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Thermal Behavior of Alkaline-Earth Metal *cyclo*-Tetraphosphates

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The effect of water vapor on the thermal behavior of alkaline-earth metal *cyclo*-tetraphosphates, $M_2P_4O_{12}\cdot nH_2O$ (n=7.0, 3.5, 5.5, and 4.0 for M=Mg, Ca, Sr, and Ba, respectively) (P_{4m}) was examined using DTA-TG, X-ray diffraction analysis, isothermal heating in an electric furnace, and HPLC-FIA. The calcination reaction of each P_{4m} proceeded via ring opening of P_{4m} with elimination of water of crystallization, followed by condensation of soluble oligophosphates (P_{oligo}) to insoluble polyphosphates ($P_{high\ poly}$). The rates of these reactions were faster for Mg_2P_{4m} than for other metal *cyclo*-phosphates. The decomposition of P_{4m} was appreciably faster in humid air than in dry air, because of the availability of water for hydrolysis and for breaking the P–O–P linkage. However, the effect of water vapor from the atmosphere was not conspicuous, since the atmosphere contains enough water (theor. 20 mg L^{-1}) for the hydrolysis of P_{4m}. The products of calcination of $Ba_2P_{4m}\cdot 4H_2O$ were hardly influenced by water vapor from the atmosphere, because the water of crystallization was not easily released in the Ba system compared with the other metal salts.

As is well known, phosphates hydrolyze or condense on heating to yield different types of phosphates.[1–19] Most of the previous works dealt with linear phosphates. In recent papers,[20–23] we reported that water vapor remarkably affected the dehydration and condensation of various phosphates, and that the thermal behavior of *cyclo*-phosphates were significantly influenced by water vapor in the atmosphere, as well as by the rate and temperature range of heating, etc. In this study, the thermal dehydration and condensation reactions of alkaline-earth metal *cyclo*-tetraphosphates were investigated by means of DTA-TG, X-ray diffraction analysis, isothermal heating in an electric furnace, and high-performance liquid chromatography-flow injection analysis (HPLC-FIA).

Experimental

Chemicals. Guaranteed reagents of $Mg(NO_3)_2\cdot 6H_2O$, $Ca(NO_3)_2\cdot 4H_2O$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, NaCl, NaOH, Na_2S, and P_2O_5 from Wako Chemical Industries, Ltd. were used. Unless otherwise stated, other chemicals were of guaranteed grade and were used without further purification.

Preparation Methods. Sodium *cyclo*-tetraphosphate tetrahydrate ($Na_4P_{4m}\cdot 4H_2O$) was prepared by methods given in the literature.[1]

Alkaline-earth metal *cyclo*-tetraphosphates, $M_2P_{4m}\cdot nH_2O$ (n=7.0, 3.5, 5.5, and 4.0 for M=Mg, Ca, Sr, and Ba, respectively) were prepared by the method similar to those described in the literatures.[8,20] Fifteen mmol of each metal nitrate was dissolved in 150 cm^3 of water, and this solution was mixed with 100 cm^3 (7.5 mmol) of a 0.075 mol dm^{-3} sodium *cyclo*-tetraphosphate aqueous solution. The precipitate was filtered off, washed with cold water, and air-dried.

Measurements. The sample solution for HPLC-FIA was prepared as follows. A 15-mg portion of a phosphate sample was dissolved in 20 cm^3 of a 0.1 mol dm^{-3} EDTA·2Na solution, and the solution was diluted to 100 cm^3 with distilled water. A 100-µL aliquot of this solution was used for HPLC-FIA. Unless otherwise noted, the analytical procedures and apparatus were essentially the same as those used in previous work.[20,21,24]

Results and Discussion

Thermal Decomposition by DTA-TG. $Ba_2P_4O_{12}\cdot 4H_2O$ $Ba_2P_{4m}\cdot 4H_2O$: Figure 1 shows the DTA-TG curves for $Ba_2P_4O_{12}\cdot 4H_2O$ at atmospheric pressure. Two endothermic peaks at 127 and 193 °C and two exothermic peaks at 222 and 487 °C were observed. A gradual lowering of the TG curve took place over a temperature range of 200 to 500 °C. A remarkable change in the DTA and TG curves was not observed above 500 °C. To clarify the reactions occurring near the endo- and exothermic peaks, the calcination products after the peaks were removed from the DTA-TG apparatus, cooled in a silica-gel desiccator, and subjected to further analysis. Figures 2 and 3 show the X-ray diffraction patterns and the liquid chromatograms of products, respectively, heated at several tempera-

