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The Synthesis and Thermal Behavior of Lithium *cyclo*-Hexaphosphate

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Lithium *cyclo*-hexaphosphate hexahydrate was made by heating a mixture of 85%-phosphoric acid and dilithium carbonate at an Li/P molar ratio of 1.4 at 200 (1 h), 275 (5 h), and then 420 °C (3 h). The thermal product was handled with a wet chemical method developed in this study. The *cyclo*-hexaphosphate was stable at room temperature (20—30 °C), while a small part of it decomposed to phosphates with shorter chain lengths above about 60 °C in air. The *cyclo*-hexaphosphate was transformed thermally to crystalline long-chain polyphosphates upon heating above 530 °C.

Some oligophosphates and long-chain polyphosphates have been made by the thermal condensation of orthophosphates. These polyphosphates have been used for water treatment, food additives, detergents, and so forth.[1] Griffith and Buxton have reported on the synthesis of lithium *cyclo*-hexaphosphate hexahydrate by heating a mixture of phosphoric acid and dilithium carbonate and then recrystallizing the *cyclo*-phosphate from the thermal product. They also indicated that the hydrated *cyclo*-phosphate could be dehydrated by heating at about 120 °C without decomposition.[2] The present authors followed up the method and found that there are several problems regarding the preparation of the hydrated and unhydrated *cyclo*-hexaphosphates. This paper describes the problems and an improvement in the preparation method for the *cyclo*-phosphate. The thermal property of the *cyclo*-phosphate was also studied.

Experimental

Preparation of Lithium *cyclo*-Hexaphosphate. According to Griffith and Buxton, a mixture of dilithium carbonate and 85%-phosphoric acid with an Li/P molar ratio of 1.4 was heated at 200 °C for 1 h and at 275 °C for 5—7 h; then, the resulting thermal product was dissolved in water and lithium *cyclo*-hexaphosphate hexahydrate was crystallized by adding methanol to the solution. The present authors found that it was difficult to prepare the *cyclo*-phosphate by this method and that it was necessary to study the effect of the mixing ratio of dilithium carbnate and 85%-phosphoric acid, the heating temperature, and the heating time for the distribution of phosphate species in the thermal product. It was also necessary to improve the wet process in order to purify the *cyclo*-phosphate from the thermal product.

Chemical Analysis. An atomic absorption analysis was used for a determination of any lithium ions in the sample solution by using a Shimadzu atomic absorption spectrophotometer (AA-646). Phosphorus was determined according to the Molybdenum Blue method.[3]

Paper Chromatography. A one-dimensional paper-chromatographic separation was employed by using acidic (for the separation of chain phosphates) and basic (for the separation of ring phosphates) solvents.[4] A sample (0.1 g) was dissolved in 10 cm^3 of a 6% aqueous disodium dihydrogen ethylenediaminetetraacetate dihydrate (Na_2H_2-edta·$2H_2O$) solution. The solution (8 mm^3) was spotted on Toyo No. 51A filter paper (2 by 50 cm). The development was run at 3 °C for 2 d.

Colorimetric Measurement of Phosphates. Every individual spot on the chromatogram was cut at its demarcation line and put into a 100-cm^3 beaker containing 10 cm^3 of 0.1 mol dm^{-3} aqueous ammonia. The phosphate extracted in aqueous ammonia was determined colorimetrically by a method described in our previous paper.[5]

HPLC Analysis. An HPLC technique (developed by Yoza) was also used for a separation and determination of any phosphate species in a sample solution.[6] Aqueous 0.26- and 0.40-mol dm^{-3} solutions of potassium chloride were run at a flow rate of 1 cm^3 s^{-1}.

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

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

TG-DTA Measurement. The TG-DTA measurement was used to study the thermal behavior of the product by using a Cho Balance TRDA-H apparatus with the heating rate of 5 °C min^{-1} in air.

