The Synthesis and Thermal Reorganization of Lithium Heptasodium *cyclo*-Octaphosphate

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Lithium heptasodium *cyclo*-octaphosphate hexahydrate, $LiNa_7P_8O_{24}\cdot 6H_2O$, has been prepared by heating lead *cyclo*-tetraphosphate tetrahydrate at 340 °C for 20 min, dissolving the thermal product in a 3% aqueous solution of tetrasodium ethylenediaminetetraacetate, and then crystallizing by the addition of lithium chloride and methanol to the solution. When the *cyclo*-octaphosphate was heated above 180 °C, it decomposed to produce phosphates with chain lenghts shorter and longer than that of the *cyclo*-octaphosphate. The thermally produced phosphates were reorganized to sodium *cyclo*-triphosphate and a small amount of insoluble polyphosphates by heating at about 300 to 350 °C. The phosphates melted at about 620 °C.

Among the many kinds of polyphosphates, di-, tri-, tetra-, penta-, *cyclo*-tri-, *cyclo*-tetra, *cyclo*-penta, *cyclo*-hexa-, *cyclo*-octa, and long-chain polyphosphates have been prepared and isolated. Polyphosphates have been used for agricultural treatment, detergents, food additives, chemical manufacturing, the ceramics industry, etc.[1–3] A dry process has usually been used for the preparation of oligo- and polyphosphates. The dry process is not favorable for the preparation of unstable polyphosphates and other techniques have been developed for making phosphates.[4] Although the synthesis of *cyclo*-octaphosphate has been reported by Schülke,[5] it has been found by the present authors that the method does not give the highest yield for the preparation of *cyclo*-octaphosphate. A modified process to make *cyclo*-octaphosphate and a thermal reorganization of the *cyclo*-phosphate were studied in the present work.

Experimental

Preparation of *cyclo*-Octaphosphate. Sodium *cyclo*-tetraphosphate tetrahydrate was made by hydrolyzing α-P_2O_5 in water cooled with ice to below 15 °C, and then adding sodium chloride to the solution. This method was modified from the original, which was proposed by Bell et al.[6] Lead *cyclo*-tetraphosphate tetrahydrate was prepared by dissolving the sodium *cyclo*-tetraphosphate in water and adding an aqueous lead nitride solution to the *cyclo*-phosphate solution. According to Schülke, sodium *cyclo*-octaphosphate hexahydrate can be obtained by heating the lead *cyclo*-tetraphosphate at 150 °C for 2 h, at 300 to 350 °C for less than 30 min, dissolving the thermal product in water together with sodium sulfide, and then adding ethanol into the resulting solution. The present authors found that the thermal product obtained with the heating process by Schülke contained only about 20 P% of *cyclo*-octaphosphate and that it was necessary to study the effects of heating temperature, heating time, and atmospheric moisture on the phosphate composition of the thermal product. It was also required to improve the wet process in order to purify the *cyclo*-octaphosphate from the thermal product.

Chemical Analysis. An atomic-absorption analysis was used for the determination of sodium and lithium ions in a sample solution by using a Shimadzu atomic-absorption spectrophotometer (AA-680). Phosphorus was determined by the Molybdenum Blue method. The water of crystallization was determined by the heating loss.

High-Performance Liquid Chromatography (HPLC). An HPLC technique was employed for the separation and determination of the phosphate species in a sample solution.[7] Aqueous 0.24, 0.40, and 0.60 mol dm^{-3} solutions of potassium chloride were used as eluents at a flow rate of 1 cm^3 min^{-1}.

^{31}P NMR Measurement. ^{31}P NMR spectrum of an aqueous phosphate solution was taken by a JNM-GX270 instrument. Phosphoric acid (85%) was used as a reference with downfield positive shifts.

X-Ray Diffractometry (XRD). An X-ray diffraction diagram of a powder sample was measured with nickel-filtered Cu $K\alpha$ radiation by using a Rigaku X-ray diffractometer (RAD-1B).

