

## Effect of Water Vapor on the Formation of Lithium *cyclo*-Hexaphosphate

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The effect of water vapor on the formation of lithium *cyclo*-hexaphosphate  $\text{Li}_6\text{P}_6\text{O}_{18}(\text{P}_{6m})$  from trilitium hydrogenpyrophosphate monohydrate  $\text{Li}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$  was investigated by means of DTA-TG, X-ray diffraction analysis, isothermal heating with electric furnace, and HPLC.  $\text{Li}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$  lost the water of crystallization at about  $180^\circ\text{C}$  to give anhydrous  $\text{Li}_3\text{HP}_2\text{O}_7$ . At  $300^\circ\text{C}$  the disproportionation of  $\text{Li}_3\text{HP}_2\text{O}_7$  anhydride to  $\text{Li}_4\text{P}_2\text{O}_7$  and  $\text{Li}_4\text{P}_4\text{O}_{12}$  ( $\text{P}_{4m}$ ) proceeded faster under humid conditions than under dry air, and subsequently  $\text{P}_{4m}$  increased with a decrease in  $\text{P}_2$  and soluble polyphosphates ( $\text{P}_{\text{poly}}$ ). At  $400^\circ\text{C}$ ,  $\text{P}_{4m}$  changed largely to  $\text{P}_{6m}$  under humid conditions. In these reaction processes, water plays an important role as catalyst in the cyclization by dehydration of the end group and in ring opening by attacking the P–O–P bond. At  $450^\circ\text{C}$ , the amounts of  $\text{P}_2$  and  $\text{P}_{6m}$  were almost equal under both humid and dry conditions, because all of  $\text{P}_{4m}$  thermally changed to  $\text{P}_{6m}$ .

It is well known that phosphates hydrolyze or condense on heating to form various kinds of phosphates.<sup>1–4)</sup> Some types of them, linear and cyclic phosphates, have been investigated from the viewpoint of their thermal behavior.<sup>5–21)</sup> These phosphates have been used for water treatment, as food additives, detergents, catalysts, and components of laser materials, and in phosphate glasses, and so forth.<sup>22–26)</sup> The practical importance of these phosphates has been reviewed.<sup>27)</sup>

In the syntheses of these phosphates, several factors including the nature of the metal, the temperature, the atmosphere, the time and rate of heating, and the state of the starting material, influence the structure and composition of the products. However, many works have been carried out on the thermal behavior of these phosphates without adequate consideration of the above-mentioned factors.

In a previous paper<sup>28)</sup> we reported that, when lead *cyclo*-tetrakisphosphate decomposed to lead *cyclo*-octaphosphate, the cyclic phosphates were prepared optimally at a low water-vapor pressure, while linear phosphates were produced at a high water-vapor pressure.

The synthesis and thermal behavior of formation of lithium *cyclo*-hexaphosphate was investigated by Griffith and Buxton in 1965.<sup>29)</sup> Schülke and Kayser reported a detailed formation mechanism in 1985.<sup>30)</sup>

Figure 1 shows the formation process of *cyclo*-hexaphosphate proposed by Schülke and Kayser.<sup>30)</sup>  $\text{Li}_3\text{HP}_2\text{O}_7$  changes to  $\text{Li}_4\text{P}_2\text{O}_7(\text{III})$  and  $\text{Li}_4\text{P}_4\text{O}_{12}(\text{II})$  by disproportionation at around  $300^\circ\text{C}$ , followed by the transformation of  $\text{Li}_4\text{P}_4\text{O}_{12}(\text{II})$  to  $\text{Li}_6\text{P}_6\text{O}_{18}(\text{I})$  at around  $400^\circ\text{C}$ . In spite of extensive works on the formation mechanism of *cyclo*-hexaphosphate, the yield of product exhibits a heavy scatter among the published results. A dominant cause for such a scatter appears to be a difference in the heating atmosphere from one experiment to another. In view of this, the effect of water vapor on the formation of lithium *cyclo*-hexaphosphate from trilitium hydrogenpyrophosphate monohydrate on heating was investigated in the present work.