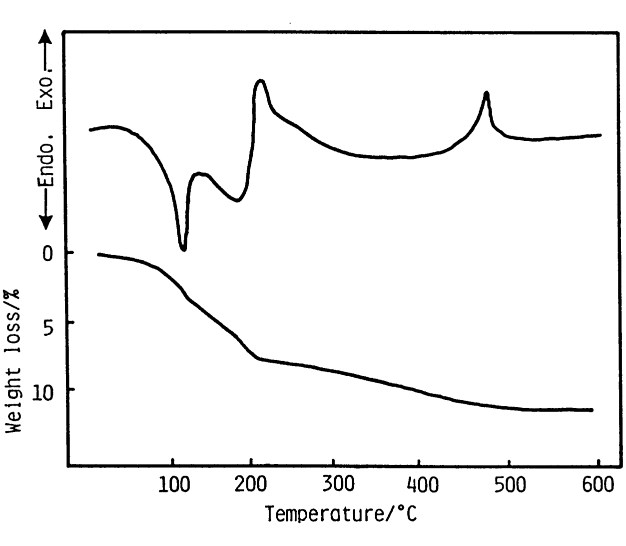

Fig. 1. DTA-TG curves for $Ba_2P_4O_{12}\cdot 4.0H_2O$.

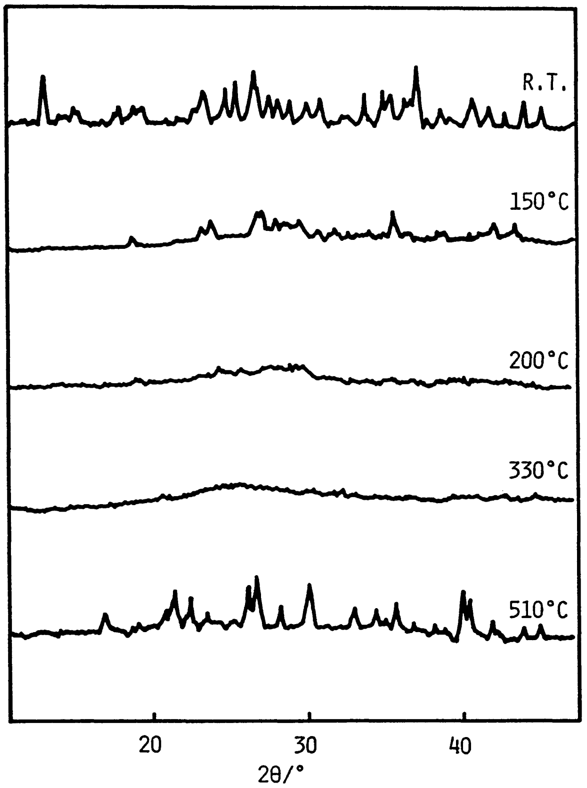

Fig. 2. X-Ray diffraction patterns of products by heating.
Sample: $Ba_2P_4O_{12}\cdot 4.0H_2O$. R. T., room temperature.

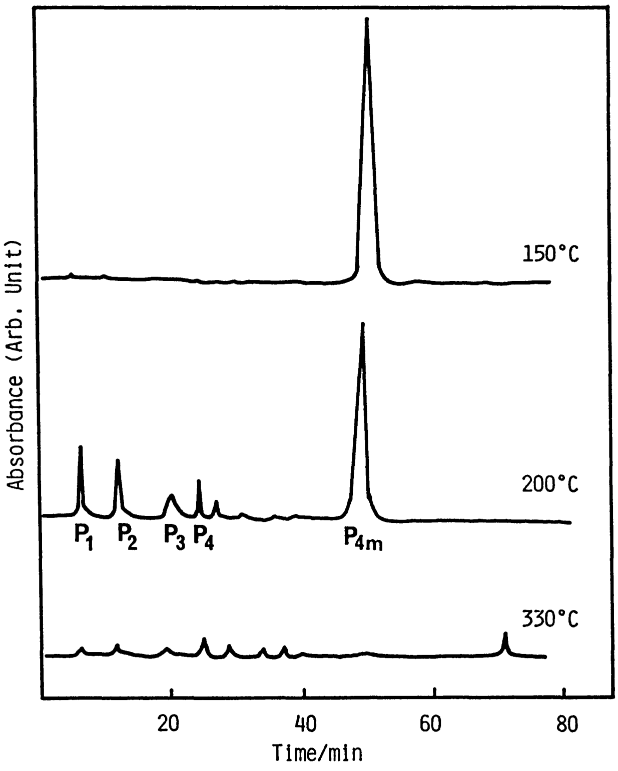

Fig. 3. Liquid chromatograms of products by heating.
Sample: $Ba_2P_4O_{12}\cdot 4.0H_2O$.

