THE SYNTHESIS AND THERMAL BEHAVIOR OF DICALCIUM *CYCLO*-TETRA- μ -IMIDO-TETRAPHOSPHATE

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Abstract

Dicalcium *cyclo*-tetra- μ -imido-tetraphosphate octahydrate has been prepared by adding aqueous calcium chloride into an aqueous *cyclo*-tetra- μ -imido-tetraphosphoric acid solution. When the *cyclo*-tetra- μ -imido-tetraphosphate was heated, release of the water of crystallization was observed and a small decomposition of the imidophosphate occurred up to 210°C. The imidophosphate decomposed to produce many kinds of condensed phosphates with or without NH and NH₂ groups at a higher temperature. The sample finally changed to calcium metaphosphate.

INTRODUCTION

Phosphazenes are very famous materials for the P-N compounds.¹⁻³ While just a few studies have been carried out for amido- and imidophosphates, because the compounds have a problem of chemical resistance. Nevertheless, amido- and imidophosphates are interesting compounds as a precursor of phosphate glass containing nitrogen, flame retardants, biochemical materials, chemical fertilizers, and so on. The present authors have published some papers on the synthesis, thermal behavior, complexation, and hydrolytic property of several amido- and imidophosphates.⁴⁻¹⁶ This paper describes the synthesis and thermal behavior of dicalcium *cyclo*-tetra- μ -imido-tetraphosphate.

EXPERIMENTAL

Preparation

Cyclo-tetraphosphazene was dissolved in 1,4-dioxane. Sodium acetate trihydrate was dissolved in water. The solutions were warmed at 45~50 °C and then mixed. The

mixed solution was reacted for 3 h at the same temperature. The white precipitate formed was quickly filtered off and washed with 70 and 90 v% aqueous ethanol solutions and then acetone. The product was dissolved in water. By passing through a column with a cation exchange resin, sodium ions in the solution were removed and then calcium chloride was added into the resulting solution. The white precipitate formed again was filtered off and treated with the a similar manner as above. The yield of the product was about 60 mol%.

Analytical Techniques

High-performance liquid chromatography(HPLC), X-ray diffractometry(XRD), ^{31}P NMR measurement, and some chemical analyses were used to investigate chemical composition of a sample. Thermogravimetry(TG) and differential thermal analysis(DTA) were employed to inquire thermal property of the dicalcium *cyclo*-tetra- μ -imido-tetraphosphate.

RESULTS AND DISCUSSION

Chemical Composition

The product exhibited only one HPLC peak and the result indicated that the product was a pure compound. The ^{31}P NMR spectrum of the product gave one singlet peak at -3.3 ppm. This means that the compound has only one kind of $\text{P}(\text{O}_2)\text{NH}$ group. The chemical analysis gave the contents for the product: P, 23.2; N, 10.6; Ca, 15.3%. The calculated contents of phosphorus, nitrogen, and calcium for dicalcium *cyclo*-tetra- μ -imido-tetraphosphate octahydrate are 23.1, 10.4, and 14.9% respectively. Accordingly, it was found that the product was dicalcium *cyclo*-tetra- μ -imido-tetraphosphate octahydrate, $\text{Ca}_2(\text{PO}_2\text{NH})_4 \cdot 8\text{H}_2\text{O}$. XRD data of the product is given in Table 1. The product was stable in air at room temperature.

TG and DTA Measurement

TG and DTA curves of $\text{Ca}_2(\text{PO}_2\text{NH})_4 \cdot 8\text{H}_2\text{O}$ are given in Figure 1. The thermal products as numbered in the figure were taken out of the furnace and served to further analysis to study thermal changes. The chemical composition of the thermal products are listed in Table 2. The first large endothermic process accompanying a rapid and large weight loss was found to be due to the release of the water of

crystallization, because thermal product 1 was composed of only *cyclo*-tetra- μ -imido-tetraphosphate and the weight loss agreed well with the release of the water of crystallization:

Table 1. XRD data of $\text{Ca}_2(\text{PO}_2\text{NH})_4 \cdot 8\text{H}_2\text{O}$

d value(Å)	I/I ₀	d value(Å)	I/I ₀
9.11	100	3.13	33
8.56	5	3.04	11
6.63	4	3.03	15
5.49	23	2.90	15
5.38	26	2.84	5
5.02	3	2.75	10
4.55	5	2.72	6
4.25	6	2.62	8
4.20	7	2.59	8
4.11	10	2.56	10
3.91	8	2.48	7
3.67	6	2.38	13
3.34	11	2.35	5
3.16	30	2.28	8

Further, the nitrogen content of thermal product 1 was the same as that of $\text{Ca}_2(\text{PO}_2\text{NH})_4$. It can be concluded from the results that thermal product 1 was anhydrous *cyclo*-tetra- μ -imido-tetraphosphate. Thermal product 2 contained imidophosphate with less nitrogen content than that of $\text{Ca}_2(\text{PO}_2\text{NH})_4$. It means that a part of *cyclo*-tetra- μ -imido-tetraphosphate is decomposed. Orthophosphate and other many kinds of condensed phosphates containing or not containing amino and imino groups were present in thermal product 3. Decomposition and reorganization of the *cyclo*-tetra- μ -imido-tetraphosphate to those condensed phosphates were considered to occur through the step. The decomposition seemed to be caused by

Figure 1. TG and DTA curves of $\text{Ca}_2(\text{PO}_2\text{NH})_4 \cdot 8\text{H}_2\text{O}$.

Table 2 Weight loss and composition of the thermal products.

Thermal product	Temp. (°C)	Wt.loss (%)	Total N(%)	Phosphates			
				<i>Cyclo-tetra-μ-imido</i>	Amido	Ortho	Others
---	---	---	10.6	100	---	---	---
1 *	210	21.3	12.7	77.8	11.3	7.6	3.3
2 *	400	23.6	7.8	18.5	10.0	4.4	67.1
3 *	560	25.2	5.6	---	14.2	24.3	61.5
4 *	650	25.7	3.9	---	23.1	9.6	63.3
5 *	770	26.0	3.6	---	29.5	15.6	54.9
6 *	850	26.2	1.1	---	---	85.6	14.4

*The samples contained a water-insoluble substance.

water in air. The following thermal reactions can be given for the step:

Thermal product 4 was insoluble in water. The water-insoluble thermal product can be considered to be highly polymelized condensed phosphates containing imino groups. MAS ^{31}P NMR spectra of the thermal products are given in Figure 2. The peak at about -10 ppm is due to $\text{P}(\text{O}_2)\text{NH}$ groups and that at about -22 ppm is given by $\text{P}(\text{O}_2)$ groups. From these results, the formation of the water-insoluble condensed phosphates can be expressed by the equation:

Figure 2. MAS ^{31}P NMR spectra of the thermal products.

At a higher temperature, the product changed to calcium metaphosphate according to the equation:

All of the thermal products finally converted to calcium metaphosphate in air above 850°C. The overall reaction of the thermal change of dicalcium *cyclo*-tetra- μ -imido-tetraphosphate is explained by the equation:

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