

The Synthesis and Thermal Property of Sodium Cyclo-octaphosphate

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ABSTRACT

Sodium cyclo-octaphosphate heptahydrate, $(\text{NaPO}_3)_8 \cdot 7\text{H}_2\text{O}$, has been made by heating lead cyclo-tetraphosphate at 340°C , dissolving the thermal product in a 3% aqueous solution of tetrasodium ethylenediaminetetraacetate, and then crystallizing it by addition of sodium chloride and acetone to the solution. When the cyclo-octaphosphate was heated up to 400°C , it decomposed to produce phosphates with both shorter and longer chain lengths. A main product at 300° to 350°C was sodium cyclo-triphosphate, and the thermal product melted at about 630°C .

INTRODUCTION

Condensed phosphates have been used for agricultural treatment, detergents, food additives, chemical manufacture, the ceramic industry, and so on. Among many kinds of condensed phosphates, di-, tri-, tetra-, penta-, cyclo-tri-, cyclo-tetra-, cyclo-hexa-, and cyclo-octaphosphates have been made and isolated [1–10]. The synthesis of cyclo-octaphosphate was reported by Schülke, but the method does not utilize the best technique for the preparation. The present authors have tried to find a modified process to prepare cyclo-octaphosphate. This article describes the method and the thermal stability of a cyclo-octaphosphate that has never been studied heretofore. Preparation of some other cyclo-octa-

phosphates by wet processes and their thermal change or phase work have already been reported [11–17].

EXPERIMENTAL

Preparation of Cyclo-octaphosphate

Sodium cyclo-tetraphosphate tetrahydrate was prepared by hydrolyzing $\alpha\text{-P}_2\text{O}_5$ in water cooled below 15°C and then adding sodium chloride to the resulting solution. The preparation technique is modified by one of the present authors (M. Watanabe) from a technique that was proposed by Bell et al. [18]. Lead cyclo-tetraphosphate tetrahydrate was obtained by dissolving sodium cyclo-tetraphosphate in water and adding an aqueous lead nitride solution to the cyclo-phosphate solution. According to Schülke, sodium cyclo-octaphosphate hexahydrate was obtained by heating lead cyclo-tetraphosphate at 150°C for 2h, then at 300° to 350°C for less than 30 min, dissolving the thermal product in water together with sodium sulfide, and then adding ethanol to the resulting solution. The thermal product obtained by the heating process by Schülke contained only about 20 P% of cyclo-octaphosphate; it was necessary to study the effect of the heating temperature and the heating time on the phosphate composition of the thermal product and to improve the wet process in order to purify the cyclo-octaphosphate.

Chemical Analysis

An atomic absorption analysis was used for determination of sodium ion in a sample solution by

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using a Shimadzu atomic absorption spectrophotometer (AA-680). Phosphorus was determined according to the molybdenum blue method. Water of crystallization was determined by heating loss.

High-Performance Liquid Chromatography (HPLC)

An HPLC technique [19] was employed for separation and determination of any phosphate species in a sample solution. Aqueous 0.24, 0.40, and 0.60 mol dm⁻³ solutions of potassium chloride were run at a flow rate of 1 cm³ min⁻¹.

³¹P NMR Measurement

A ³¹P NMR spectrum of an aqueous phosphate solution was taken by use of a JNM-GX270 instrument. Phosphoric acid (85%) was used as a reference with the positive shifts being downfield.

X-Ray Diffractometry (XRD)

An X-ray diffraction diagram of a powder sample was measured with nickel-filtered Cu K_α radiation by using a Rigaku X-ray diffractometer, RAD-1B.

Thermogravimetry (TG) and Differential Thermal Analysis (DTA)

TG-DTA data were recorded on a Rigaku TG-DTA apparatus with a heating rate of 5°C min⁻¹ in dry air.

