Syntheses and Thermal Reactions of Alkaline Earth
Cyclo-hexaphosphates

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Alkaline earth cyclo-hexaphosphates were prepared by wet chemical processes. All these
cyclo-hexaphosphates contained water of crystallization. When the cyclo-hexaphosphates
were heated, the following thermal changes were observed.

\[
\begin{align*}
\text{Dehydration} & & M_3(PO_3)_6 \cdot nH_2O \rightarrow M_3(PO_3)_6 \cdot (n-x)H_2O + xH_2O \\
\text{Hydrolysis} & & nM_3(PO_3)_6 + 3H_2O \rightarrow 3MnH_2P_2O_6n+1 \\
\text{Condensation} & & MnH_2P_2O_6n+1 \rightarrow [M(PO_3)_2]_n + H_2O
\end{align*}
\]

Where M stands for alkaline earth metals. The final thermal products above 500 to 600°C
were metaphosphates and one can write the overall reaction for the changes:

\[
nM_3(PO_3)_6 \cdot nH_2O \rightarrow 3Mn(PO_3)_2n + nH_2O
\]

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Key words: Cyclo-hexaphosphate, Synthesis, Thermal property

1 Introduction

Condensed phosphates are well known materials, which are used in the fields of water treatment,
food additives, detergents, biomaterials, electroceramics, optoceramics, chemical fertilizers\(^1\)\(^-\)\(^5\). Among many kinds of condensed phosphates, only several phosphates (di-, tri-, cyclo-
tri-, cyclo-tetra-, cyclo-hexa-, cyclo-octa-, cyclo-de-caphosphates, and highly polymerized condensed phosphates) have been made and isolated. There have been many papers on di-,
tri-, cyclo-tri-, cyclo-tetra-, and long chain poly-
phosphates including phosphate glasses, but
only a few papers on the other oligophosphates
have been published. Some cyclo-hexaphosphates
have been made and the thermal behavior and hydrolytic property of the compounds were studied\(^6\)\(^-\)\(^11\). This paper describes wet-
chemical syntheses and thermal reactions of alkaline earth cyclo-hexaphosphates.

2 Experimental

2.1 Preparation

Lithium cyclo-hexaphosphate dihydrate was prepared by the method described in a previous
paper\(^7\). The cyclo-hexaphosphate (1 g) was dissolved in water (10 cm\(^3\)). Alkaline earth cyclo-
hexaphosphates were prepared by using the cyclo-hexaphosphate solution. Magnesium cyclo-
hexaphosphate was prepared by adding magnesium dichloride hexahydrate (1.2 g) into the cyclo-
hexaphosphate solution with stirring. Methanol (10 cm\(^3\)) was added into the solution. The white precipitate was filtered off, washed with 60–90
v\% aqueous solutions of methanol and meth-
anol, and then dried in atmosphere. The wash-
ing was done carefully not to remove water of crystallization in the product. The yield was
about 0.5 g. Calcium, strontium, and barium cyclo-hexaphosphates were made by adding calci-
um dichloride (1.3 g), strontium dichloride hexa-
hydrate (2.4 g), or barium dichloride dihydrate
(2.0 g) into the lithium cyclo-hexaphosphate solution with stirring. The precipitate was washed with 60–90 v% aqueous solutions of acetone and dried in atmosphere. The yields of calcium, strontium, and barium cyclo-hexaphosphates were 0.6, 0.7, and 0.8 g, respectively.

2.2 Chemical analysis
Determination of alkaline earth metal and phosphorus in a sample was achieved by the atomic absorption spectrophotometric analysis (Shimazu AA-680) and Molybdenum Blue colorimetric method, respectively. The amount of water of crystallization was determined by heating weight loss.

2.3 X-ray diffractometry (XRD)
An XRD diagram of a powdered sample was taken with nickel filtered Cu Kα radiation by using a Rigaku RAD–1B diffractometer.

2.4 High-performance liquid chromatography (HPLC)
A phosphate sample (0.01 g) was dissolved in a 3% aqueous solution (10 cm³) of tetrasodium ethylenediaminetetraacetate tetrahydrate (EDTA) and the phosphate solution (100 mm³) was injected into a column. The HPLC technique developed by Baba et al11)–13) was employed by using 0.24, 0.40, 0.45, and 0.60 mol/dm³ solutions of potassium chloride as eluents.

