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The Effect of Water Vapor on the Thermal Decomposition of Various Tin(IV) *cyclo*-Phosphates

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The process of the thermal decomposition of various tin(IV) *cyclo*-phosphates, $SnP_4O_{12}\cdot 4H_2O$(P_{4m}), $Sn_3(P_6O_{18})_2\cdot 12H_2O$ (P_{6m}), and $Sn_2P_8O_{24}\cdot 5H_2O$(P_{8m}), was investigated using X-ray analysis, DTA-TG, and HPLC-FIA. P_{4m} lost the water of crystallization at about 105 °C. In the region of 400—500 °C, P_{4m} changed to *cyclo*-triphosphate (P_{3m}) without any other species of phosphates. Therefore, the change of P_{4m} to P_{3m} probably proceeded as a radical reaction. At temperatures above 580 °C, P_{3m} changed to insoluble polyphosphates ($P_{high\ poly}$). P_{6m} lost the water of crystallization at about 110 °C. In the region of 500—570 °C, P_{6m} changed to $P_{high\ poly}$ through P_{3m}. P_{8m} lost the water of crystallization at about 140 °C. At about 255 °C, P_{8m} decomposed to oligo phosphates($n<8$)(P_{oligo}), soluble polyphosphates($15<n<20$)(P_{poly}), and amorphous insoluble polyphosphates ($P^*_{high\ poly}$). Under a higher water vapor pressure, these decomposition and subsequent condensation reactions proceeded rather faster than in a lower one. At about 300 °C, $P^*_{high\ poly}$ changed to P_{3m} again. At higher temperatures, P_{3m} changed to $P_{high\ poly}$.

It is well-known that, upon heating, phosphates hydrolyze or condense to form various kind of phosphates.[1-13] These reactions are affected by the kind of metal, the atmosphere, the temperature, the time and rate of heating, etc., thus resulting in the formation of different phosphates. In a previous paper,[14] we reported the effect of water vapor on the thermal decomposition of lead *cyclo*-tetraphosphate. As regards the thermal decomposition of tin(IV) *cyclo*-phosphates, though, little work has been reported. Therefore, in this paper, we wish to present the experimental results of the atmospheric dependence of the thermal decomposition of tin(IV) *cyclo*-phosphates and also discuss the mechanisms of their thermal decomposition. The process of the thermal decomposition of *cyclo*-phosphates was investigated by means of X-ray analysis, thermal analysis (DTA-TG), and high performance liquid chromatography-flow injection analysis (HPLC-FIA).

Experimental

Chemicals. The tin(IV) *cyclo*-phosphates—$SnP_4O_{12}\cdot 4H_2O$ (P_{4m}), $Sn_3(P_6O_{18})_2\cdot 12H_2O$($P_{6m}$), and $Sn_2P_8O_{24}\cdot 5H_2O$ (P_{8m})— were prepared by methods similar to those described in the literature.[5,14-16] Tin(IV) *cyclo*-triphosphate(P_{3m}) could not be obtained by the above method. Unless otherwise stated, guaranteed reagents were used without further purification. The analytical procedures and apparatus were essentially the same as those used in the previous paper.[14]

Results and Discussion

Thermal Decomposition of $SnP_4O_{12}\cdot 4H_2O$ (P_{4m}). Figure 1 shows the DTA-TG curves of P_{4m} at atmospheric pressure. Three endothermic peaks at about 70 and 105 (with a weight loss), and at 580 °C, and an exothermic peak at about 630 °C were observed. To clarify these thermal changes at each temperature, X-ray measurements of the products on heating were performed. Figure 2 shows the X-ray diffraction patterns of products heated at various temperatures in an electric furnace for 30 min. In the 300—450 °C region, no change in the X-ray diffraction patterns was observed. In the 495—510 °C region, though, some new peaks began to appear. In the 610—660 °C region, other new peaks began to appear, gradually increasing with the heating temperature. From the X-ray diffraction pat-

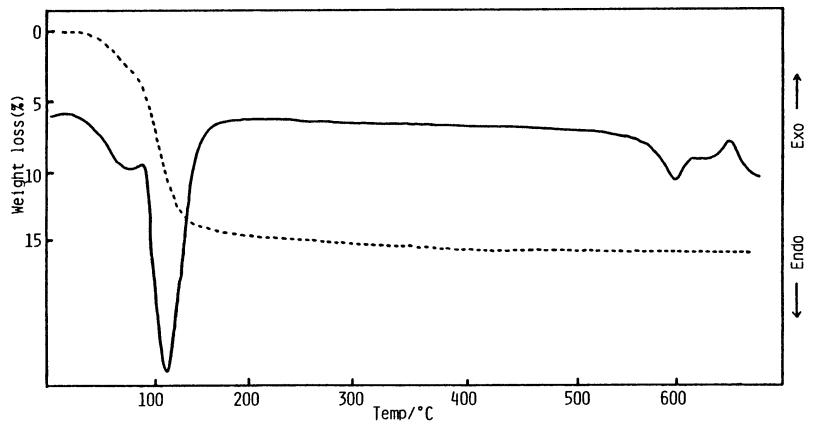


Fig. 1. DTA-TG curves of $SnP_{4m}\cdot 4H_2O$. Solid line: DTA, dotted line: TG.