RESULTS AND DISCUSSION

Heating Temperature and Heating Time

Lead cyclo-tetraphosphate tetrahydrate was heated at a temperature between 300 and 460°C for 20 min. The phosphate composition of the thermal product is listed in Table 1. The result shows that a suitable temperature range for the formation of lead cyclo-octaphosphate lies between 340° and 400°C and that the cyclo-octaphosphate content is about 80 P%. At a lower temperature the content of polyphosphates with shorter chain lengths increased, and at a higher temperature the content of polyphosphates with longer chain lengths increased. It was unnecessary to preheat the lead cyclo-tetraphosphate at 150°C for 2 h as Schülke described in his paper. Dependence on heating time for the phosphate composition of the thermal product at 340°C is shown in Table 2. A heating time of 10 to 20 min was seen to be appropriate.

Purification of the Cyclo-octaphosphate

The thermal product obtained by heating the lead cyclo-tetraphosphate at 340°C dissolved but little

TABLE 1 Composition of Polyphosphates in the Thermal Products Heated at 300°, 340°, 360°, 400°, and 460°C for 20 min

| Heating temp (°C) | Phosphates (P%) | | | |
|-------------------|----------------------|-------------|------------|-----------------------|
| | Lowpoly ^a | Cyclo-tetra | Cyclo-octa | Highpoly ^b |
| 300 | 17.8 | 7.1 | 73.6 | 1.5 |
| 340 | 14.5 | — | 79.8 | 5.7 |
| 360 | 11.6 | — | 81.6 | 6.9 |
| 400 | 10.4 | — | 84.5 | 5.1 |
| 460 | 14.9 | — | 24.2 | 60.9 |

^a Polyphosphates with chain lengths shorter than the length of pentaphosphate.

^b Polyphosphates with chain lengths longer than the length of tetraphosphate.

in water. However, it was soluble in an aqueous solution of ethylenediaminetetraacetate. The thermal product (4 g) was dissolved in 200 cm³ of a 3% tetrasodium ethylenediaminetetraacetate tetrahydrate (Na₄-edta·4H₂O) solution and a residue (high-polyphosphates) was filtered off. Sodium chloride (40 g) was added to the filtrate, and a white precipitate (cyclo-octa- and highpolyphosphates) that resulted was removed by filtration. Acetone (30 cm³) was added to the filtrate and a white precipitate was obtained. The precipitate (1.4 g) was dissolved in 150 cm³ of water, and acetone (60 cm³) was added to the solution. A white precipitate was obtained, collected by filtration, washed with acetone, and dried in an air bath at 50°C. The process is shown in Figure 1. Chemical analysis of the product showed the following contents: P, 25.9; Na, 19.2; H₂O, 13.6%. The calculated contents for (NaPO₃)₈·7H₂O are as follows: P, 26.3; Na, 19.5; H₂O, 13.4%. A ³¹P NMR spectrum of the product showed only one peak at δ -21.2. HPLC profiles of the product and ortho-, di-, tri-, cyclo-tri-, cyclo-tetra-, and cyclo-hexa-

TABLE 2 Composition of Polyphosphates in the Thermal Products Heated at 340°C

| Heating time (min) | Phosphates (P%) | | | |
|--------------------|----------------------|-------------|------------|-----------------------|
| | Lowpoly ^a | Cyclo-tetra | Cyclo-octa | Highpoly ^b |
| 5 | 39.7 | 36.4 | 23.3 | 0.7 |
| 10 | 14.5 | 0.2 | 80.9 | 4.5 |
| 20 | 10.5 | — | 79.8 | 9.7 |
| 30 | 9.6 | — | 77.7 | 12.7 |

^a Polyphosphates with chain lengths shorter than the length of pentaphosphate.

^b Polyphosphates with chain lengths longer than the length of tetraphosphate.

