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Effect of Water Vapor on the Thermal Behavior of Manganese *cyclo*-Tetraphosphate

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As a part of an investigation on the effect of water vapor on the thermal behavior of *cyclo*-phosphates, $Mn_3H_2(P_4O_{12})_2 \cdot 9.5H_2O$ $Mn_3H_2(P_{4m})_2 \cdot 9.5H_2O$ was examined by means of DTA-TG,X-ray analysis, and HPLC-FIA. $Mn_3H_2(P_{4m})_2 \cdot 9.5H_2O$ lost the water of crystallization at about 145 °C. In a temperature range 165—265 °C, $Mn_3H_2(P_{4m})_2$ anhydride decomposed to form oligophosphates(P_{oligo}). At temperatures below 200 °C, the amounts of P_{oligo} were more abundant under humid conditions than under dry conditions. At 265—450 °C,P_{oligo} changed partially into polyphosphates (P_{poly}) and insoluble highpolyphosphates($P_{high\ poly}$). The dehydration and condensation reactions proceeded faster under dry conditions than under humid conditions, where gradual water evolution was noted over the temperature range of 265 to 450 °C. The stable crystalline $P_{high\ poly}$,$Mn(PO_3)_2$, was produced at temperatures above 450 °C, where the product was not affected by the water vapor.

It has been well documented that phosphates hydrolyze or condense upon heating to form various kinds of phosphates .[1-18] Most of the previous works dealt with linear phosphates, and a systematic investigation on the thermal behavior of *cyclo*-phosphates as the starting material has scarcely been reported. We found that the thermal behavior of *cyclo*-phosphates are significantly influenced by water vapor in the atmosphere, as well as by the kind of the metal, the rate and temperature range of heating, etc.[19-25] Manganese phosphates are used as catalysts and in phosphate glasses.[26-31] Lee and Browne reported that $Mn(NH_4)P_2O_7$(manganese violet) decomposed into $Mn_2(P_4O_{12})$ and $Mn_3(P_3O_9)_2$.[32] Lavrov et al. described the conditions for the formation of cyclic $M_2P_4O_{12} \cdot xH_2O$ and $M_4O_8O_{24} \cdot yH_2O$ (M=Mn, Ni, Cd) and their thermal behaviors.[33] In this work, the thermal behavior of manganese *cyclo*-tetraphosphate was studied in detail to clarify the effect of the atmosphere, under dynamic and isothermal conditions with a DTA-TG apparatus and an electric furnace, respectively.

Experimental

Chemicals. Guaranteed reagents of $Mn(NO_3)_2 \cdot 6H_2O$, NaCl, NaOH, P_2O_5, acetone, and methanol from Wako Pure Chemical Industries, Ltd. were used. Unless otherwise noted, guaranteed reagents were used without further purification. Sodium *cyclo*-tetraphosphate tetrahydrate ($Na_4P_{4m} \cdot 4H_2O$) was prepared according to the literature.[1] Trimanganese dihydrogenbis(*cyclo*-tetraphosphate) hydrate $Mn_3H_2(P_{4m})_2 \cdot 9.5H_2O$ was prepared by a method similar to those described in the literature[8,19] Twenty mmol(9.5984 g) of $Na_4P_{4m} \cdot 4H_2O$ was dissolved in 200 cm^3 of water, and the solution was mixed with 200 cm^3 (40 mmol) of a 0.2 mol dm^{-3} manganese nitrate aqueous solution. When the mixture became slightly turbid, adequate amounts of methanol and acetone were added, followed by stirring for 1h. The precipitate was filtered off,

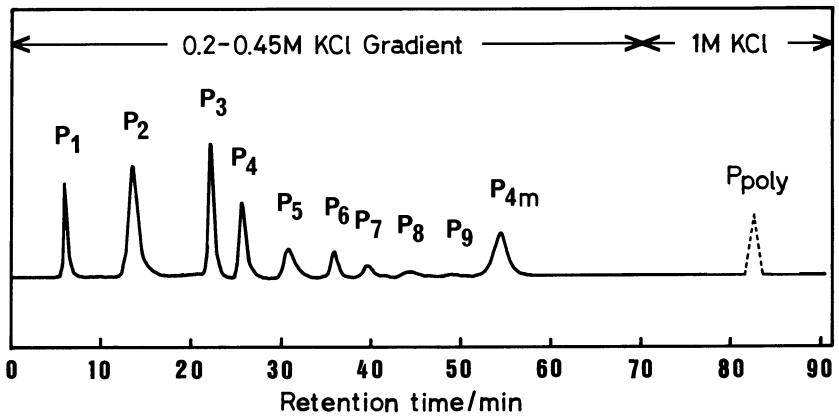

Fig. 1. HPLC profiles for products obtained at 165°C in air of 90% relative humidity. P_1, P_2, P_3, P_4, P_5, P_6, P_7, P_8, P_9, P_{4m}, and P_{poly} represent ortho-, pyro-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, *cyclo*-tetra-, and soluble polyphosphates (n=15—20, absent in this sample), respectively.

washed with cold water, and air-dried.