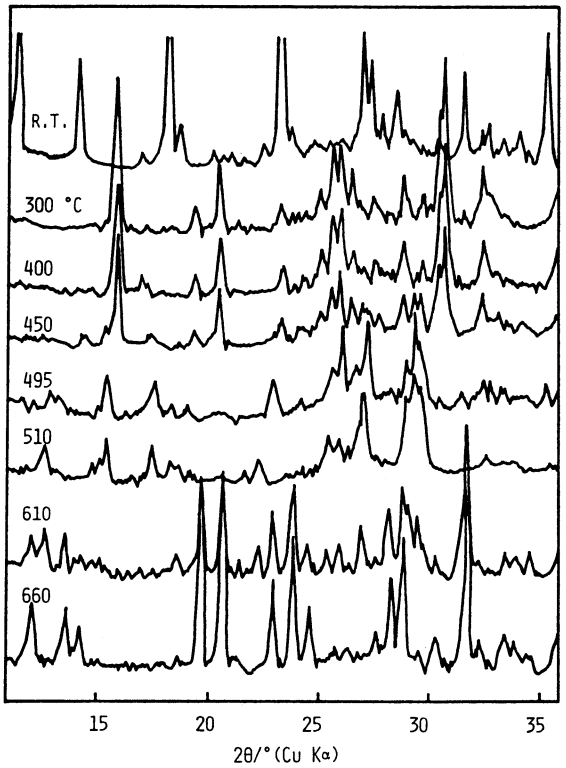


Fig. 2. X-Ray diffraction patterns of products on heating. Sample: $SnP_{4m}\cdot 4H_2O$.

terns and HPLC, it seems that P_{4m} dehydrated to form an anhydride at about 105 °C and that it thereafter remained unchanged up to 450 °C. At temperatures above 500 °C, P_{4m} began to decompose and changed to P_{3m} and/or $P_{high\ poly}$. Although the DTA-TG curves do not have a definite peak in Fig. 1, P_{4m} gradually decomposed above 500 °C. Therefore, the influence of water vapor upon thermal decomposition was investigated at 400 and 450 °C. Table 1 shows the changes in the amounts of phosphates in the samples heated at each temperature. At 400 °C in a dry air atmosphere (r.h.=0%), 35% of the starting material has already changed to P_{3m}, while in the 15—90% range of relative humidity (at 25 °C), about 12—15% of the starting material changed to P_{3m}. At 450 °C in a dry air atmosphere (r.h.=0%), most of the P_{4m} changed to P_{3m}, while in r.h.=15—90, 30—36% of that remained unchanged. From the X-ray diffraction pattern and the HPLC of the product heated at 610 °C, the endothermic peak at 580 °C shows the phase transition of P_{3m} to $P_{high\ poly}$, while the exothermic peak at 630 °C shows the crystallization of $P_{high\ poly}$. When P_{4m} changed to P_{3m}, no other species of phosphates except P_{4m} and P_{3m} were observed, indicating that its rearrangement probably proceeded radically.[17] For a reason similar to that noted above and from the fact that no weight change was observed in the TG curve (Fig. 1), the change of P_{3m} to $P_{high\ poly}$ probably proceeded radically.

Table 1. Changes in the Amounts of Phosphates (Starting Material: P_{4m})

Temp/°C	Compound R.H./%	P_{oligo} %	P_{4m} %	p_{3m} %	P_{poly} %	$P_{high\ poly}$ %
400	0	0	65.0	35.0	0	0
	15	0	84.3	15.7	0	0
	90	0	87.7	12.3	0	0
450	0	0	4.9	95.1	0	0
	15	0	30.9	69.1	0	0
	90	0	36.4	63.6	0	0