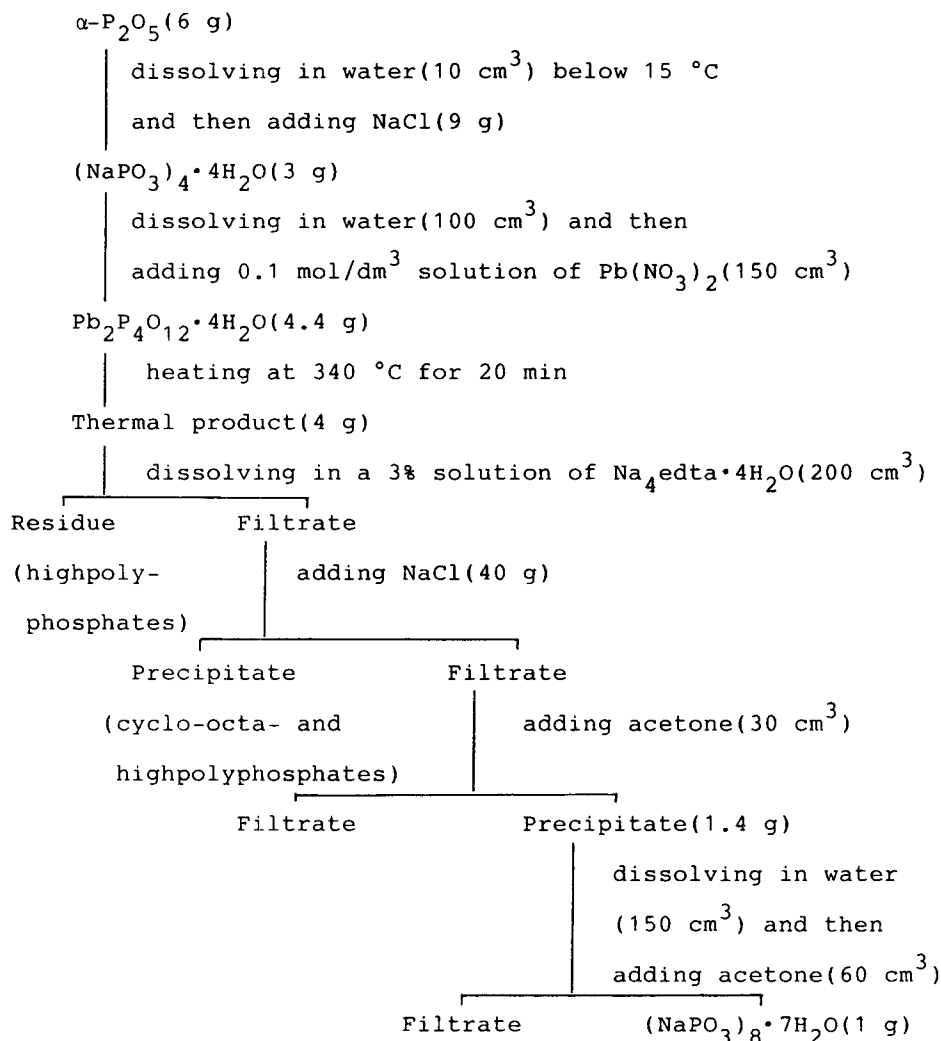
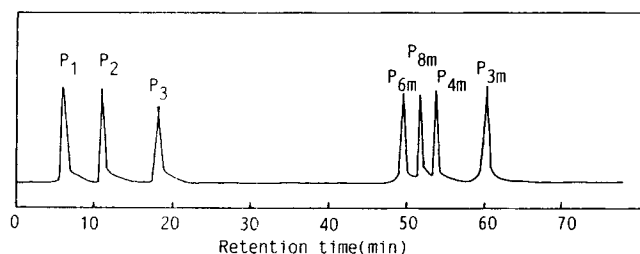


FIGURE 1 Synthetic process of sodium cyclo-octaphosphate heptahydrate.

phosphates are shown in Figure 2. The position of the HPLC peak of the product is in accord with that of cyclo-octaphosphate shown in a previous paper [20]. From these results, the product was concluded to be sodium cyclo-octaphosphate heptahydrate,

$(\text{NaPO}_3)_8 \cdot 7\text{H}_2\text{O}$. X-ray diffraction data of the cyclo-octaphosphate are presented in Table 3, together with those of sodium cyclo-octaphosphate hexahydrate, $(\text{NaPO}_3)_8 \cdot 6\text{H}_2\text{O}$, which is described in a JCPDS card, No. 28-1127. The cyclo-octaphosphate was stable at room temperature (15° to 30°C) and was easily soluble in water.