### Experimental

**Chemicals.** Trilitium hydrogenpyrophosphate monohydrate  $\text{Li}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$  was prepared by the method given in the literature.<sup>30)</sup> Guaranteed reagent sodium pyrophosphate decahydrate ( $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) was used after double recrystallization. Other chemicals were of guaranteed reagent from Wako Chemical Industries, Ltd. and were used without further purification.

**Determination of Lithium, Phosphorus, and the Water of Crystallization.** Atomic absorption analysis was used for the determination of lithium ion in the sample solution with a Hitachi atomic absorption spectrophotometer Model 207. The total amount of phosphorus in phosphates was determined by absorptiometry after hydrolyzing the condensed phosphates with dilute hydrochloric acid. The condensed phosphates obtained by calcination were separated by HPLC, and then each phosphate was determined by the Molybdenum Blue Method.<sup>18,20,21,28,31)</sup> The amount of the water of crystallization was calculated from the weight loss in TG curves. Other analytical procedures and apparatus were essentially the same as those used in previous works.<sup>18,28)</sup>

### Results and Discussion

**Thermal Decomposition of the Phosphates Examined by DTA-TG.** Figure 2 shows the DTA-TG curves for

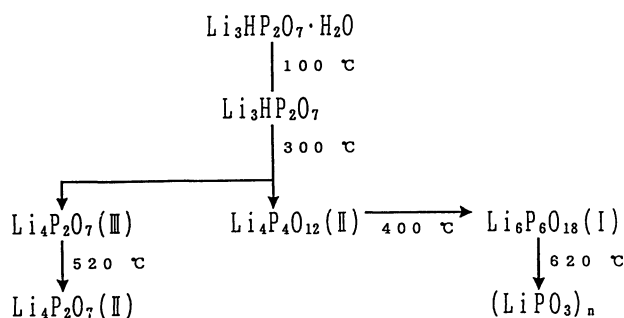


Fig. 1. Thermal dehydration processes of  $\text{Li}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$  as described by Schülke and Kayser.

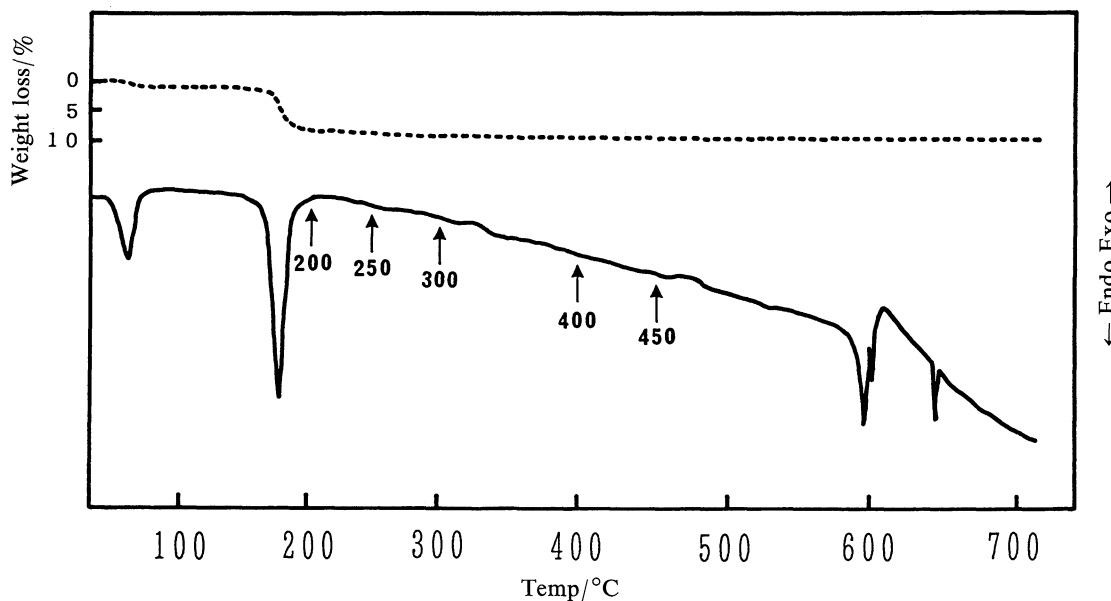


Fig. 2. DTA-TG curves for  $\text{Li}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ . Solid line: DTA, dotted line: TG.