Thermogravimetry (TG) and Differential Thermal Analysis (DTA). TG-DTA measurements were carried out in air using a Rigaku TG-DTA apparatus with a heating rate of 5 °C min^{-1}.

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	9.3
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 that of pentaphosphate. b) Polyphosphates with chain lengths longer than that of tetraphosphate.

Results and Discussion

Heating Temperature, Heating Time, and Humidity. Lead *cyclo*-tetraphosphate tetrahydrate was heated at a temperature between 300 and 460 °C for 20 min in dry air. The dry air was prepared by passing air through glass tubes containing silica gel and phosphorus pentaoxide. The phosphate composition of the thermal product is listed in Table 1. The results show 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%.

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	9.3
30	9.6	—	77.7	12.7

a) Polyphosphates with chain lengths shorter than that of pentaphosphate. b) Polyphosphates with chain lenghts longer than that of tetraphosphate.

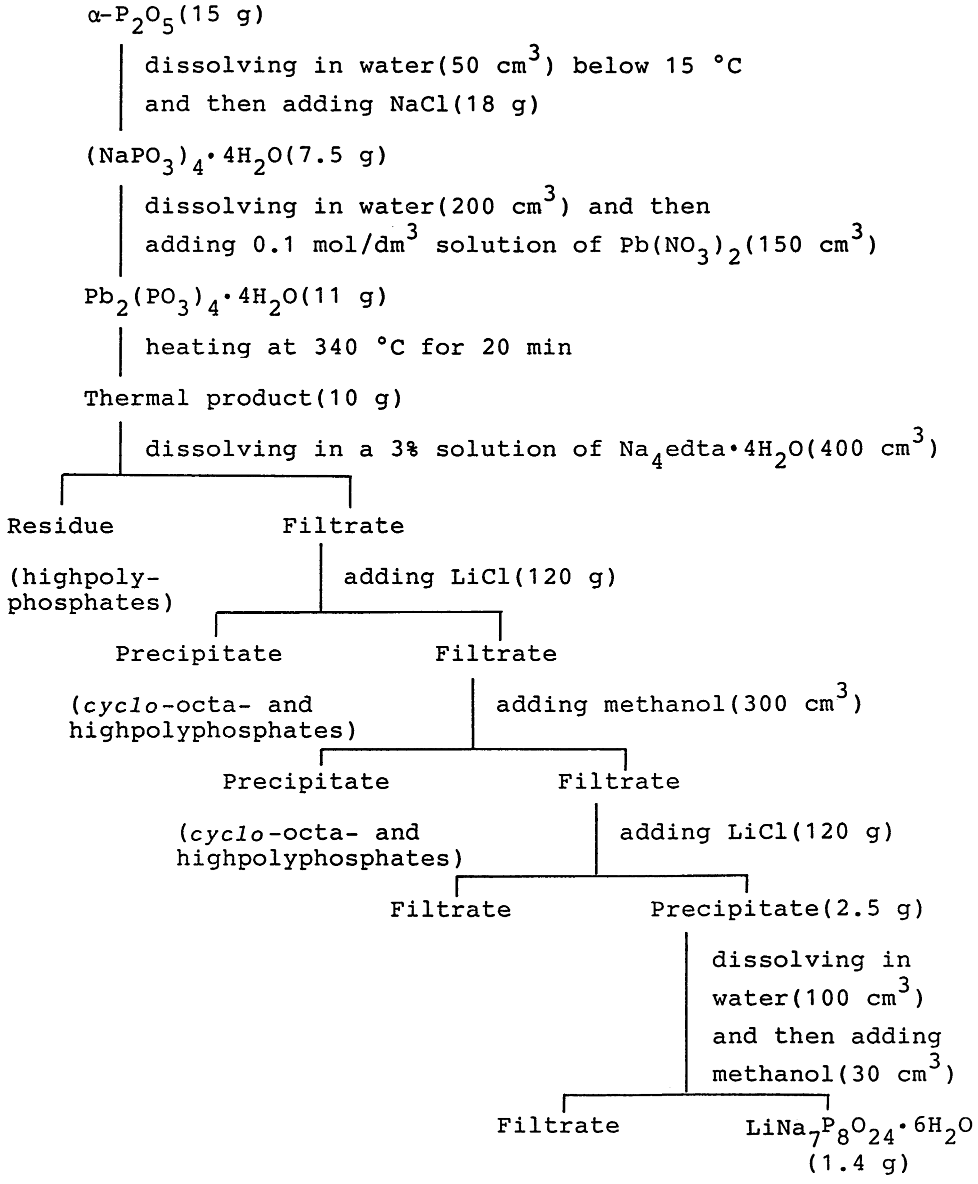

Fig. 1. Synthetic process of *cyclo*-octaphosphate.

At a lower temperature, the content of polyphosphates with shorter chain lengths increased. The content of polyphosphates with longer chain lengths increased at a higher temperature. Schülke described in his paper that the lead *cyclo*-tetraphosphate was preheated at 150 °C for 2 h, but there was not any need to heat the lead *cyclo*-tetraphosphate at that temperature. The dependence on the 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 seemed to be appropriate. In the case of preparation in air without drying, the content of highpolyphosphates increased at temperatures between 300 and 460 °C.