FIGURE 2 HPLC profiles of polyphosphates. P₁: Orthophosphate, P₂: diphosphate, P₃: triphosphate, P_{3m}: cyclo-triphosphate, P_{4m}: cyclo-tetraphosphate, P_{6m}: cyclo-hexaphosphate, P_{8m}: cyclo-octaphosphate (product obtained in this study).



TG-DTA Measurement

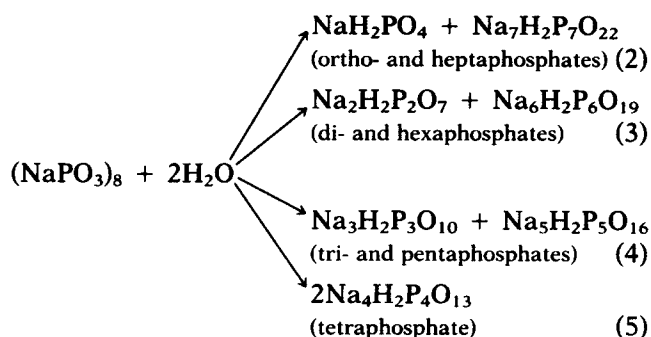
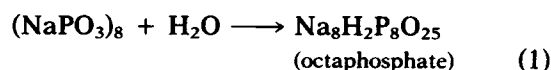
TG and DTA curves of sodium cyclo-octaphosphate heptahydrate are shown in Figure 3. The thermal products (as numbered in Figure 3) were taken out of a furnace and subjected to further analysis in order to study thermal reactions of the cyclo-octaphosphate. The results of chemical analysis and XRD measurement of the thermal products are listed in Table 4. The ³¹P NMR spectra of the thermal products are shown in Figure 4. The first large endothermic reaction accompanying a large amount of weight loss at about 150°C seemed to be due to

TABLE 3 X-ray Diffraction Data of Cyclo-octaphosphate

| $(\text{NaPO}_3)_8 \cdot 7\text{H}_2\text{O}$ (this study) | | $(\text{NaPO}_3)_8 \cdot 6\text{H}_2\text{O}$ (JCPDS 28-1127) | |
|---|---------|--|---------|
| $d(\text{\AA})$ | hkl_0 | $d(\text{\AA})$ | hkl_0 |
| 10.593 | 10 | 5.348 | 100 |
| 6.402 | 15 | 6.329 | 80 |
| 5.310 | 100 | 5.208 | 60 |
| 5.229 | 16 | 4.902 | 60 |
| 4.891 | 4 | 4.808 | 60 |
| 3.633 | 15 | 3.937 | 60 |
| 3.542 | 4 | 3.650 | 60 |
| 3.445 | 7 | 3.344 | 60 |
| 3.229 | 4 | 3.195 | 60 |
| 3.195 | 13 | 3.077 | 60 |
| 3.023 | 6 | 2.959 | 60 |
| 2.869 | 11 | 2.907 | 60 |
| 2.741 | 19 | 2.625 | 60 |
| 2.654 | 7 | 8.264 | 40 |
| 2.621 | 13 | 3.257 | 40 |
| 2.300 | 8 | 2.762 | 40 |
| 2.212 | 3 | 2.494 | 40 |
| 2.151 | 5 | 2.439 | 40 |
| 2.126 | 6 | | |
| 1.973 | 8 | | |
| 1.771 | 3 | | |
| 1.668 | 6 | | |

removal of water of crystallization of the cyclo-octaphosphate. The result listed in Table 4 indicates that the cyclo-octaphosphate had been converted to phosphates with shorter or longer chain lengths. The formation of phosphates with shorter chain