2.5 Thermogravimetry (TG) and differential thermal analysis (DTA)
TG and DTA curves of phosphate samples were recorded on a Rigaku TAS–100 apparatus at a heating rate of 5°C/min in dry air.

3 Results and discussion
3.1 Magnesium cyclo-hexaphosphate
The result of HPLC analysis showed that the product was cyclo-hexaphosphate. The contents of magnesium, phosphorus, and water of crystallization of the product were 8.7, 21.0, and 34.0%, respectively. The calculated contents of magnesium, phosphorus, and water of crystallization of Mg₃(PO₃)₆·15H₂O are 8.9, 22.8, and 33.1%, respectively. Accordingly, the product was magnesium cyclo-hexaphosphate pentadecahydrate. The XRD data of the product are shown in Table 1. TG and DTA curves of Mg₃(PO₃)₆·15H₂O are given in Fig. 1. Thermal products as numbered in the figure were removed from a furnace and subjected to further analysis to study thermal changes. The results of chemical and XRD analyses for the thermal products are listed in Table 2. A large endothermic reaction accompanying a large weight loss below 200°C was due to the removal of water of crystallization. The result in Table 2 shows that the degradation of the cyclo-hexaphosphate to ortho- and polyphosphates with chain lengths shorter than that of hexaphosphate took place at the same time. Condensation and/or reorganization of the cyclo-hexaphosphate and the thermally produced phosphates to form polyphosphates to chain lengths longer than that of hexaphosphate can also be considered at this step. Thermal product 1 was X-ray diffractometrically amorphous. The following thermal changes may occur at this thermal step (up to 200°C).

Dehydration

\[
\text{Mg}_3(\text{PO}_3)_6 \cdot 15\text{H}_2\text{O} \rightarrow \text{Mg}_3(\text{PO}_3)_6 \cdot (15 - x)\text{H}_2\text{O} + x\text{H}_2\text{O} \quad (1)
\]

0 < x ≤ 15

General equation for hydrolysis

\[
\text{nMg}_3(\text{PO}_3)_6 + 3\text{H}_2\text{O} \rightarrow 3\text{Mg}_n\text{H}_2\text{P}_{2n}\text{O}_{6n+1} \quad (2)
\]
Gradual weight loss up to about 600°C seemed to be due to the dehydration and condensation. Thermal products 2 and 3 showed weak XRD peaks and they had a low solubility. The result can be explained by the formation of highly polymerized condensed phosphates through the heating process. The exothermic reaction at about 600°C was caused crystallization of the amorphous condensed phosphates to magnesium metaphosphate, because thermal product 4 gave an XRD pattern of the metaphosphate (JCPDS No. 27-1273). Thermal products obtained above 600°C were insoluble in water. An endothermic reaction at about 750°C was due to melting of a part of the product and the last endothermic peak was caused by melting of the whole product. The overall thermal reaction of Mg₃(PO₄)₆·15H₂O can be expressed by the following equation:

\[
\text{Mg₃(PO₄)₆·15H₂O → 3Mg₃(PO₄)₂·5H₂O + Mg₂(PO₄)₂·8H₂O + HPO}_₄^{─} + 15\text{H₂O}
\]

3.2 Calcium cyclo-hexaphosphate

HPLC analysis exhibited only one peak at the reasonable retention time for cyclo-hexaphosphate. Chemical analysis showed that contents of calcium, phosphorus, and water of the product were 17.6, 26.4, and 12.5%, respectively. Calculated contents of calcium, phosphorus, and water of Ca₃(PO₄)₆·5H₂O are 17.6, 27.2, and 13.2%, respectively. It was found that the product was calcium cyclo-hexaphosphate pentahydrate. XRD data of the product are given in Table 3. TG and DTA curves of the cyclo-hexaphosphate are indicated in Fig. 2. Analytical data of the calcium cyclo-hexaphosphate is listed in Table 4. The first endothermic reaction accompanying a rapid weight loss was caused by removal of water of crystallization. The analyti-
The results of Table 4 showed that a slight amount of the cyclo-hexaphosphate decomposed to phosphates with chain lengths shorter than that of hexaphosphate and reorganized to condensed phosphates with chain lengths longer than that of hexaphosphate. The similar thermal changes to reactions 1 to 3 can be written for the thermal process at this step (up to 130°C). These thermal changes progressed at a higher temperature up to about 600°C. The thermally produced phosphates were amorphous because thermal products 7 to 10 did not give any XRD peak other than those of calcium cyclo-hexaphosphate pentahydrate. The exothermic peak at about 600°C was due to crystallization of these phosphates to calcium metaphosphate (JCPDS No. 17-0500). Thermal products obtained after the exothermic reaction was insoluble in water. The overall thermal reaction of the cyclo-hexaphosphate can be expressed as follows:

\[ nCa_3(PO_3)_6 \cdot 5H_2O \rightarrow 3Ca_n(PO_3)_{2n} + 5nH_2O \]  