Purification of the *cyclo*-Octaphosphate. According to Schülke, the thermal product produced by heating the lead *cyclo*-tetraphosphate at between 300 and 350 °C dissolved in water. The thermal product obtained by heating the lead *cyclo*-tetraphosphate at 340 °C in this study dissolved only slightly in water and was soluble in an aqueous solution of ethylenediaminetetraacetate. The thermal product (10 g) was dissolved in 400 cm^3 of an aqueous 3% tetrasodium ethylenediaminetetraacetate tetrahydrate($Na_4edta\cdot 4H_2O$) solution, and a residue (highpolyphosphates) was filtered off. Lithium chloride (120 g) was added to the filtrate and a white precipitate (*cyclo*-octa- and highpolyphosphates) was removed by filtration. Methanol (300 cm^3) was added to the filtrate and a precipitate was filtered off. Lithium chloride (120 g) was put in the filtrate, resulting in a white precipitate (2.5 g), which was then dissolved in 100 cm^3 of water; methanol (30 cm^3) was added to the solution. About 1.4 g of a white precipitate was filtered off, washed with methanol, and dried in an air bath at 50 °C. This process is shown in Fig. 1. Found: P, 28.7; Na, 18.1; Li, 0.6; H_2O, 11.5%. Calcd for $LiNa_7P_8O_{24}\cdot 6H_2O$: P, 27.3; Na, 17.7; Li, 0.8; H_2O, 11.9%. The ^{31}P NMR spectrum of the product showed only one peak due to a middle PO_4 group at −21.5 ppm. This result indicates that the product is cyclic phosphate. The HPLC peaks of the product and several known phosphates (ortho-, di-, tri-, *cyclo*-tri-, *cyclo*-tetra-, and *cyclo*-hexaphosphates) are shown in Fig. 2. The position of the HPLC peak of the product was in accord with that of *cyclo*-octaphosphate, as shown in another paper.[8] According to these results, it was concluded that the product was lithium heptasodium *cyclo*-octaphosphate hexahydrate, $LiNa_7P_8O_{24}\cdot 6H_2O$. X-Ray diffraction data of the product are presented in Table 3, together with those of lithium *cyclo*-octaphosphate hexahydrate (JCPDS card, No. 28-0577). The *cyclo*-octaphosphate was stable at room temperature (15 to 30 °C) and had low solubility to water (about 1.9 at 20 °C).