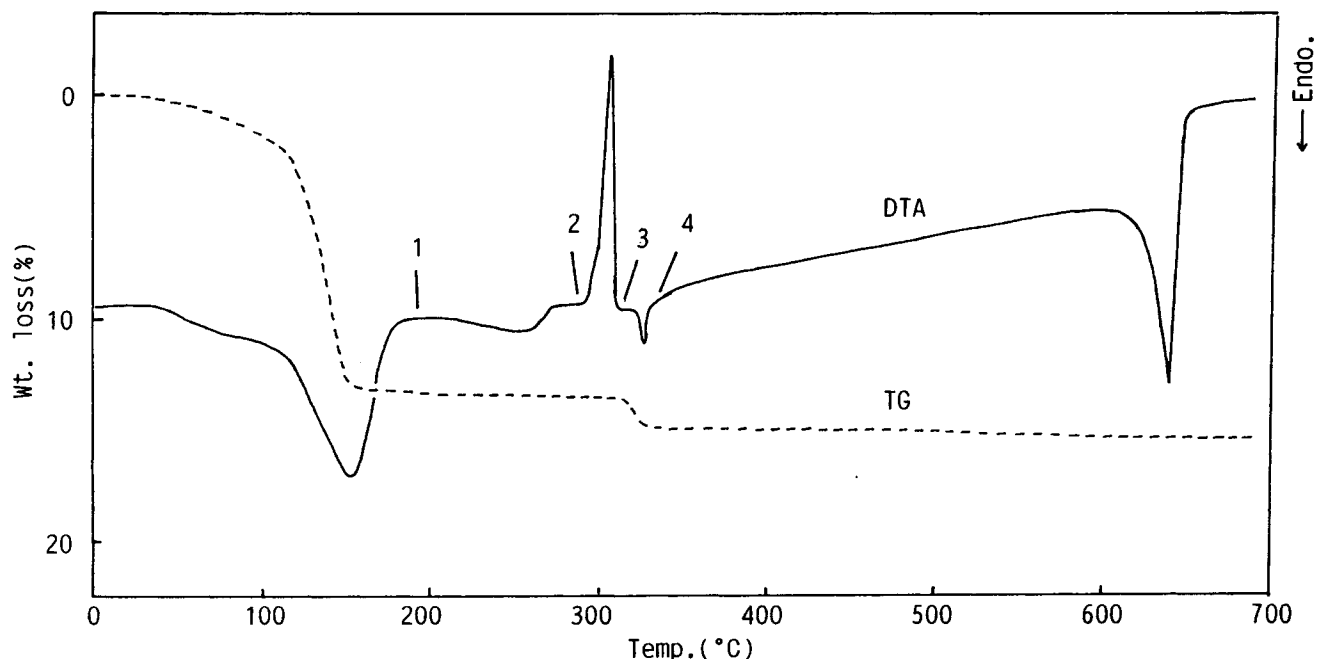
lengths can be explained by hydrolysis of the cyclo-octaphosphate as follows:



Reorganization of the cyclo-octaphosphate to high-polyphosphate can be written as follows:



^{31}P NMR peaks at about $\delta - 10$ and -22 are due to end and middle PO_4 groups, respectively. The NMR data of thermal product 1 shown in Figure 4 agree well with those shown in Table 4. The thermal product 1 was X-ray diffractometrically amorphous. Because the cyclo-octaphosphate content in the thermal product 2 decreased, the above conversion to phosphates with shorter or longer chain lengths seemed to proceed by successive heating up to 300°C . After a large exothermic reaction at about 310°C , the thermal product 3 showed an XRD pattern of

FIGURE 3 TG and DTA curves of $(\text{NaPO}_3)_8 \cdot 7\text{H}_2\text{O}$.