Results and Discussion

Li/P Molar Ratio and Reaction Temperature. The process of the synthesis of *cyclo*-hexaphosphate developed by Griffith and Buxton is shown in Fig. 1. Mixtures of 85%-orthophosphoric acid and dilithium carbonate with Li/P ratios of 1.0—1.5 were heated in the same manner as that of Griffith and Buxton. The compositions of the phosphate species of these thermal products are shown in Table 1. (The values listed in Tables 1—4 are average values for, at least, three times.) The main product was high polyphosphate or diphosphate. The content of *cyclo*-hexaphosphate was at most 19.0% at an Li/P ratio of 1.4. The resulting thermal products were again heated at 350 or 420 °C for 3 h. The compositions of the phosphate species of the thermal products are listed in Tables 2 and 3, respectively. The content of *cyclo*-hexaphosphate increased when the thermal products were reheated at 350 and 420 °C. The *cyclo*-phosphate content at 420 °C was higher than that at 350 °C. The best Li/P ratio was 1.4, in agreement with the result of Griffith

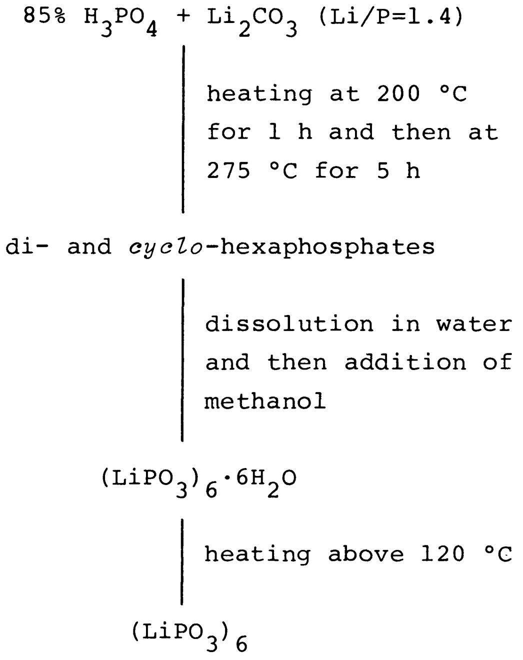

Fig. 1. Synthetic process of *cyclo*-hexaphosphate by Griffith and Buxton.

Table 1. Compositions of the Thermal Products Heated at 200 °C for 1 h and at 275 °C for 5 h

Li/P	Phosphates/P%				
	Ortho	Di	Tri	*cyclo*-Hexa	Higher
1.0	3.9	4.8	—	—	91.3
1.1	3.4	29.6	2.8	—	64.2
1.2	—	45.0	—	11.6	43.4
1.3	—	68.0	—	13.5	18.5
1.4	—	74.7	—	19.0	6.3
1.5	—	81.4	—	11.5	7.1

Table 2. Compositions of the Thermal Products Heated at 200 °C for 1 h, at 275 °C for 5 h, and then at 350 °C for 3 h

Li/P	Phosphates/P%				
	Ortho	Di	Tri	*cyclo*-Hexa	Higher
1.0	—	—	—	—	100
1.1	—	11.8	—	2.9	85.3
1.2	—	18.6	—	16.1	65.3
1.3	—	36.2	—	36.4	27.4
1.4	—	31.0	—	35.2	33.8
1.5	—	33.9	—	31.3	34.8

Table 3. Compositions of the Thermal Products Heated at 200 °C for 1 h, at 275 °C for 5 h, and then at 420 °C for 3 h

Li/P	Phosphates/P%				
	Ortho	Di	Tri	*cyclo*-Hexa	Higher
1.0	—	—	—	—	100
1.1	—	13.8	—	—	86.2
1.2	—	22.6	—	15.3	62.1
1.3	—	28.1	—	39.5	32.4
1.4	—	29.6	—	44.4	26.0
1.5	—	37.2	—	25.1	37.7

Table 4. The Effect of Heating Temperature on the Composition of the Thermal Product with Li/P Ratio of 1.4[a)]

t/°C	Phosphates/P%				
	Ortho	Di	Tri	*cyclo*-Hexa	Higher
300	—	63.7	—	26.1	10.7
320	—	37.1	—	35.5	27.4
350	—	31.0	—	35.2	33.8
370	—	27.7	—	43.7	28.6
400	—	29.9	—	40.0	30.1
420	—	29.6		44.4	26.0
450	—	28.1	—	33.3	38.6

a) The thermal product was preheated at 200 °C for 1 h and at 275 °C for 5 h.

and Buxton. The effect of the reaction temperature on the content of the *cyclo*-phosphate was studied for the thermal product with an Li/P ratio of 1.4 (prepared by Griffith and Buxton's method). The results are shown in Table 4. The best reaction temperature seemed to be 420 °C. The either product at a temperature higher or lower than 420 °C showed a decrease in the *cyclo*-phosphate content.