Table 3. X-Ray Diffraction Data of *cyclo*-Octaphosphates

$LiNa_7P_8O_{24}\cdot 6H_2O$ (this study)		$(LiPO_3)_8\cdot 6H_2O$ (JCPDS 28-0577)	
d(Å)	I/I_0	d(Å)	I/I_0
8.450	44	9.259	75
8.261	36	8.403	75
5.427	45	7.692	25
5.310	74	6.993	100
5.211	28	5.291	100
4.833	30	4.902	25
4.444	23	4.505	100
4.211	85	3.546	25
4.122	26	3.484	25
3.917	40	3.425	75
3.847	35	3.289	50
3.821	25	3.185	25
3.511	41	3.115	50
3.385	25		
3.240	67		
3.204	63		
2.983	48		
2.932	77		
2.855	35		
2.843	57		
2.804	43		
2.769	100		
2.710	79		
2.665	33		
2.455	37		
1.645	26		

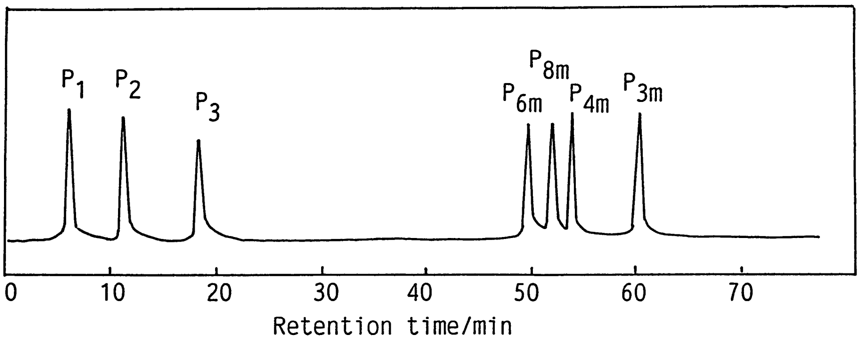

Fig. 2. HPLC profiles of polyphosphates.
P_1: Orthophosphate, P_2: diphosphate, P_3: triphosphate, P_{3m}: *cyclo*-triphosphate, P_{4m}: *cyclo*-tetraphosphate, P_{6m}: *cyclo*-hexaphosphate, P_{8m}: *cyclo*-octaphosphate (product obtained in this study).

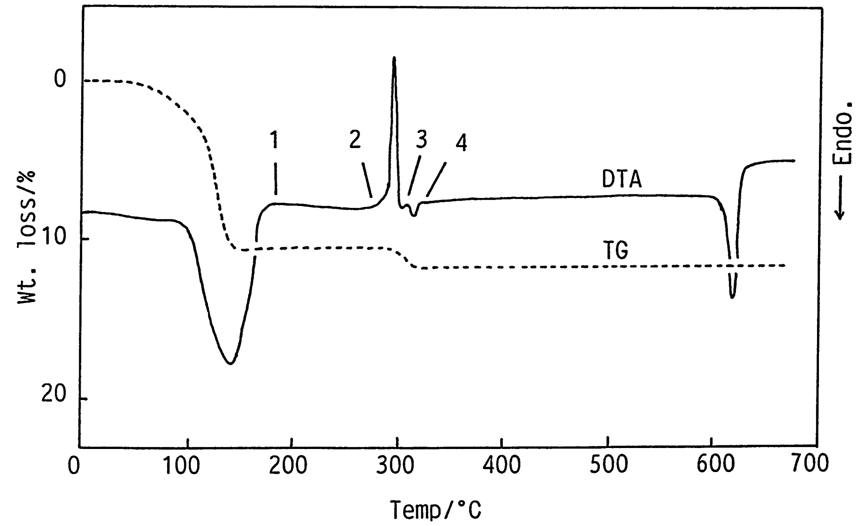

Fig. 3. TG and DTA curves of $LiNa_7P_8O_{24}\cdot 6H_2O$.