$\text{Li}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$  at atmospheric pressure. Endothermic peaks are noted at about 50, 180, 600, and 640°C. From the HPLC analytical results, the first endothermic peak accompanying a small weight loss at 50°C seemed to be due to liberation of absorbed acetone, and/or methanol, and/or water, since no change took place in the X-ray diffraction pattern of  $\text{Li}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ . The second endothermic peak with a large weight loss at 180°C was attributed to elimination of the water of crystallization. HPLC analysis showed that anhydrous  $\text{Li}_3\text{HP}_2\text{O}_7$  alone was present in the sample heated at 200°C. No change in the TG curve occurred at temperatures above 300°C. From the HPLC analysis, the products were found to be  $\text{P}_2$ ,  $\text{P}_{4m}$ , and  $\text{P}_{\text{poly}}$  at 300°C,  $\text{P}_2$ ,  $\text{P}_{4m}$ , and  $\text{P}_{6m}$  at 400°C, and  $\text{P}_2$  and  $\text{P}_{6m}$  at 500°C. The sample melted at around 600°C. HPLC results indicated that  $\text{P}_{6m}$  and  $\text{P}_2$ , and  $\text{P}_{4m}$  and  $\text{P}_2$  were present before and after the endothermic peak at 600°C, respectively. Lithium metaphosphate (polymetaphosphate) was observed after the endothermic peak at 640°C.

**Isothermal Change.** Although the DTA-TG curves do not exhibit definite peaks in the 200–500°C region in Fig. 2,  $\text{P}_2$  gradually changed to  $\text{P}_{4m}$  and/or  $\text{P}_{6m}$  and/or  $\text{P}_{\text{poly}}$ . Therefore, the influence of water vapor on the thermal decomposition was examined by heating  $\text{Li}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$  at 200, 250, 300, 400, or 450°C for 1 h in air of 0 or 90% (at 25°C) relative humidity. Figure 3 shows the X-ray diffraction patterns of the sample heated in dry air. In the 200–300°C region, the diffraction lines of  $\text{Li}_3\text{HP}_2\text{O}_7$  anhydride are dominant. At 400°C, the characteristic diffraction lines of  $\text{P}_2(\text{III})$  at  $2\theta=21.2^\circ$ , and  $\text{P}_{4m}(\text{II})$  at  $2\theta=17.5, 26.8,$  and  $30.3^\circ$  began to appear. At 450°C, the diffraction lines of  $\text{P}_{4m}(\text{II})$  disappeared, and those of  $\text{P}_{6m}(\text{I})$  at  $2\theta=18.6, 19.2, 22.4, 23.7,$  and  $33.6^\circ$ , and  $\text{P}_2(\text{II})$  at  $21.2, 27.4, 28.5, 35.6,$  and