tures. In Fig. 2, the peak intensity of the anhydrous phase at 150 °C was gradually decreased with raising temperature and the product heated at 200 °C gave the X-ray difraction pattern of an amorphous phase. In view of the HPLC data at 150 °C, the P_{4m} ring structure was reserved. Therefore, the endothermic peak at 127 °C was assumed to reflect partial dehydration of the water of crystallization. The X-ray diffraction patterns of the products at a temperature range 193—330 °C were similar to that of an amorphous solid phase, as seen in Fig. 2. The HPLC trace shown in Fig. 3 suggests that decomposition of the P_{4m} ring to oligophosphates (P_{oligo}) such as ortho- (P_1), pyro- (P_2), tri- (P_3), and tetraphosphate (P_4) and the condensation of P_{oligo} to soluble polyphosphates (P_{poly}, P_5—P_{20}) occurred in the amorphous solid phase. No peak was seen in HPLC trace for product heated at 510 °C, because an insoluble polyphosphate ($P_{high\ poly}$) newly formed at this temperature. The thermal product at 510 °C showed an X-ray diffraction pattern characteristic of $Ba(PO_3)_2$. It seems that crystal growth was too slow to give one particular X-ray diffraction pattern, since under dynamic conditions the consecutive transformations of phosphates did not reach their equilibrium state, so that the X-ray diffraction pattern reflected an amorphous phase.

$Sr_2P_4O_{12}\cdot 5.5H_2O$ $Sr_2P_{4m}\cdot 5.5H_2O$: Figure 4 shows the DTA-TG curves for $Sr_2P_4O_{12}\cdot 5.5H_2O$ at atmospheric pressure. Two large endothermic peaks at about 120 and 160 °C accompanied by a weight loss are apparently due to elimination of the water of crystallization. A gradual lowering of the TG curve is noted over a temperature range of 200—400 °C. The calcinated samples were prepared in a similar manner to the barium salt and subjected to further analysis. The results of HPLC and X-ray diffraction analysis are

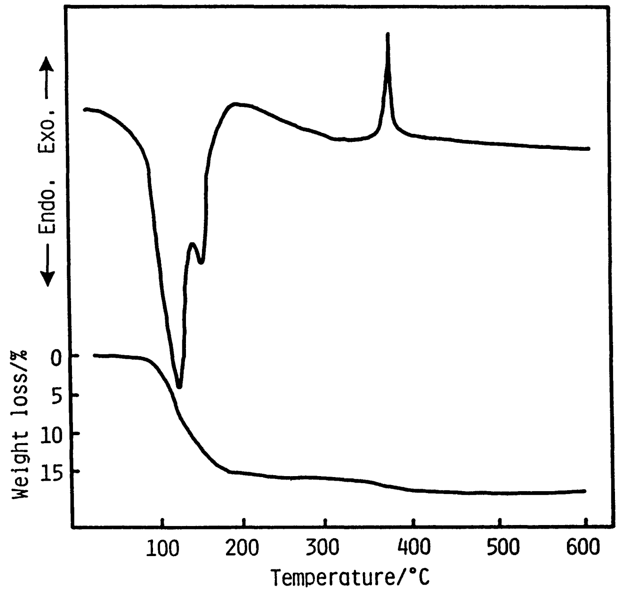

Fig. 4. DTA-TG curves for $Sr_2P_4O_{12}\cdot 5.5H_2O$.

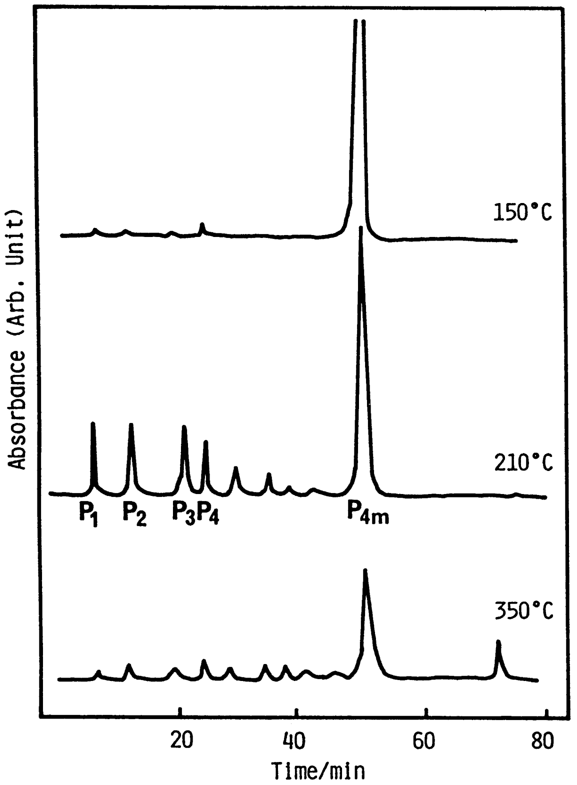

Fig. 5. Liquid chromatograms of products by heating. Sample: $Sr_2P_4O_{12} \cdot 5.5H_2O$.