Table 4. Composition of the Thermal Products

Thermal product	Temp/°C	Wt. loss/%	XRD	Phosphates/P%						
				Ortho	Di	Tri	*cyclo*-Tri	*cyclo*-Hexa	*cyclo*-Octa	Higher
1	180	10.2	AM[a]	1.4	3.9	4.1	—	4.4	60.0	26.2
2	270	10.4	AM	1.0	2.1	2.6	12.4	3.8	30.7	47.4
3	310	10.4	$(NaPO_3)_3$	2.7	10.1	3.6	62.5	—	10.4	10.7
4	340	11.5	$(NaPO_3)_3$	0.4	1.0	0.8	93.3	—	2.5	2.0

a) AM stands for amorphous substance.

TG and DTA Measurements. TG and DTA curves of lithium heptasodium *cyclo*-octaphosphate hexahydrate are shown in Fig. 3. The thermal products (as numbered in Fig. 3) were removed from a furnace and subjected to further analysis in order to study thermal reactions within the temperature ranges. The chemical compositions of the thermal products are listed in Table 4. The first large endotherm accompanying a large weight loss seemed to be due to an elimination of the water of crystallization. The result in Table 4 shows that the decomposition of the *cyclo*-octaphosphate to phosphates with chain lengths longer and shorter than that of *cyclo*-octaphosphate occurs at the same time. The following thermal reactions can be written for the endothermic process:

$$(MPO_3)_8\cdot 8H_2O \longrightarrow (MPO_3)_8\cdot(8-x)H_2O \quad (0<x\leqslant 8) \qquad (1)$$

$$(MPO_3)_8 + H_2O \longrightarrow \underset{\text{(octaphosphate)}}{M_8H_2P_8O_{25}} \qquad (2)$$

$$\begin{array}{lll} & \nearrow MH_2PO_4 + M_7H_2P_7O_{22} & (3)\\ & \quad \text{(ortho- and heptaphosphates)} & \\ & \nearrow M_2H_2P_2O_7 + M_6H_2P_6O_{19} & (4)\\ (MPO_3)_8 + 2H_2O & \quad \text{(di- and hexaphosphates)} & \\ & \searrow M_3H_2P_3O_{10} + M_5H_2P_5O_{16} & (5)\\ & \quad \text{(tri- and pentaphosphates)} & \\ & \searrow 2M_4H_2P_4O_{13} & (6)\\ & \quad \text{(tetraphosphate)} & \end{array}$$

$$(MPO_3)_8 \longrightarrow \underset{\text{(}cyclo\text{-hexaphosphate)}}{4/3(MPO_3)_6} \qquad (7)$$

$$n(MPO_3)_8 \longrightarrow \underset{\text{(highpolyphosphates)}}{8(MPO_3)_n.} \qquad (8)$$

Here, M stands for sodium and/or lithium. Since the content of highpolyphosphates with chain lengths longer than that of octaphosphate was high at this step, thermal reaction 8 seemed to be preferencial. According to the successive heatings to 270 °C, the content of the highpolyphosphates increased even more. Reaction 8 was also considered to be preferable to the other degradations through heating. Thermal products 1 and 2 were X-ray diffractometrically amorphous. After a large exothermic change at about 300 °C, the *cyclo*-triphosphate content increased. The following reorganization can be responsible for the change:

$$(MPO_3)_n \longrightarrow n/3(MPO_3)_3. \qquad (9)$$

A small endothermic peak accompanying a small amount of weight loss was observed at about 330 °C. Thermal product 4 gave 93.3 P% of *cyclo*-triphosphate content and all other phosphate contents decreased through the heating. Therefore, reaction 9 progressed at this step, along with a small heating loss which may have been caused by the following condensation of the phosphates with hydrogen to *cyclo*-triphosphate:

$$M_nH_2P_nO_{3n+1} \longrightarrow n/3(MPO_3)_3 + H_2O. \qquad (10)$$

Thermal products 3 and 4 gave an X-ray diffraction diagram of sodium *cyclo*-triphosphate in accord with the phosphate composition given in Table 4. Since no other X-ray diffraction peaks were observed, phosphates containing lithium may be amorphous.

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