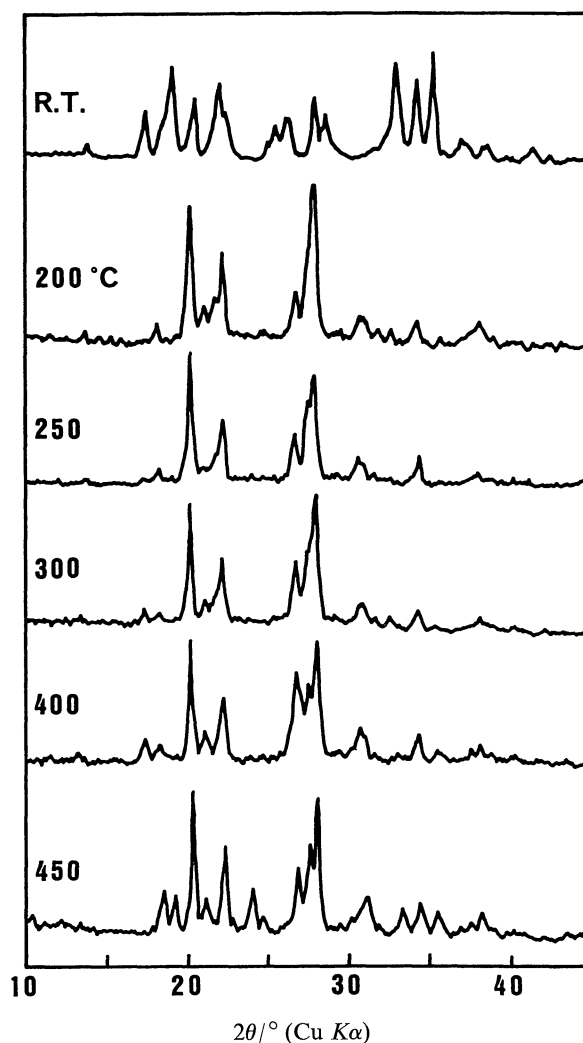


Fig. 3. X-Ray diffraction patterns of products in the course of heating. Sample:  $\text{Li}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ , relative humidity: 0%. R.T. is room temperature.

Table 1. Changes in the Amounts of Phosphates (Starting Material:  $\text{Li}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ )

Temp/°C	Compound <sup>a)</sup> R.H. <sup>b)</sup> /%	P <sub>2</sub>	P <sub>4m</sub>	P <sub>6m</sub>	P <sub>poly</sub>
		%	%	%	%
200	0%	93.5			6.5
	90%	96.5			3.5
250	0%	88.0	7.9		4.1
	90%	90.1	8.7		1.2
300	0%	79.4	15.9		4.7
	90%	69.7	28.4	1.9	
400	0%	66.3	30.8	2.9	
	90%	65.7	17.9	16.4	
450	0%	65.0		35.0	
	90%	65.1		34.9	

a) P<sub>4m</sub>, P<sub>6m</sub>, and P<sub>poly</sub> represent *cyclo*-tetra-, *cyclo*-hexa-, and polyphosphates, respectively. P<sub>2</sub> represents the sum of diphosphates of  $\text{Li}_3\text{HP}_2\text{O}_7$  and  $\text{Li}_4\text{P}_2\text{O}_7$ . P% denotes the percentage of phosphorus atoms present in these phosphate anions. b) Relative humidity at 25 °C.

38.0° began to appear. The persistence of the diffraction lines of  $\text{Li}_3\text{HP}_2\text{O}_7$  anhydride at 450 °C in Fig. 3 indicates that the starting material remains even at this temperature.

Table 1 summarizes the changes in the amounts of phosphorus compounds in the samples. At 200–250 °C, a decrease in the amount of P<sub>2</sub> is accompanied by a 5-% level formation of P<sub>poly</sub>. The condensation reaction was somewhat faster in dry air than in humid air. At 250 °C, P<sub>4m</sub> was formed at about 8% in both dry air and humid air: the influence of atmosphere is hence negligible at this temperature. At 300 °C, P<sub>4m</sub> increased with a decrease in P<sub>2</sub>. In 90% relative humidity this trend was significant, and further P<sub>6m</sub> was formed in a slight amount and P<sub>poly</sub> was lost. At 400 °C, a fairly large amount of P<sub>4m</sub> was converted into P<sub>6m</sub>, particularly in 90% relative humidity. At 450 °C, the amounts of P<sub>2</sub> and P<sub>6m</sub> were almost equal under both atmospheric conditions, since all the P<sub>4m</sub> formed by the disproportionation changed to P<sub>6m</sub>.

These results clearly show that a dry atmosphere is more favorable for the dehydration reaction at temperatures below about 300 °C, while a humid atmosphere is more favorable for the thermal process at above 300 °C where P<sub>2</sub> and P<sub>poly</sub> change to P<sub>4m</sub> and further to P<sub>6m</sub>. In the processes at above 300 °C, water most probably plays a role of catalyst; the water molecule accelerates the ring opening by attacking the P–O–P bond, and promotes the diffusion and recombination of the radicals formed by the ring opening.

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