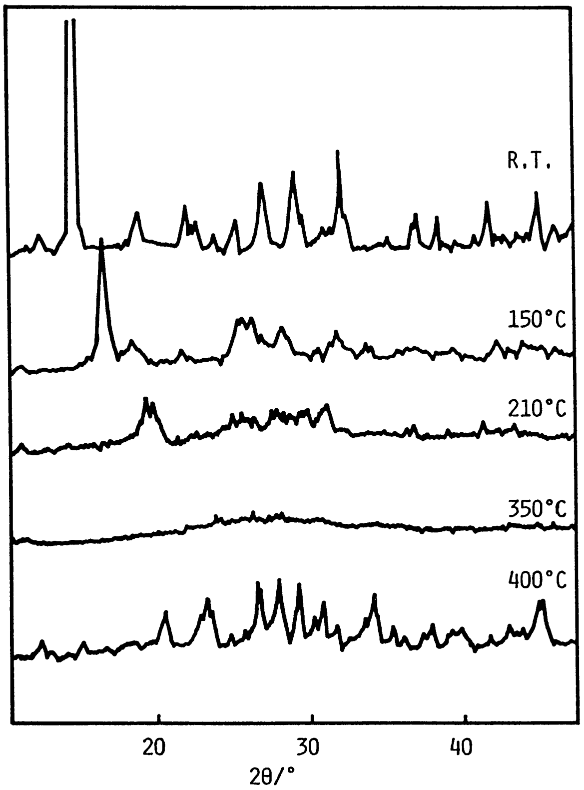

Fig. 6. X-Ray diffraction patterns of products by heating.
Sample: $Sr_2P_4O_{12} \cdot 5.5H_2O$.

shown in Figs. 5 and 6. According to the HPLC trace at 150 °C shown in Fig. 5, more than 90% of P_{4m} remained at this temperature, and the decomposition of P_{4m} to P_{oligo} was less than 10%. As seen in Fig. 6, the X-ray diffraction lines of the thermal products at temperatures from 210 to 350 °C gradually decreased by a rise in temperature and finally changed to an amorphous phase. HPLC results indicate that the decomposition of P_{4m} and the condensation of P_{oligo} to P_{poly} took place continuously. The sample heated at 400 °C did not

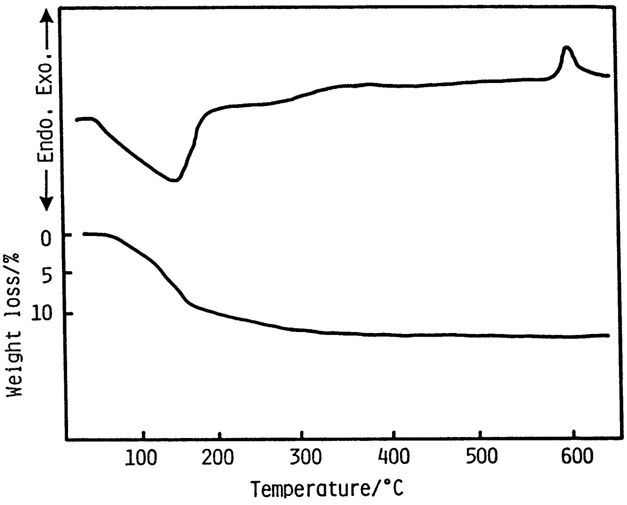

Fig. 7. DTA-TG curves for $Ca_2P_4O_{12} \cdot 3.5H_2O$.

