)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 spectograph. The chemical shifts are reported relative to external 85% phosphoric acid, with the positive shifts being downfield.

2 · 6 Thermogravimetry (TG) and differential thermal analysis (DTA)

Thermal characteristics were analyzed by TG–DTA technique using Rigaku and/or Seiko-Kindenshi TG–DTA apparatus in air at a heating rate of 10°C min\(^{-1}\).

3 Results and discussion

3 · 1 Disodium dihydrogentetra-\(\mu\)-imido-cyclo-tetraphosphate

Product A gave one HPLC peak in Fig. 1. The product is a pure compound. The retention time is reasonably assigned to tetra-\(\mu\)-imido-cyclo-tetraphosphate in comparison with that of other known phosphates. The \(31\)P NMR spectrum of the product exhibited one singlet peak at \(-3.5\) ppm. The compound contains a kind of P02(NH) group. Found: Na, 11.6; P, 30.8; N, 13.9%. Calcd for Na\(_2\)H\(_2\)(PO\(_2\)NH)\(_4\)·2H\(_2\)O: Na, 11.6; P, 31.3; N, 14.1%. Therefore, product A is proved to be disodium dihydrogentetra-\(\mu\)-imido-cyclo-tetraphosphate dihydrate Na\(_2\)H\(_2\)(PO\(_2\)NH)\(_4\)·2H\(_2\)O. The XRD data of the compound are listed in Table 1. The product was soluble in water and stable at room temperature.

TG and DTA curves of Na\(_2\)H\(_2\)(PO\(_2\)NH)\(_4\)·2H\(_2\)O are shown in Fig. 2. The thermal products as numbered in Fig. 2 were removed from a furnace and subjected to further analysis to study thermal changes. The results are given in Table 2 and Fig. 3. The compound was stable below 125°C. A small amount of weight loss with a small endothermal peak at a temperature lower than 100°C was considered to be due to the
release of adsorbed water. A large amount of weight loss and a large endothermic peak at about 150 to 200°C were due to the removal of the water of crystallization. The content of tetra-μ-imido-cyclo-tetraphosphate in thermal product 2, however, was about 16% and that of other phosphate species in the thermal product was more than 80%. Accordingly, the reorganization and decomposition of the tetra-μ-imido-cyclo-tetraphosphate to other phosphates occurred simultaneously within the temperature range. The proposed general thermal reaction for the process are:

Dehydration

\[ \text{Na}_2\text{H}_2(\text{PO}_2\text{NH})_4\cdot 2\text{H}_2\text{O} \rightarrow \text{Na}_2\text{H}_2(\text{PO}_2\text{NH})_4\cdot (2-x)\text{H}_2\text{O} + x\text{H}_2\text{O} \quad (0 < x \leq 2) \]  

(1)

Reorganization

\[ n[ (\text{NaH})_{1/2}\text{PO}_2\text{NH}_2 ] \rightarrow 4[ (\text{NaH})_{1/2}\text{PO}_2\text{NH}_2 ] \text{n} \]  

(2)

Substitution

\[ [(\text{NaH})_{1/2}\text{PO}_2\text{NH}_2 ]_n + m\text{H}_2\text{O} \rightarrow (\text{NaH})_{(1/2)n}\text{P}_n\text{O}_{2m+n} + (\text{NH})_{n-m} + m\text{NH}_3 \text{n} \]  

(n > m)  

(3)

Decomposition at bridging oxygen

\[ (\text{NaH})_{(1/2)n}\text{P}_n\text{O}_{2n+m} + (\text{NH})_{n-m} + \text{H}_2\text{O} \rightarrow \text{Na}_1(1/2)(\text{H})_{(1/2)n} + 2\text{P}_n\text{O}_{2n+m+1} + (\text{NH})_{n-m} \text{m} \]  

(4)

Decomposition at an imino group

\[ (\text{NaH})_{(1/2)n}\text{P}_n\text{O}_{2n+m} + (\text{NH})_{n-m} + \text{H}_2\text{O} \rightarrow \text{Na}_1(1/2)(\text{H})_{(1/2)n} + \text{P}_n\text{O}_{2n+m+1} + (\text{NH})_{n-m} - \text{NH}_2 \text{n} \]  

(n > m + 1)  

(5)

Overall reaction of formation of orthophosphate

\[ [(\text{NaH})_{1/2}\text{PO}_2\text{NH}_2 ]_n + 2n\text{H}_2\text{O} \rightarrow (n/3)(\text{NaH})_{3/2}\text{PO}_4 + (2/3)n\text{H}_2\text{PO}_4 + n\text{NH}_3 \]  

(6)

<table>
<thead>
<tr>
<th>Thermal product</th>
<th>Temp. (°C)</th>
<th>Wt. loss (%)</th>
<th>Total N(%)</th>
<th>Tetra-ortho-phosphate</th>
<th>Ortho</th>
<th>Others</th>
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<tbody>
<tr>
<td>1</td>
<td>125</td>
<td>1.4</td>
<td>14.0</td>
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<tr>
<td>2</td>
<td>200</td>
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<td>13.6</td>
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<td>3</td>
<td>270</td>
<td>11.9</td>
<td>8.9</td>
<td>-</td>
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<td>82.5</td>
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<tr>
<td>4*</td>
<td>350</td>
<td>12.7</td>
<td>4.5</td>
<td>-</td>
<td>44.3</td>
<td>55.7</td>
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</table>