Purification of the *cyclo*-Hexaphosphate. The highest content of the *cyclo*-phosphate in the thermal products was about 45% and a purification of the *cyclo*-phosphate was required. Griffith and Buxton described how *cyclo*-phosphate was purified by dissolving the thermal product in water and then adding methanol to the solution. The thermal product obtained by heating at 420 °C for 3 h did not dissolve in water, but dissolved in a 1% ethylenediaminetetraacetic acid (H_4edta) solution of pH 9. The pH of the solution was controlled with a 1-mol dm^{-3} aqueous lithium hydroxide solution. The thermal product (7.3 g) was dissolved in 100 cm^3 of a H_4edta solution and the residue (di- and highpolyphosphates) was filtered off. Methanol (110 cm^3) was added to the filtrate and a white precipitate was removed by filtration. Lithium chloride (8 g) was added to the filtrate. A small amount of white precipitate (*cyclo*-hexa- and highpolyphosphates) was filtered off; then, lithium chloride (18.5 g) was added to the filtrate. A white precipitate was obtained by filtration, washed with 75 vol% aqueous acetone, and dried in air. The process is shown in Fig. 2. Found: P, 29.5; Li, 6.8;

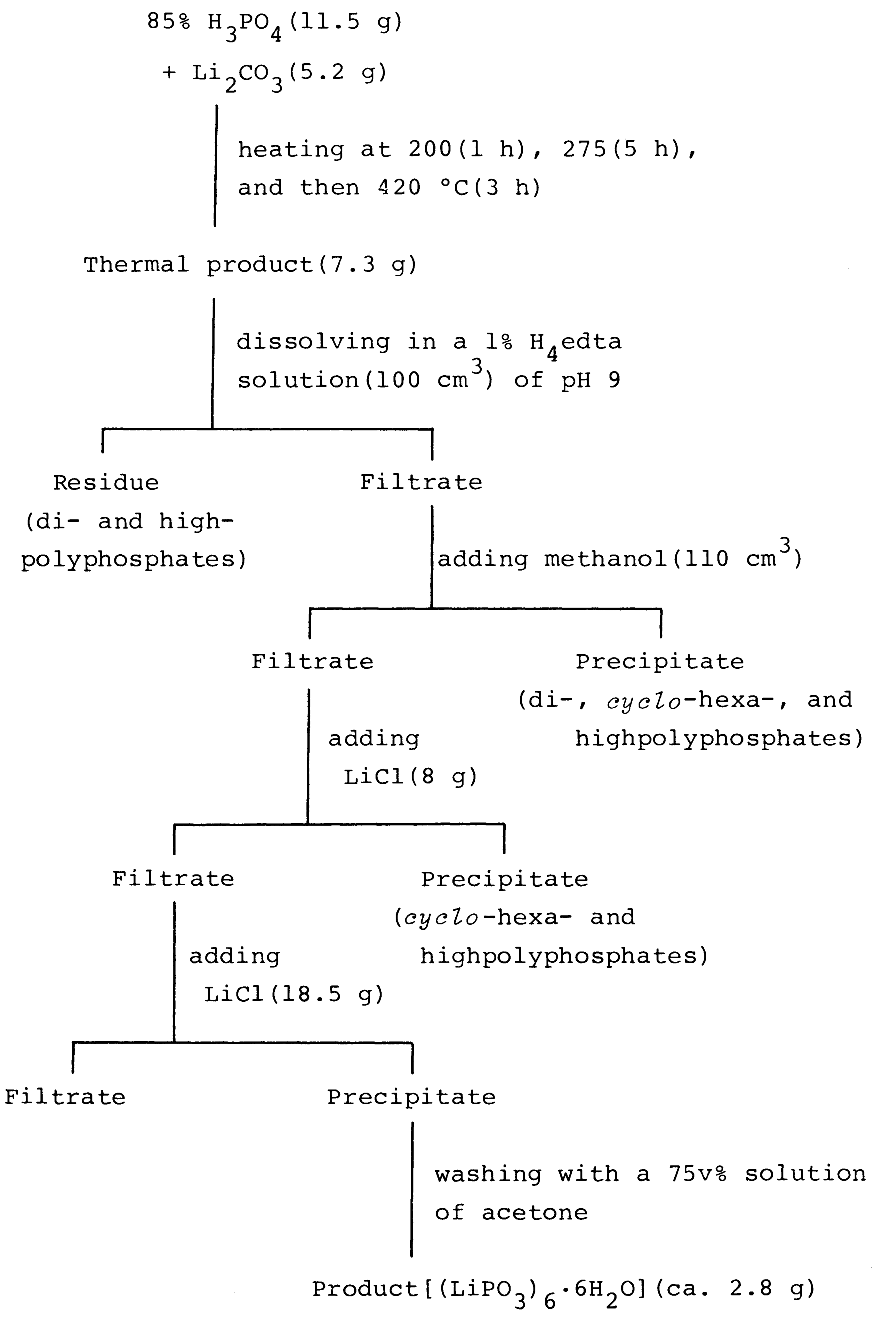

Fig. 2. Synthetic process of *cyclo*-hexaphosphate hexahydrate.

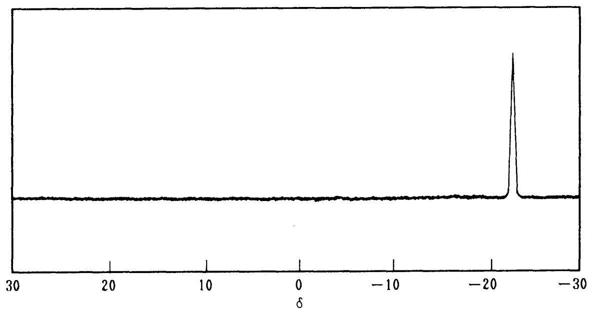

Fig. 3. ^{31}P NMR spectrum of $(LiPO_3)_6 \cdot 6H_2O$.

H_2O, 17.5%. Calcd for $(LiPO_3)_6 \cdot 6H_2O$: P, 29.8; Li, 6.7; H_2O, 17.3%. The ^{31}P NMR spectrum of the product shown in Fig. 3 exhibited only one singlet at −22.6 ppm and the peak is due to a middle-PO_4 group. The product also gave only one HPLC peak in the profile. Accordingly, the product is lithium *cyclo*-hexaphosphate hexahydrate, $(LiPO_3)_6 \cdot 6H_2O$. The X-ray diffraction data of *cyclo*-phosphate are presented in Table 5, together with the data of Griffith and Buxton. They gave a rough order of intensity of the peak without the I/I_0 value. The yield of the product was about 30%. The *cyclo*-phosphate was stable at room

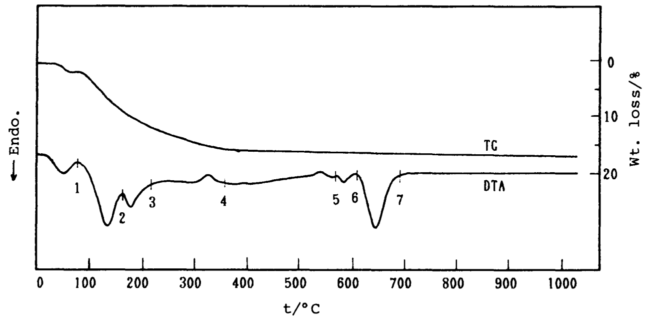

Fig. 4. TG and DTA curves of $(LiPO_3)_6 \cdot 6H_2O$.