Thermal Decomposition of $Sn_3(P_6O_{18})_2\cdot 12H_2O$ (P_{6m}). Figure 3 shows the DTA-TG curves of P_{6m} at atmospheric pressure. Five endothermic peaks, at about 60 and 110 (with a weight loss), and at 550, 570, and 610 °C, were observed. From the results of HPLC, P_{6m} remained unchanged up to the 500 °C region, while in the region near 560 °C it completely decomposed to a mixture of P_{oligo}, P_{3m}, and $P_{high\ poly}$. Figure 4 shows the X-ray diffraction patterns of products heated at various temperatures in an electric furnace for 30 min. In the 210—500 °C region, only the peaks for anhydride were observed. In 570 °C, the diffraction pattern changed to another pattern, that of $P_{high\ poly}$. The higher the temperature, the more intense the peaks became. Table 2 shows the changes in the amounts of phosphates in the samples heated at 500 and 570 °C. At 500 °C, the temperature before the endothermic peak in Fig. 3, we expected a remarkable effect of the water vapor upon the decomposition of

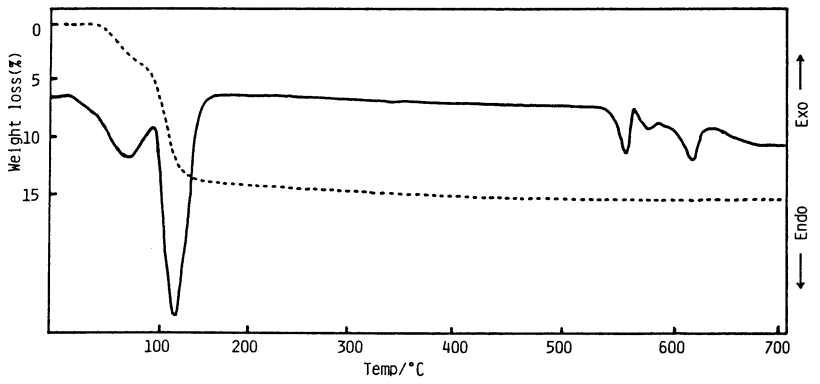


Fig. 3. DTA-TG curves of $Sn_3(P_{6m})_2\cdot 12H_2O$. Solid line: DTA, dotted line: TG.

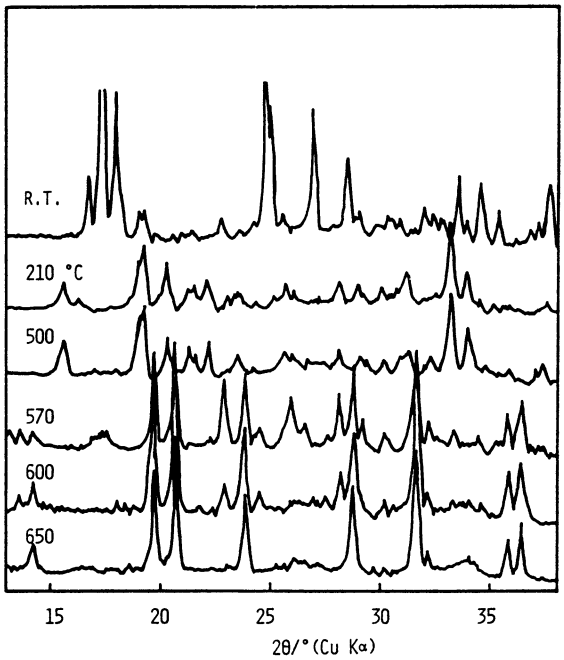


Fig. 4. X-Ray diffraction patterns of products on heating. Sample: $Sn_3(P_{6m})_2 \cdot 12H_2O$.

Table 2. Changes in the Amounts of Phosphates (Starting Material: P_{6m})

Temp/°C	Compound R.H./%	P_{oligo} %	P_{6m} %	P_{3m} %	P_{poly} %	$P_{high\ poly}$ %
500	0	0	84.6	15.4	0	0
	15	0	88.1	11.9	0	0
	90	0	91.0	9.0	0	0
570	0	1.7	0	44.5	1.4	52.4
	15	11.2	0	28.9	2.7	57.2
	90	5.6	0	30.3	1.9	62.2

P_{6m}. In a dry air atmosphere (r.h.=0%), the amounts of P_{6m} decreased and P_{3m} was formed in about a 15% yield. In a 15—90% relative humidity atmosphere (at 25 °C), P_{3m} was formed in about a 10% yield. The ratio of the amounts of P_{3m} to P_{6m} decreased with the increase in the humidity. At 570 °C, the P_{6m} completely disappeared throughout the humidity region and considerable amounts of P_{3m} and $P_{high\ poly}$ were produced along with some soluble linear phosphates (P_{oligo} and P_{poly}). The amount of $P_{high\ poly}$ in r.h.=15—90% was larger than that in r.h.=0%, while that of P_{3m} had an opposite tendency. It seems from the above results that P_{3m} begins to decompose and changes to $P_{high\ poly}$ at 550—570 °C, while P_{3m} completely decomposes at 610 °C near an endothermic peak and $P_{high\ poly}$ forms in a large quantity. When P_{6m} changed to $P_{high\ poly}$ through P_{3m}, scarcely no other species of phosphates were found in these reaction processes (maximum of P_{oligo}=10%). Consequently, these rearrangements probably proceed in the same manner as is the case with the P_{3m} system.

