Effect of Water Vapor on the Transformation of *cyclo*-Tetraphosphate

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Synopsis. The effect of water vapor on the process of transformation of sodium *cyclo*-tetraphosphate $Na_4P_4O_{12}(P_{4m})$ to sodium *cyclo*-triphosphate $Na_3P_3O_9(P_{3m})$ was investigated by means of DTA-TG, X-ray diffraction analysis, isothermal heating with an electric furnace, and HPLC. The transformation of P_{4m} to P_{3m} proceeded by a radical reaction via different reaction pathways in dry and humid air.

Phosphates hydrolyze or condense on heating to form various kinds of phosphates.[1—11] These reaction processes are affected by many factors including the kind of metal, the ratio of metal to phosphorus, and the duration and rate of heating.

The water vapor pressure is also an important factor in thermal reaction of phosphates. In this study, the effect of water vapor on the thermal transformation of P_{4m} to P_{3m} was investigated.

Experimental

Chemicals. Sodium *cyclo*-tetraphosphate tetrahydrate ($P_{4m}\cdot 4H_2O$) was prepared by the method given in the literature.[1] P_{4m} was prepared by heating of its hydrate at 100 and 150 °C for 2 h and 1 h, respectively. Unless otherwise stated, guaranteed-grade reagents were used without further purification. The analytical procedures and apparatus were essentially the same as those in previous works.[12—15]

Results and Discussion

Thermal Decomposition of P_{4m} Examined by DTA-TG. Figure 1 shows the DTA-TG curves for P_{4m} at atmospheric pressure. Except for a slight decrease by dehydration of adsorbed water, there was no weight loss in the TG curve over the temperature range examined. In the DTA curve, a small exothermic peak at around 500 °C was due to the transformation of P_{4m} to P_{3m} and the endo- and exothermic peaks at about 600 °C due to decomposition of P_{3m}. The influence of water vapor was investigated under the isothermal conditions in a temperature range from 400 to 500 °C.

Isothermal Change. Figure 2 shows the X-ray diffraction patterns of the samples heated for 1 h at several temperatures and humidities. The diffraction lines of P_{4m} remained unchanged at 400 °C. At 420 °C the lines changed partially to those of P_{3m}(I) (JCPDS Card 11-0648) in dry air, while in humid air to P_{3m}(I′), which has a crystal structure different from that of P_{3m}(I).[16,17] The transformation of P_{4m} to P_{3m}(I′) has not been reported. At 450 °C P_{4m} changed completely into each type of P_{3m}. Table 1 shows the changes in the amounts of phosphorus compounds in the samples heated at several temperatures. At 420 °C in a dry air atmosphere (r. h.=0%), about 56% of P_{4m} already changed to P_{3m}, while in air of 90% relative humidity at (25 °C), about 21% of P_{4m} changed to P_{3m}. Since the TG curve indicated no weight change, and since no oligophosphates were detected in the 400—500 °C region, it seems

Table 1. Changes in Phosphate Composition (Starting Material: P_{4m})

Temp	Relative humidity	P_{4m}	P_{3m}
°C	%	%	%
400	0	100.0	0
	90	100.0	0
420	0	44.3	55.7
	90	79.3	20.7
450	0	0	100.0
	90	0	100.0

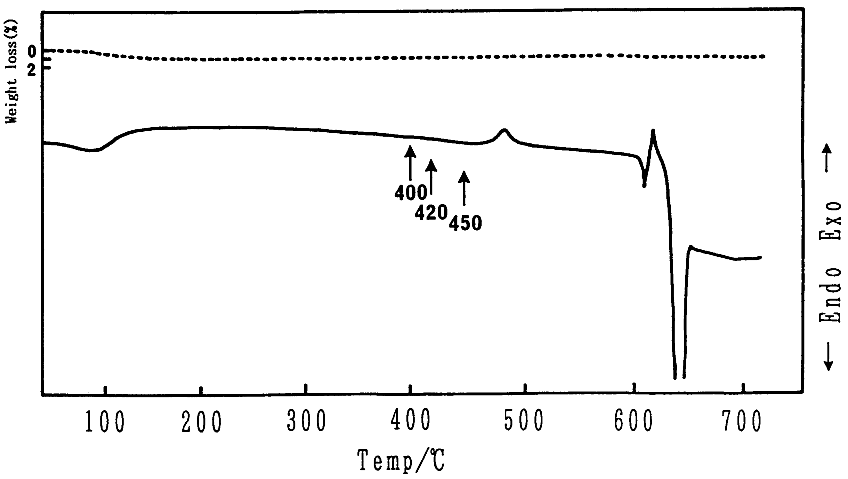

Fig. 1. DTA-TG curves for $Na_4P_4O_{12}$ anhydride. Solid line: DTA, dotted line: TG.

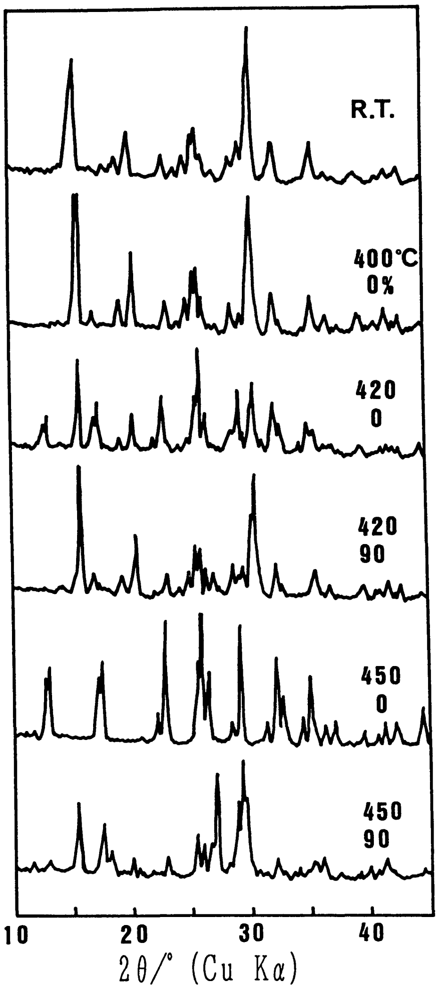

Fig. 2. X-Ray diffraction patterns of the products on heating in two different atmospheres (relative humidities of 0% and 90%). Sample: $Na_4P_4O_{12}$ anhydride. R. T., room temperature.

that the transformation of P_{4m} to P_{3m} proceeds by a radical process.[14] It is interesting to note that P_{4m} transformed to $P_{3m}(I')$ under a humid atmosphere as follows:

$$P_{4m} \begin{cases} \xrightarrow{\text{in dry air}} P_{3m}(I) \\ \xrightarrow[\text{in humid air}]{} P_{3m}(I') \end{cases}$$

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