Determination of Manganese, Phosphorus, and the Water of Crystallization. X-Ray fluorescence analysis(XRF) was used to determine manganese and phosphorus in the samples with a Rigaku Automatic X-Ray Fluorescence Analyzer System 3080 E. The manganese was determined also by titration with EDTA.[34] The total amount of phosphorus in phosphates was determined by absorptiometry after hydrolyzing the condensed phosphates with dilute hydrochloric acid. The codensed phosphates obtained by calcination were separated by HPLC as shown in Fig. 1, and then each phosphate was determined by the Molybdenum Blue Method.[19-25,35] The amount of the water of crystallization was calculated from the weight loss in TG curves.

Found : Mn/P,0.389(XRF), 0.382(EDTA titrn.); P,23.76; Mn, 16.09%. Calcd for $Mn_3H_2(P_4O_{12})_2 \cdot 9.5H_2O$, Mn/P, 0.375; P,25.55; Mn,17.00%.

Other analytical procedures and apparatus were essentially the same as those in previous works.[19,20]

Results and Discussion

Thermal Decomposition by DTA-TG. Figure 2 shows the DTA-TG curves of $Mn_3H_2(P_{4m})_2 \cdot 9.5H_2O$ at atmospheric pressure. Two endothermic peaks at 66 and 140 °C and two exothermic ones at 225 and 450—500 °C were observed. A gradual decrease in the TG curve was noted over a temperature range of 200 to 500 °C. Above 520 °C, the DTA and TG curves remained essentially unchanged. Table 1 summarizes the changes in the amounts of phosphates in the samples heated at a series of temperatures. From the HPLC analytical results at 165 °C, namely at the end of the endothermic peak with a large weight loss at 140 °C, the weight loss was attributed to the loss of the water of crystallization. Thus, $Mn_3H_2(P_{4m})_2 \cdot 9.5H_2O$ existed as anhydride at 165 °C. At 265 °C, a considerable amount of the P_{4m} began to decompose and changed into short-chain phosphates(n=1—4) and P_{oligo}. At 450 °C, significant amounts of P_{poly} and $P_{high\ poly}$ were formed with a decrease in the short-chain phosphates, P_{oligo}, and P_{4m}. At 540 °C, $P_{high\ poly}$ was produced almost quantitatively.

Isothermal Change. Based upon the results described above, $Mn_3H_2(P_{4m})_2 \cdot 9.5H_2O$ dehydrated to its anhydride at 165 °C and the latter decomposed to P_{oligo}, and then condensed to P_{poly} and further to $P_{high\ poly}$ with a rise of temperature. These changes proceeded continuously, and the equilibrium was not reached instantly. The influence of water vapor upon thermal decomposition was examined by heating $Mn_3H_2(P_{4m})_2 \cdot 9.5H_2O$ at various temperatures for 1 h in air of 0 or 90% (at 25 °C) relative humidity. Figures 3 and 4 show the X-ray diffraction patterns of products heated at various temperatures and atmospheres in an electric furnace. In the 165—265 °C