Thermal Decomposition of $Sn_2P_8O_{24} \cdot 5H_2O$ (P_{8m}). Figure 5 shows the DTA-TG curves of P_{8m} at atmospheric pressure. Four endothermic peaks — at about 65, 140, 270, and 635 °C — were observed. A large exothermic peak was shown at 320 °C. The endothermic peaks with a weight loss at 65 and 140 °C are attributable to the dehydration of the water of crystallization. From the results of the X-ray analysis and the HPLC of products heated at various temperatures, it seems that P_{8m} existed in anhydride at 180 °C and decomposed to P_{oligo} and $P^*_{high\ poly}$ in the 250—300 °C region, except for the changing of P_{8m}, in part, to P_{3m}. At higher temperatures, P_{3m} decomposed and then condensed $P_{high\ poly}$. Table 3 shows the changes in the amounts of phosphates in the samples heated at sev-

Table 3. Changes in the Amounts of Phosphates (Starting Material: P_{8m})

Temp/°C	Compound R.H./%	P_{oligo} %	P_{8m} %	P_{3m} %	P_{poly} %	$P^*_{high\ poly}$ %
255	0	23.8	18.9	3.9	26.8	26.6
	15	11.7	0	5.7	3.5	79.1
	90	15.5	0	5.7	3.5	75.3
300	0	5.0	0	84.8	1.6	14.8
	15	17.2	0	6.3	1.6	81.0
	90	26.9	0	7.6	2.1	69.5

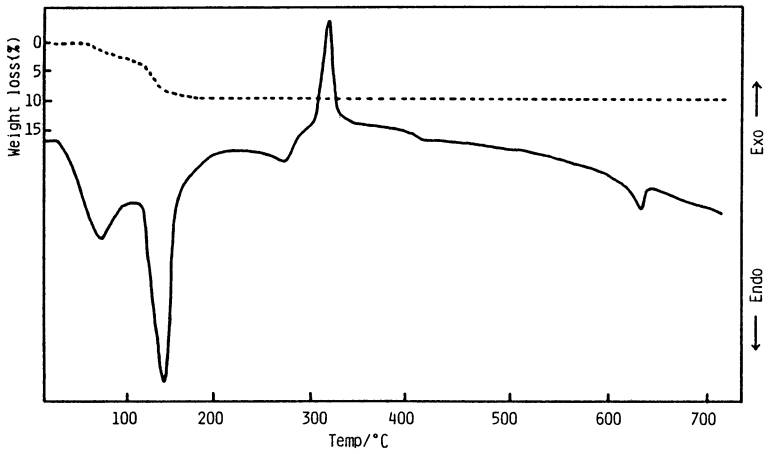
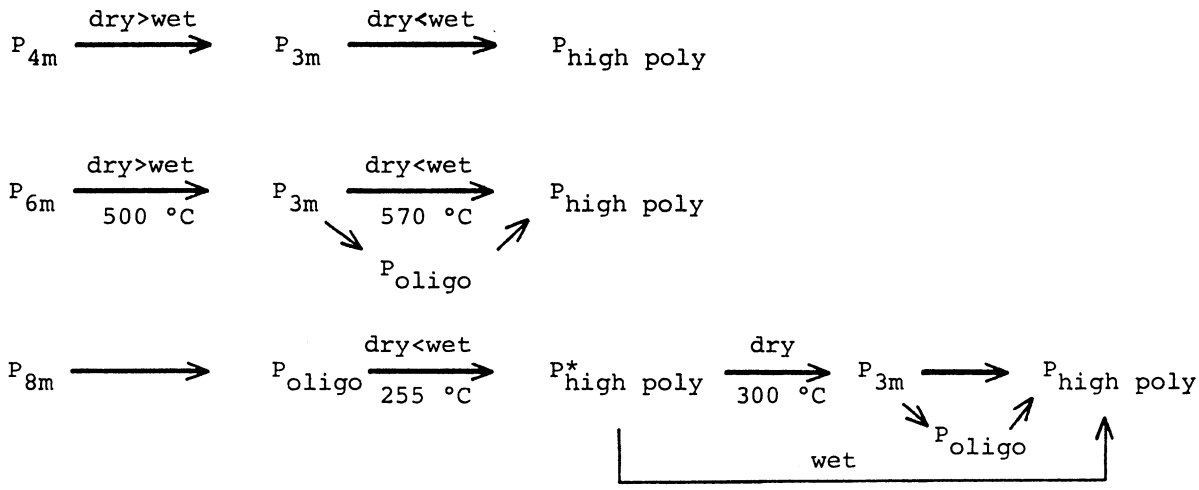