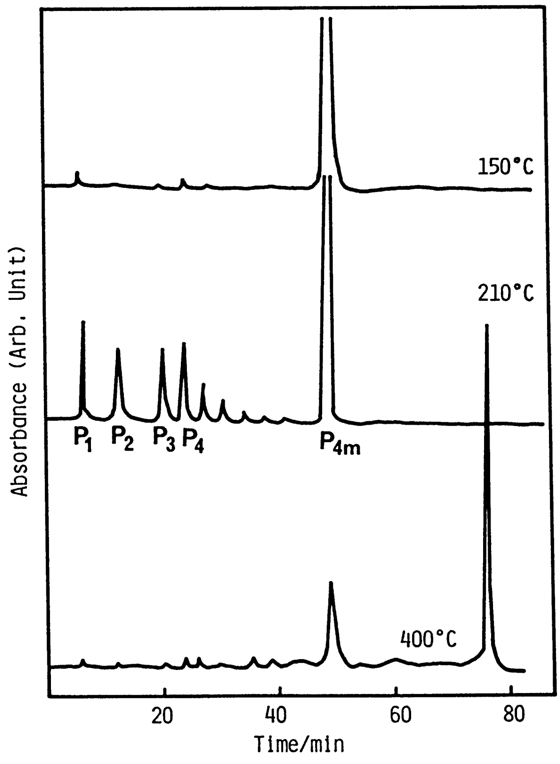

Fig. 8. Liquid chromatograms of products by heating. Sample: $Ca_2P_4O_{12} \cdot 3.5H_2O$.

dissolve by the EDTA treatment. It seems that insoluble polyphosphates ($P_{\text{high poly}}$) were newly formed through dehydration and condensation reactions. The thermal product at 400 °C showed a characteristic X-ray diffraction pattern in agreement with that of $Sr(PO_3)_2$. Accordingly, the exothermic peak at 390 °C should reflect the crystallization of $Sr(PO_3)_2$.

$Ca_2P_4O_{12}\cdot 3.5H_2O$ $Ca_2P_{4m}\cdot 3.5H_2O$: Figure 7 shows the DTA-TG curves for $Ca_2P_4O_{12}\cdot 3.5H_2O$ at atmospheric pressure. The samples were prepared as described above and subjected to further analysis. The results are shown in Figs. 8 and 9. The large endothermic peak at 150 °C accompanying a weight loss may be due mainly to the release of the water of crystallization. The TG curve was gradually lowered over a temperature range of 150—350 °C. According to the HPLC data at 150 °C shown in Fig. 8, P_{4m} remained almost in an anhydride state. At 210 °C, a significant amount of P_{4m} decomposed to P_{oligo} and further condensed to P_{poly}. The sample heated at 650 °C did not dissolve by the EDTA treatment. It seems that large amounts of insoluble polyphosphates ($P_{\text{high poly}}$) were formed through the dehydration and condensation reactions. The X-ray diffraction patterns of products heated at 650 °C (Fig. 9) agreed with that of $Ca(PO_3)_2$. Therefore, the exothermic peak at 589 °C reflects the crystallization of $Ca(PO_3)_2$.

$Mg_2P_4O_{12}\cdot 7.0H_2O$ $Mg_2P_{4m}\cdot 7.0H_2O$: Figure 10 shows the DTA-TG curves for $Mg_2P_4O_{12}\cdot 7.0H_2O$ at atmospheric pressure. Two large endothermic peaks at 95 and 155 °C accompanying a weight loss seemed to be mainly caused by elimination of the water of crystallization. A gradual lowering of the TG curve took place over a temperature range of 200—450 °C. According to the HPLC result at 230 °C shown in Fig. 11, large

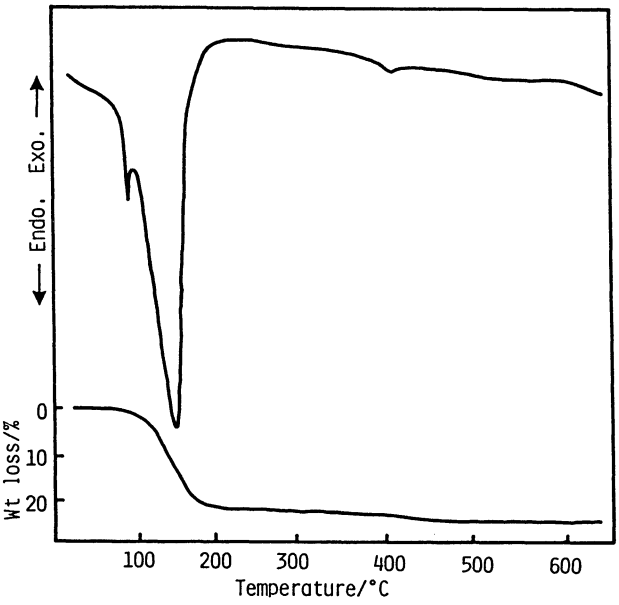

Fig. 10. DTA-TG curves for $Mg_2P_4O_{12}\cdot 7.0H_2O$.