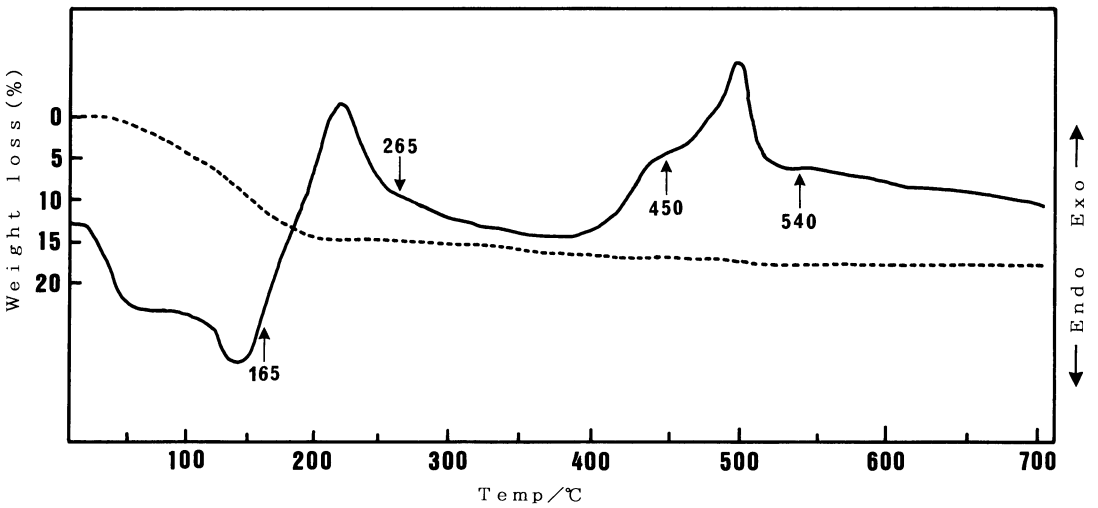

Fig. 2. DTA-TG curves for $Mn_3H_2(P_{4m})_2 \cdot 9.5H_2O$. Solid line: DTA, dotted line: TG.

Table 1. Changes in the Amounts of Phosphorus Compounds in the Samples Heated at a Series of Temperatures, as Determined by DTA-TG

Compound[a] Temp/°C	P_1 %	P_2 %	P_3 %	P_4 %	P_{oligo} %	P_{4m} %	P_{poly} %	$P_{high\ poly}$ %
165	0.9	0	0.8	2.6	0	95.7	0	0
265	2.7	8.8	12.2	11.9	47.7	14.4	2.3	0
450	1.4	1.2	1.6	1.8	11.7	2.6	36.4	43.3
540	0	0	0	0	0	1.3	5.6	93.1

a) P_1, P_2, P_3, P_4, P_{oligo}, P_{4m}, P_{poly}, and $P_{high\ poly}$ represent ortho-, pyro-, tri-, tetra-, oligo-(chain length, n=5—14), *cyclo*-tetra-, soluble poly-, and insoluble highpolyphosphates, respectively.

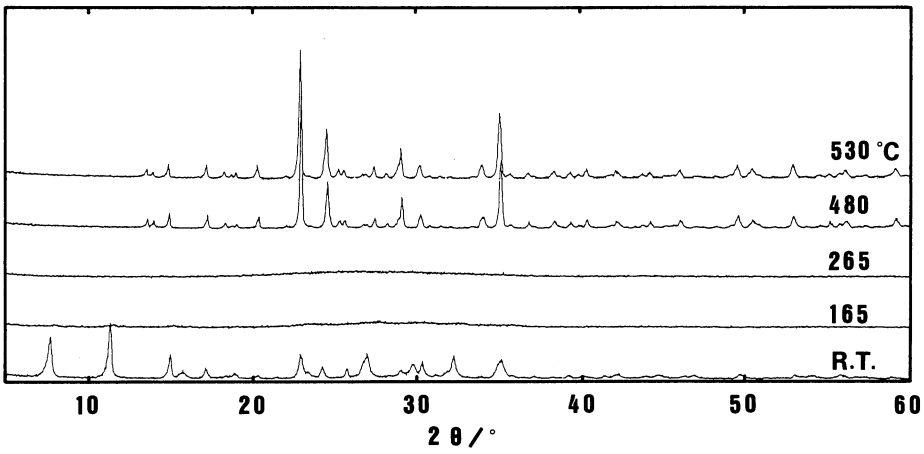

Fig. 3. X-Ray diffraction patterns of products obtained by heating at 0% relative humidity. Sample: $Mn_3H_2(P_{4m})_2 \cdot 9.5H_2O$. R.T., room temperature.