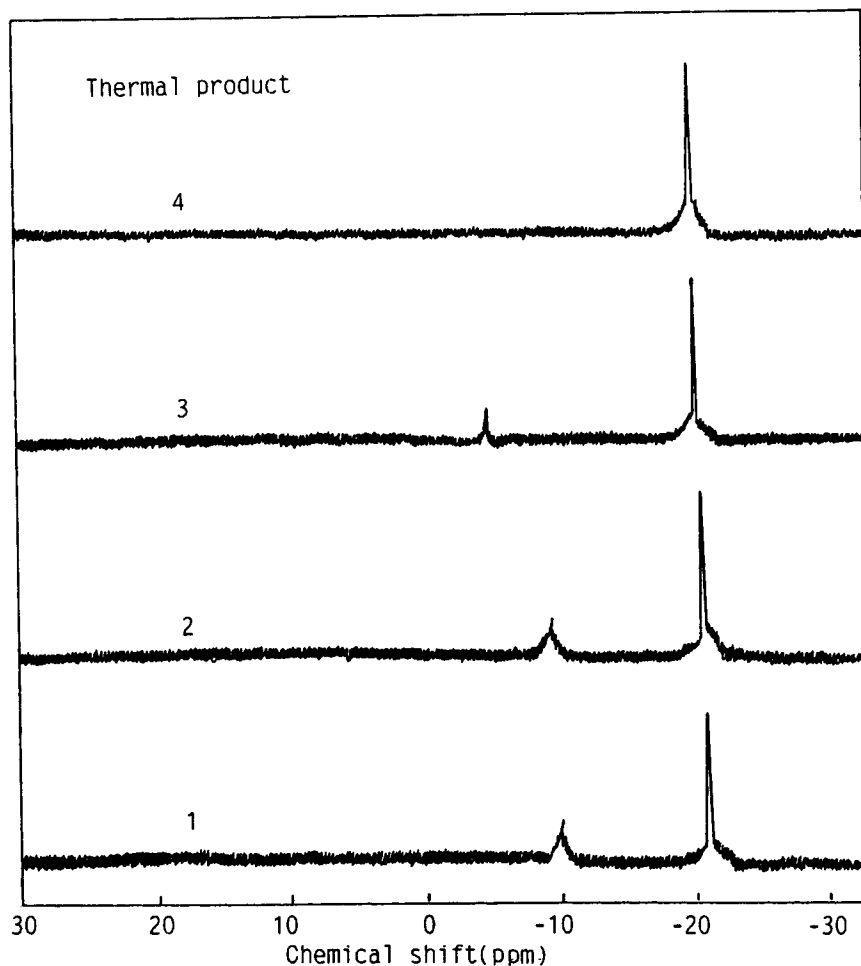


FIGURE 4 ^{31}P NMR spectra of the thermal products of $(\text{NaPO}_3)_8 \cdot 7\text{H}_2\text{O}$.

sodium cyclo-triphosphate, $(\text{NaPO}_3)_3$. Therefore, the exotherm is due to crystallization of the amorphous phosphates to sodium cyclo-triphosphate. The phosphate content of thermal product 3 in Table 4 supports the conclusion. A ^{31}P NMR peak at about $\delta -5$ is associated with the end PO_4 group of diphosphate, and an NMR peak at about $\delta -10$ is caused by the end PO_4 group of the phosphates with chain lengths longer than that of diphosphate. The phosphate content of thermal product 3 in Table 4

is in good agreement with the ^{31}P NMR data of the thermal product. A small endothermic reaction accompanying a small amount of weight loss was observed after the exotherm associated with the formation of sodium cyclo-triphosphate. Thermal product 4 showed an XRD diagram of sodium cyclo-triphosphate, but cyclo-triphosphate content decreased and highpolyphosphate content increased. Accordingly, condensation of the phosphates produced by Equations 1 to 5 and reorganization

TABLE 4 Composition of the Thermal Products

| Thermal product | Temp (°C) | XRD | Phosphates (P%) | | | | | |
|-----------------|-----------|---------------------|-----------------|------|-----|-----------|------------|--------|
| | | | Ortho | Di | Tri | Cyclo-tri | Cyclo-octa | Higher |
| 1 | 180 | AM ^a | 2.2 | 4.4 | 4.8 | — | 61.3 | 27.3 |
| 2 | 270 | AM | 4.1 | 6.7 | 3.5 | 12.4 | 10.8 | 62.5 |
| 3 | 310 | $(\text{NaPO}_3)_3$ | 3.1 | 10.0 | 0.2 | 85.2 | 1.5 | — |
| 4 | 340 | $(\text{NaPO}_3)_3$ | 3.4 | 6.2 | 0.3 | 63.1 | — | 27.0 |

^a AM, amorphous substance.

of the cyclo-triphosphate to high-polyphosphates according to reactions similar to that shown in Equation 6 seemed to occur through the endotherm. The degree of polymerization of the high-polyphosphates was considered to be high because the thermal product did not show any ^{31}P NMR peak associated with the end PO_4 group of polyphosphates. The last large endotherm was caused by fusion of the polyphosphates produced by heating to about 630°C .

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