Table 5. X-Ray Diffraction Data of $(LiPO_3)_6 \cdot 6H_2O$

(This study)		(Griffith and Buxton)	
d/Å	I/I_0	d/Å	I/I_0
7.22	28	6.91	—
6.67	5	5.53	—
6.28	100	4.39	—
5.47	45	3.40	—
4.68	40	2.96	—
4.23	60		
4.18	7		
4.09	45		
3.92	60		
3.83	4		
3.74	4		
3.71	6		
3.62	11		
3.53	35		
3.13	30		
2.94	80		
2.90	13		
2.88	16		
2.72	30		
2.63	4		
2.58	7		
2.41	6		
2.39	4		
2.35	6		
2.33	20		
2.26	5		

temperature (20—30 °C), with a solubility of 3.03 at 20 °C.

TG-DTA Measurement. TG and DTA curves of lithium *cyclo*-hexaphosphate hexahydrate are shown in Fig. 4. The thermal products (as numbered in Fig. 4) were taken out of a furnace and subjected to further analysis in order to study the thermal reactions of the *cyclo*-phosphate. The first endothermic peak accompanying a small amount of weight loss seemed to be due to the removal of the adsorbed water, since the product showed an X-ray diffraction pattern of $(LiPO_3)_6 \cdot 6H_2O$. However, the results listed in Table 6 indicate that a small part of the *cyclo*-phosphate decomposed to diphosphate:

$$(LiPO_3)_6 + 3H_2O \longrightarrow 3Li_2H_2P_2O_7. \qquad (1)$$

The water in the above equation might have come from the water of crystallization of the *cyclo*-phosphate. The next big endothermic reaction accompanying the weight loss was considered to be due to an elimination of the water of crystallization along with a simultaneous decomposition of the *cyclo*-phosphate. The third small endothermic peak accompanying the weight loss may have been caused by an elimination of the rest water of crystallization, and a condensation of the phosphates to phosphates with longer chain lengths, since the content of ortho-, di-, and triphosphate in the thermal product decreased and that of *cyclo*-hexaphosphate increased after the endothermic reaction. A small exothermic peak was observed at about 330 °C. As Table 6 shows, most parts of the thermal products of Nos. 2—4 were *cyclo*-hexaphosphate; the weight loss of thermal product No. 4 agrees well with the following dehydration:

$$(LiPO_3)_6 \cdot 6H_2O \longrightarrow (LiPO_3)_6 + 6H_2O. \qquad (2)$$

Thermal product No. 4 gave a different X-ray diffraction diagram than those of Nos. 2 and 3. Therefore, the exothermic reaction can be attributed to a transition of *cyclo*-hexaphosphate. The X-ray diffraction pattern of No. 4 agreed with that of anhydrous lithium *cyclo*-hexaphosphate by Griffith and Buxton. After the next exothermic reaction at about 530 °C, the

Table 6. Composition and Weight Loss of the Thermal Products of $(LiPO_3)_6 \cdot 6H_2O$

Sample No.	Wt. loss	X-Ray dif.	Phosphates/P%				
			Ortho	Di	Tri	*cyclo*-Hexa	Higher
1	2.8	SM	—	1.0		99.0	—
2	10.9	UK	1.1	1.9	3.4	93.6	—
3	13.4	UK	1.0	1.4	2.2	95.4	—
4	17.2	$(LiPO_3)_6$	—	2.0	—	98.0	—
5	17.3	$LiPO_3$ JCPDS 26-1177	—	6.6	—	7.1	86.3
6	17.3	JCPDS 26-1177	—	14.2	—	—	85.8
7	17.3	AM	—	—	—	—	100

SM, UK, and AM stand for the starting material, an unknown substance, and an amorphous species respectively.

crystalline *cyclo*-hexaphosphate transformed to crystalline lithium methaphosphate (highpolyphosphate). The thermal product was sintered through the next small endothermic reaction at about 590 °C. The metaphosphate melted at about 650 °C. Griffith and Buxton reported that the *cyclo*-hexaphosphate hexahydrate can be dehydrated by heating above 120 °C and pure anhydrous *cyclo*-hexaphosphate can be prepared. According to the above results, a samll part of the *cyclo*-hexaphosphate hexahydrate is decomposed to phosphates with shorter chain lengths by heating above about 60 °C and pure anhydrous *cyclo*-hexaphosphate can not be prepared by heating the hexahydrate.

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