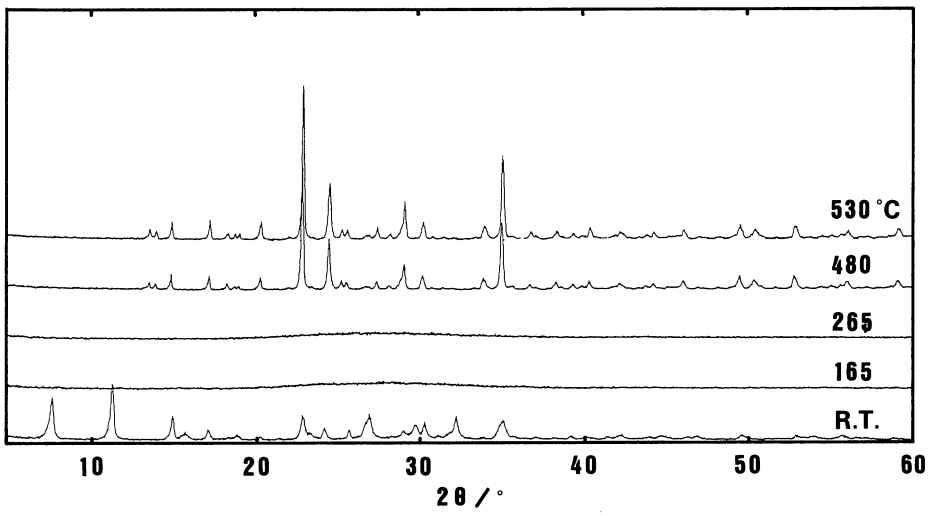

Fig. 4. X-Ray diffraction patterns of products obtained by heating at 90% relative humidity. Sample: $Mn_3H_2(P_{4m})_2 \cdot 9.5H_2O$. R.T., room temperature.

Table 2. Changes in the Amounts of Phosphorus Compounds in the Samples Heated at a Series of Temperatures at 0 or 90% Relative Humidities (R.H.) for 1 h

Temp °C	Compound[a] R.H./%	P_1 %	P_2 %	P_3 %	P_4 %	P_{oligo} %	P_{4m} %	P_{poly} %	$P_{high\ poly}$ %
165	0	6.3	16.1	14.2	9.9	21.8	31.7	0	0
	90	9.6	23.3	17.1	12.5	22.0	15.5	0	0
265	0	2.0	6.2	8.6	9.2	50.8	3.1	20.1	0
	90	3.6	9.1	10.9	11.2	48.4	5.1	11.7	0
450	0	0.4	0	0	0	0	0.4	0.3	98.9
	90	0.3	0.2	0	0	0	0.8	0.4	98.3
480	0	0.3	0.2	0	0	0	0.7	0.2	98.6
	90	0.2	0.3	0	0	0	1.1	0.4	98.0
500	0	0.3	0	0	0	0	1.3	0.4	98.0
	90	0.5	0.4	0	0	0	2.2	0.2	96.7
530	0	0.2	0	0	0	0	0.5	0.2	99.1
	90	0.9	0.4	0	0	0	0.5	0.5	97.7

a) See footnote to Table 1 for abbreviation of the products.

region, no diffraction lines were observed. It seems that $Mn_3H_2(P_{4m})_2 \cdot 9.5H_2O$ dehydrated into its anhydride, and further thermal dehydration resulted in the formation of P_{oligo}. At 480 °C, the diffraction patterns of $P_{high\ poly}$ appeared and remained unchanged up to 800 °C. As seen in Figs.3 and 4, both X-ray diffraction patterns changed in a similar manner over the temperature range from room temperature to 530 °C and finally became to that of $P_{high\ poly}$, $Mn(PO_3)_2$.

Table 2 shows the changes in the amounts of phosphorus compounds in the samples heated at several temperatures. At 165 °C, the temperature after the endothermic peak in Fig. 2, P_1, P_2, P_3, P_4, and P_{oligo} were formed accompanying a decrease of P_{4m}. The decomposition reaction was faster in humid air than in dry air. At 265 °C, P_{4m} almost disappeared, and considerable amounts of P_{oligo} (about 50%) and P_{poly} (about 12—20%) were produced. The condensation reaction was faster in dry air than in humid air. At 450 °C, P_{4m} almost disappeared to give insoluble $P_{high\ poly}$. Above 450 °C, no remarkable difference was noted for the amounts and species of products between the dry and humid air.

It is clear from these results that at temperatures below about 200 °C, the humid conditions are more favorable for the decomposition of P_{4m}, probably because water molecules attack the P–O–P linkage and accelerate the ring opening reaction and hydrolysis. At 265 °C, at which the short-chain phosphates formed could be condensed, the dry conditions are more favorable for liberation of the water molecules formed by dehydration. Therefore, the condensation reaction in dry air proceeds faster than in humid air. Above 450 °C, all the phosphates formed by the decomposition reaction changed thermally to a stable $P_{high\ poly}$, and consequently the effect of water vapor was not observed.

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