(5)

3.3 Strontium cyclo-hexaphosphate

HPLC analysis for the product gave the result that the product was cyclo-hexaphosphate. Contents for strontium, phosphorus, and water of the product were 30.4, 21.7, and 11.3%, respectively. Calculated contents of strontium, phosphorus, and water for \( Sr_3(PO_3)_6 \cdot 5H_2O \) were 31.8, 22.5, and 10.9%, respectively. From the results, the product was found to be strontium cyclo-hexaphosphate pentahydrate. XRD data of the product are given in Table 5. TG and DTA curves of \( Sr_3(PO_3)_6 \cdot 5H_2O \) are indicated in Fig. 3. The results of chemical analysis of the thermal products as numbered in Fig. 3 are listed in Table 6. The first endothermic reaction accompanying a rapid weight loss was caused by removal of the water of crystallization. The weight loss at this step corresponds to the dehydration:

\[ Sr_3(PO_3)_6 \cdot 5H_2O \rightarrow Sr_3(PO_3)_6 \cdot H_2O + 4H_2O \]  

(6)

The XRD pattern of thermal product 13 may be due to the strontium cyclo-hexaphosphate monohydrate. The analytical data in Table 5 shows that about 30 P% of the cyclo-hexaphosphate decomposed and reorganized to other phosphates at this stage. The similar thermal changes to equations 2 and 3 are available for

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Table 4 Analytical data of the thermal products of \( Ca_3(PO_3)_6 \cdot 5H_2O \).

<table>
<thead>
<tr>
<th>Thermal product</th>
<th>Temp. (°C)</th>
<th>Wt. loss (%)</th>
<th>XRD</th>
<th>Phosphates (P%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1P</td>
</tr>
<tr>
<td>7</td>
<td>130</td>
<td>5.0</td>
<td>ST</td>
<td>0.3</td>
</tr>
<tr>
<td>8</td>
<td>260</td>
<td>8.0</td>
<td>ST</td>
<td>3.4</td>
</tr>
<tr>
<td>9</td>
<td>390</td>
<td>11.9</td>
<td>ST</td>
<td>2.6</td>
</tr>
<tr>
<td>10</td>
<td>540</td>
<td>12.4</td>
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<td>2.1</td>
</tr>
<tr>
<td>11</td>
<td>630</td>
<td>12.5</td>
<td>Ca(PO_3)_2</td>
<td>—</td>
</tr>
<tr>
<td>12</td>
<td>930</td>
<td>12.5</td>
<td>Ca(PO_3)_2</td>
<td>—</td>
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</tbody>
</table>

1P, 2P, 3P, 4P, and 6M stand for ortho-, di-, tri-, tetra-, and cyclo-hexaphosphates, respectively.

ST exhibits the starting material, \( Ca_3(PO_3)_6 \cdot 5H_2O \).

Thermal products 11 and 12 were insoluble in water and a 3% aqueous EDTA solution.

Table 5 XRD data of \( Sr_3(PO_3)_6 \cdot 5H_2O \).

<table>
<thead>
<tr>
<th>d value(A)</th>
<th>I/I_0</th>
<th>d value(A)</th>
<th>I/I_0</th>
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<tr>
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<td>7.33</td>
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<tr>
<td>5.69</td>
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</tr>
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<td>4.87</td>
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<td>2.61</td>
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<tr>
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<td>2.35</td>
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<td>2.31</td>
<td>8</td>
</tr>
<tr>
<td>3.07</td>
<td>12</td>
<td>2.27</td>
<td>35</td>
</tr>
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</table>
the step. The thermal changes progressed as heating temperature increased. Thermal product 14 was X-ray diffractometrically amorphous and its soluble part was about 60%. After a sharp exothermic peak at about 560°C, thermal product 15 gave an XRD pattern of strontium metaphosphate form I (JCPDS No. 12-0360). Therefore, the exothermic process was due to crystallization of the amorphous phosphates to the strontium metaphosphate. Thermal product 16 indicated an XRD pattern of strontium metaphosphate form I and thermal product 17 gave XRD patterns due to strontium metaphosphate forms I and II (JCPDS No. 12-0366). A small endothermic change at about 800°C was caused by the phase transition of a part of the metaphosphate from form I to II. The phase transition progressed as temperature increased because thermal product 18 exhibited only one XRD pattern of strontium metaphosphate form II. Soluble parts of thermal products 15 to 18 were only several percents.