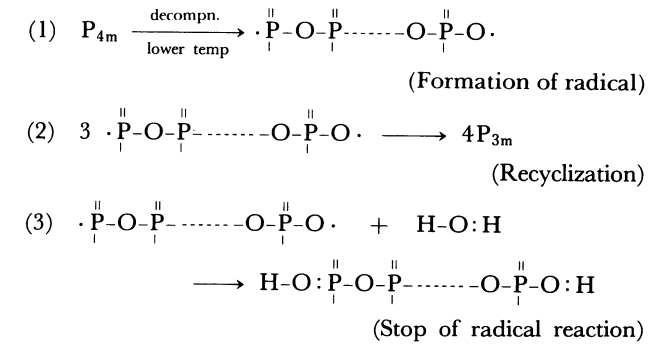
Fig. 5. DTA-TG curves of $Sn_2P_{8m} \cdot 5H_2O$. Solid line: DTA, dotted line: TG.

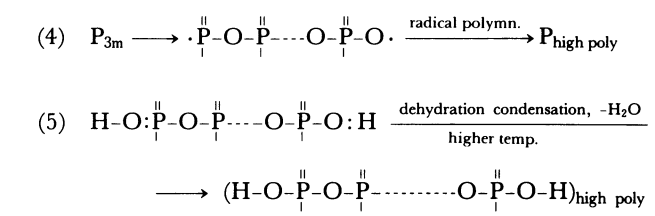


Scheme 1.

eral temperatures. At 255 °C in a dry air atmosphere (r.h.=0%), about 80% of the P_{8m} has already changed to P_{oligo}, P_{poly}, and $P^*_{high\ poly}$ in about equal quantities, while in a relative humidity of 15—90% (at 25 °C) the P_{8m} disappeared completely, while $P^*_{high\ poly}$ was formed in a large quantity. Further, at 300 °C in a dry air atmosphere (r.h.=0%), P_{3m} formed again in about a 85% yield with the decrease in P_{oligo}, P_{poly} and $P^*_{high\ poly}$, while in a relative humidity of 15—90% (at 25 °C), no remarkable change was observed in the amounts of phosphates as compared with the results at 255 °C. In the humid atmosphere, there might be a path of $P^*_{high\ poly}$ to $P_{high\ poly}$ without going through P_{3m}.

Based upon the results described above, the process of the thermal decomposition of tin(IV) *cyclo*-phosphates under several humid atmospheres may be summarized schematically as in Scheme 1. In a previous paper,[17] Takenaka et al. reported that, in a humid atmosphere, the radicals formed from P_{4m} may be considered to combine with water molecules in the atmosphere, so the water molecules could be expected to inhibit the radical polymerization. In this work, when P_{4m} decomposed in a humid atmosphere, the amount of the P_{3m} was small compared with that in a dried atmosphere. Consequently, P_{3m} is produced by the recyclization of the radicals which result from the cleavage of P_{4m}. Therefore, the mechanisms of P_{4m} to $P_{high\ poly}$ through P_{3m} may be considered to be as follows:





Since no P_{oligo} was detected, and since the TG curve indicated no weight change, at a lower temperature, it seems that the thermal reaction of P_{4m} to P_{3m} proceeds mainly according to Processes (1) and (2), while at a higher temperature the thermal polymerization of P_{3m} to $P_{high\ poly}$ proceeds mainly by Process (4), not Process(5). In the case of P_{6m}, the thermal reactions probably proceed by similar mechanisms except for the formation of a small amount of P_{oligo}.

On the other hand, P_{8m} decomposes at a rather low temperature (at about 250 °C) compared with the other two *cyclo*-phosphates. Consequently, it can be said that the water vapor very much influenced the thermal reaction and that P_{oligo} is formed by Process (3), followed by the change to $P^*_{high\ poly}$ by means of the dehydration-condensation reaction (Process (5)). $P^*_{high\ poly}$ in a dry air atmosphere (r.h.=0%) changed radically to $P_{high\ poly}$ through P_{3m} by means of Process (4), while in a humid atmosphere it probably crystallizes or changes to $P_{high\ poly}$ by means of the dehydration-condensation reaction (Process (5)).

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