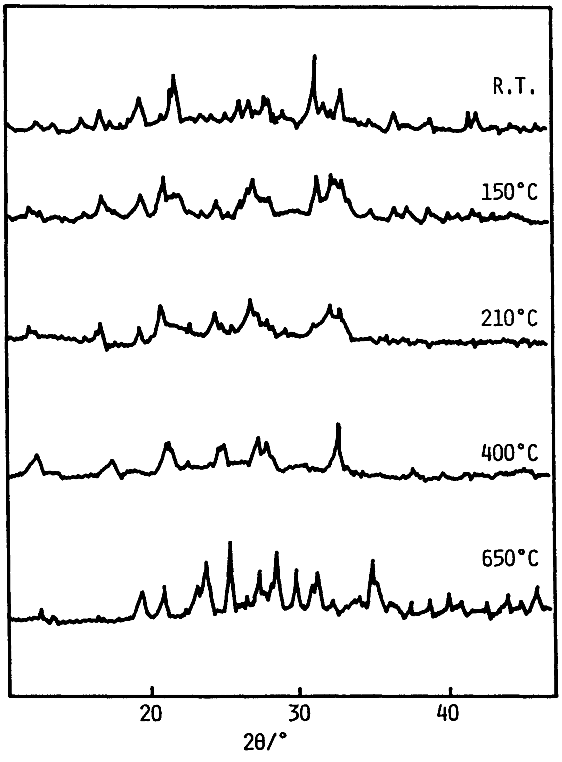

Fig. 9. X-Ray diffraction patterns of products by heating.
Sample: $Ca_2P_4O_{12}\cdot 3.5H_2O$.

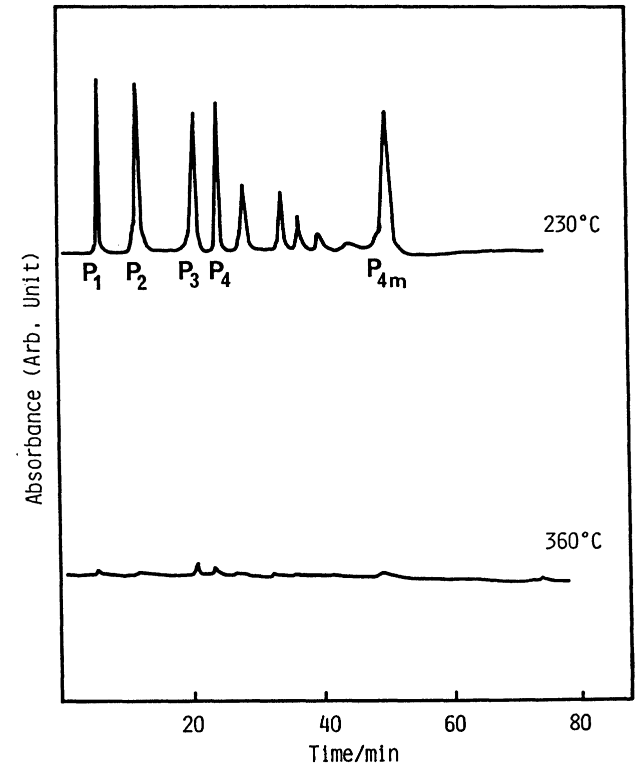

Fig. 11. Liquid chromatograms of products by heating.
Sample: $Mg_2P_4O_{12}\cdot 7.0H_2O$.

amounts of P_{4m} already decomposed to P_{oligo}. It is obvious that around this temperature the dehydration and decomposition of P_{4m} and the condensation of decomposed products of P_{4m} to P_{poly} are taking place during calcination. It is a characteristic feature of the Mg system that decomposition of P_{4m} proceeded faster than other three systems at a similar temperature. At 360 °C, no definite peaks were observed in HPLC. Therefore, it is clear that a large amount of polyphosphates ($P_{high\ poly}$) was formed through the dehydration and condensation, because the product heated at this temperature did not dissolve by the EDTA treatment. As seen in Fig. 12, the thermal products heated at 360 °C newly exhibited definite diffraction lines and they gradually increased with a rise in temperature. The X-ray diffraction lines coincided in position with those of $Mg(PO_3)_2$.