The overall thermal change for he strontium cyclo-hexaphosphate can be written as follows:

\[
n\text{Sr}_3(\text{PO}_3)_6\cdot5\text{H}_2\text{O} \rightarrow 3\text{Sr}_n(\text{PO}_3)_{3n}+5n\text{H}_2\text{O}
\]  

(7)

3.4 Barium cyclo-hexaphosphate

HPLC analysis showed that the product was cyclo-hexaphosphate. Contents of barium, phosphorus, and water of the product were 39.5, 18.2, and 14.0%, respectively. Calculated contents of barium, phosphorus, and water of Ba\(_3\) (PO\(_3\))\(_6\cdot8\text{H}_2\text{O}\) were 40.0, 18.0, and 14.0%, respectively. Accordingly, the product was found to be barium cyclo-hexaphosphate octahydrate. XRD data of the product are given in Table 7. TG and DTA curves of the barium cyclo-hexaphosphate are indicated in Fig. 4. Analytical results of the thermal products as numbered in Fig. 4 are listed in Table 8. The first endothermic change accompanying a large weight loss up to 150°C was taken place by elimination of a part of the water of crystallization. The weight loss corresponds to the dehydration process:

\[
\text{Ba}_3(\text{PO}_3)_6\cdot8\text{H}_2\text{O} \rightarrow \text{Ba}_3(\text{PO}_3)_6\cdot2\text{H}_2\text{O}+6\text{H}_2\text{O}
\]  

(8)

Thermal products 19 and 20 gave the same new XRD pattern and the pattern can be assigned to barium cyclo-hexaphosphate dihydrate. According to analytical result in Table 8, a part of the cyclo-hexaphosphate decomposed and reorganized to other phosphates at the thermal step up to about 240°C. The similar thermal changes
Thermal products 19 and 20 were soluble in water. The second broad endothermic reaction was caused by dehydration of the rest of the water of crystallization. Through the thermal step, reorganization of phosphates to highly polymerized condensed phosphates was progressed. A part of the thermal product was crystalline barium metaphosphate (JCPDS No. 29-9141) because thermal product 21 gave weak XRD peaks due to the metaphosphate. A small exothermic peak at about 440°C was caused by crystallization of amorphous phosphates to the barium metaphosphate. Thermal product 22 exhibited strong XRD peaks of the barium metaphosphate. Thermal products obtained above 500°C was insoluble in water. The last endothermic process at about 850°C was due to melting of the metaphosphate. The overall thermal reaction of the barium cyclo-hexaphosphate can be described by the equation:

\[
n\text{Ba}_3\left(\text{PO}_3\right)_6\cdot 8\text{H}_2\text{O} \rightarrow 3\text{Ba}_9\left(\text{PO}_3\right)_{2n} + 8n\text{H}_2\text{O}
\]  

(9)

**References**


アルカリ土類シクロ六リン酸塩の合成と加熱変化

渡辺 誠・桝井 誠・加藤 浩二・盛 秀彦
（中部大学工学部工業化学科）

アルカリ土類シクロ六リン酸塩を湿式法により合成した。これらのシクロ六リン酸塩は全て結晶水を含有しており、加熱をするときの変化が観察された。

脱水

\[ M_3(PO_3)_6 \cdot nH_2O \rightarrow M_3(PO_3)_6 \cdot (n-x)H_2O + xH_2O \]

加水分解

\[ nM_3(PO_3)_6 + 3H_2O \rightarrow 3M_nH_2P_{2n}O_{6n+1} \]

総合

\[ M_{6n+1}H_2P_{2n}O_{6n+1} + [M(PO_3)_2]_n + H_2O \]

M はアルカリ土類金属を示す。これらのシクロ六リン酸塩の500～600°Cでの最終加熱生成物はメタリン酸塩であった。この反応に対する全反応はつきの式によってあらわすことができる。

\[ nM_3(PO_3)_6 \cdot nH_2O \rightarrow 3M_n(PO_3)_2n + nH_2O \]