* The thermal product contained a water-insoluble substance (solubility: 36%).
Condensation

\[ 2(\text{NaH})_{(1/2)}P_2O_{2n+m}(\text{NH})_{2-n} \rightarrow \text{Na}_n\text{H}_{n-2}P_2O_{4n+2m-1}(\text{NH})_{2(n-m)} + \text{H}_2\text{O} \quad (n > 2) \]  

\[ 2\text{Na}_{(1/2)}\text{H}_{(1/2)n+2}P_2O_{2n+m+1}(\text{NH})_{n-m} \rightarrow \text{Na}_n\text{H}_{n-2}P_2O_{4n+2m+1}(\text{NH})_{2(n-m)} + \text{H}_2\text{O} \]  

The weight loss and nitrogen content of thermal product 2 resulted in an almost 2 in equation 1. Accordingly, the main reaction of the process was dehydration and reorganization described above. Since the weight loss of thermal products 3 and 4 increased and the nitrogen contents of the thermal products decreased, the substitution, decomposition, and condensation reactions progressed through the thermal processes. Thermal product 4 contained a water-insoluble substance. The substance may be highly polymerized condensed phosphates containing imino groups. All of the thermally produced phosphates were X-ray diffractometrically amorphous within the temperature range.

The HPLC analysis and $^{31}$P NMR measurement of product B gave the same results as those of product A. Found: P, 34.7; N, 23.6%. Calcd for $(\text{NH}_4)_2\text{H}_2(\text{PO}_2\text{NH})_4$: P, 35.4; N, 24.9%. Based on the results, product B was confirmed to be anhydrous diammonium dihydrogen-teta-μ-imido-cyclo-tetraphosphate, $(\text{NH}_4)_2\text{H}_2(\text{PO}_2\text{NH})_4$. The XRD data of the product are given in Table 3. The compound was soluble in water and stable at room temperature.

TG and DTA curves of $(\text{NH}_4)_2\text{H}_2(\text{PO}_2\text{NH})_4$ are shown in Fig. 4. The analytical results of the thermal products numbered in Fig. 4 are listed in Table 4 and the XRD diagrams of the thermal products are given in Fig. 5. The ammonium tetra-μ-imido-cyclo-tetraphosphate was stable up to 180°C. Thermal product 6 contained about...
30 P% of the tetra-μ-imido-cyclo-tetraphosphate and a large amount of the imidophosphate converted to other phosphates at 180 to 240°C. The weight loss of the process was due to the removal of NH₃ of NH₄ groups from the substance, because of the nitrogen content decrease in the thermal product. From these results, the same reorganization as in equation 2 may take place through the process and it can be expressed by the equation:

\[ n(NH_4)_2H_2(PO_2NH)_4 \rightarrow (NH_4)_{2n-x}H_{2n+x}(PO_2NH)_{4n+x}NH_3 \quad (2n > x) \] (9)

The weight loss and decrease in nitrogen content of thermal product 7 may be caused by the release of NH₃ of NH₄ groups in the thermal product and the above reorganization progressed through the thermal process. Because thermal products 6 and 7 showed the XRD pattern of \((NH_4)_2H_2(PO_2NH)_4\), the thermally produced phosphates in the products were amorphous. Thermal product 8 contained a large quantity of orthophosphate and the same substitution and decomposition as those in equations 3 to 6 may take place through the endothermic process. Thermal product 8 also contained a water-insoluble substance. The substance seemed highly polymerized condensed phosphate with imino groups. The XRD data of the product are listed in Table 5. The weight of the thermal product kept decreasing above 240°C and all of that was finally sublimed higher than 600°C. The diammonium dihydrogentetra-μ-imido-cyclo-tetraphosphate had a higher stability than the disodium dihydrogentetra-μ-imido-cyclo-tetraphosphate dihydrate.

### Table 5 XRD data of the water-insoluble thermal product of \((NH_4)_2H_2(PO_2NH)_4\).

<table>
<thead>
<tr>
<th>d value(Å)</th>
<th>I/I₀</th>
<th>d value(Å)</th>
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<tr>
<td>3.458</td>
<td>27</td>
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</table>

### References
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テトラ-μ-イミド-cyclo-テトラリン酸二水素ニナトリウムおよびニアンモニウムの合成と熱的性質

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テトラ-μ-イミド-cyclo-テトラリン酸四ナトリウム水溶液のpHを、塩酸で2.0に調整することによって、テトラ-μ-イミド-cyclo-テトラリン酸二水素ニナトリウムニ水和物を合成した。この化合物は125℃以下では安定であったが、これ以上の温度では分解し、いろいろなイミドポリリン酸塩を生じた。

テトラ-μ-イミド-cyclo-テトラリン酸水溶液のpHをアンモニア水で10以上にした後、さらに塩酸で5.0以下に調整することによって、テトラ-μ-イミド-cyclo-テトラリン酸ニアンモニウム無水物を合成した。生成物は180℃までは安定であったが、これ以上の温度では分解し、イミノ基を含むいろいろな総合リ
ン酸塩を生じた。