Isothermal Change. In view of the above-mentioned results, the thermal transformation of alkaline-earth metal *cyclo*-tetraphosphates, $M_2P_4O_{12}\cdot nH_2O$ (n=7.0, 3.5, 5.5, and 4.0 for M=Mg, Ca, Sr, and Ba, respectively), proceeded via dehydration, decomposition, and condensation. These reactions took place continuously, and did not reach equilibrium instantly. To examine the influence of water vapor on the thermal decomposition of $M_2P_4O_{12}\cdot nH_2O$, their isothermal decompositions were carried out in dry and humid air at various temperatures. Each $M_2P_4O_{12}\cdot nH_2O$ was heated at 200 °C for 30 min. The relationships between the amounts of various phosphates formed and the amounts of water vapor are shown in Figs. 13 through 16. P% denotes the percentage of phosphorus atoms present in these phosphate anions. The influence of the amount of water vapor on the products was not remarkable in a 20—110 mg L^{-1} range of water vapor. It is probable that there is enough water (theor. 20 mg L^{-1}) in the atmosphere for the hydrolysis of P_{4m}. However, a characteristic change was noted between the dry and the humid air. In dry air, the hydrolysis of P_{4m} was

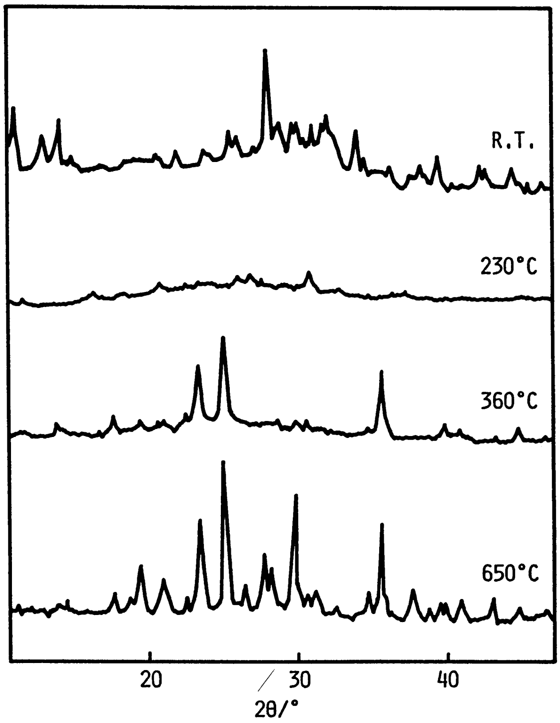

Fig. 12. X-Ray diffraction patterns of products by heating.
Sample: $Mg_2P_4O_{12}\cdot 7.0H_2O$.

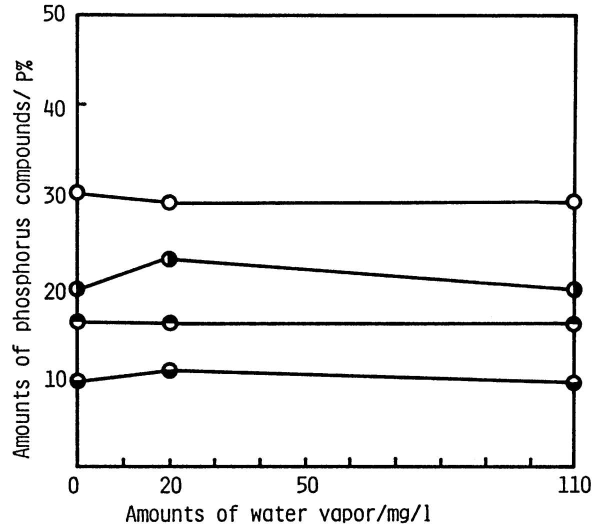

Fig. 13. Relationships between the amounts of phosphates and water vapor for the sample heated at 200 °C for 30 min.
Sample: $Ba_2P_4O_{12}\cdot 4.0H_2O$. ○: P_{4m}, ◒: P_1, ◑: P_2, ◓: P_3.
P % denotes the percentage of phosphorus atoms present in these phosphate anions.

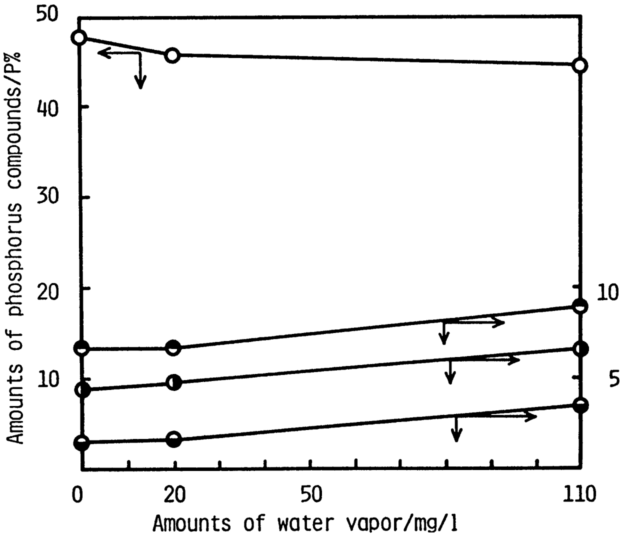

Fig. 14. Relationships between the amounts of phosphates and water vapor for the sample heated at 200 °C for 30 min.
Sample: $Sr_2P_4O_{12}\cdot 5.5H_2O$. ○: P_{4m}, ◒: P_1, ◑: P_2, ◓: P_3.

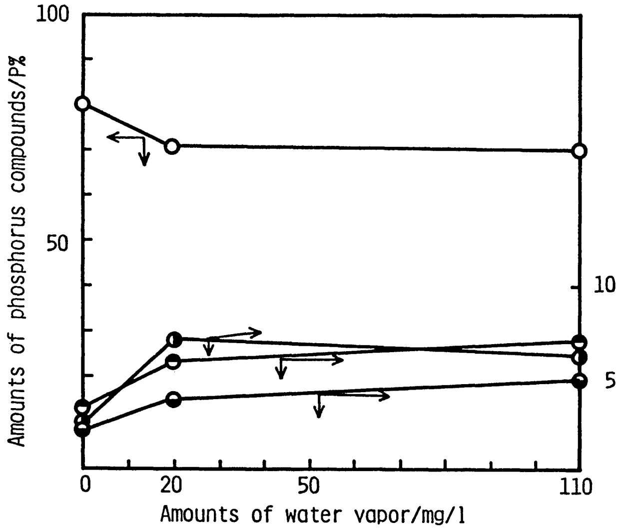

Fig. 15. Relationships between the amounts of phosphates and water vapor for the sample heated at 200 °C for 30 min.
Sample: $Ca_2P_4O_{12}\cdot 3.5\ H_2O$. ○: P_{4m}, ◒: P_1, ◑: P_2, ◓: P_3.

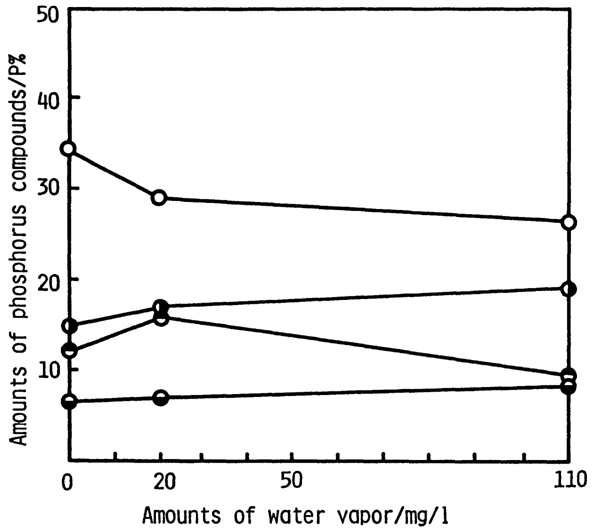

Fig. 16. Relationships between the amounts of phosphates and water vapor for the sample heated at 200 °C for 30 min.
Sample: $Mg_2P_4O_{12}\cdot 7.0H_2O$. ○: P_{4m}, ◒: P_1, ◑: P_2, ◓: P_3.

depressed, since there was not enough water necessary for hydrolysis and for breaking the P–O–P linkage. In the Ba system shown in Fig. 1, release of the water of crystallization took place at a higher temperature than in other three systems, so that the effect of water from the atmosphere was hardly discernible. According to the present results, the thermal decomposition and condensation processes may be formulated as follows:

$$M_2P_4O_{12}\cdot nH_2O \longrightarrow M_2P_4O_{12} \qquad (1)$$

(M: Ba, Sr, Ca, Mg)

$$M_2P_4O_{12} \longrightarrow P_{\mathrm{oligo}} \qquad (2)$$

$$P_{\mathrm{oligo}} \longrightarrow P_{\mathrm{poly}} \qquad (3)$$

$$P_{\mathrm{poly}} \longrightarrow P_{\mathrm{high\ poly}} \qquad (4)$$

The thermal reactions in the first stage proceed continuously according to Processes (1) and (2), followed by Processes (3) and (4) simultaneously. The decomposition of $M_2P_4O_{12}\cdot nH_2O$ to P_{oligo} proceeds faster in humid air than in dry air. In this work, pure anhydrides could not be obtained by heating or freeze-drying of the hydrates of *cyclo*-tetraphosphates.

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