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The Thermal Decomposition of Ammonium Zinc Trihydrogenbis(phosphate) Monohydrate $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$

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Synopsis. $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$[NZHP] was prepared by a wet method. NZHP was gradually decomposed to di-(P_2) and oligophosphates (n=3—9: P_{oligo}). A part of the formation of P_{oligo} involved hydrolysis of the –P–O–P– linkages of P_2, which was accerelated by humidity. γ-$Zn_2P_2O_7$ partially crystallized from P_2. Above 350 °C, NZHP was changed to long-chain β-$Zn(PO_3)_2$.

Ammonium zinc phosphate, $(NH_4)ZnPO_4$, and its hydrates are known with regard to gravimetric determinations of zinc.[1,2] They have also been studied regarding thermal decomposition.[3–7]

It has been indicated in the literatures[8,9] that zinc *cyclo*-tetraphosphate, $Zn_2P_4O_{12}$, with an eight-membered ring anion was formed through dehydration-condensation of zinc bis(dihydrogenphosphate) dihydrate $Zn(H_2PO_4)_2 \cdot 2H_2O$.

Frazier et al.[10] reported the formation and X-ray diffraction data of $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$[NZHP]. Since its molar ratio of zinc to phosphorus is 1/2, like that of $Zn(H_2PO_4)_2 \cdot 2H_2O$, NZHP is thought to produce zinc metaphosphates with long-chain or eight-membered ring anions.

Although the thermal decomposition of $(NH_4)ZnPO_4$ has been well studied, as mentioned above, that of NZHP has been reported only by Acharyya and Roy.[11] However, they did not refer to any method for separating and identifying, phosphate anions.[11] The purpose of the present work was to investigate the thermal decomposition of NZHP with regard to the effect of humidity and the formation of zinc *cyclo*-tetraphosphate. Analysis of the various phosphate anions was performed by means of HPLC-FIA (HPLC-flow injection analysis), similar to in previous work.[12–14]

Experimental

NZHP was prepared by a method different from that described in Ref. 11. Forty grams of phosphoric acid were mixed with 80 cm^3 of distilled water. Two grams of zinc oxide were added to the diluted phosphoric acid solution to dissolve. The pH of the solution was adjusted to three with concentrated aqueous ammonia; it was then allowed to stand for four days at room temperature. The formed precipitate was filtered off, and washed with cold water, 50% (v/v) ethanol–water, and then acetone. The product was air-dried. It was characterized by X-ray diffractometry,[10] and by determinations of phosphorus, nitrogen[12–14] and zinc.[2]

Streams of dry N_2 gas and of two kinds of humid air (50 $cm^3\,min^{-1}$) were employed in order to investigate the effect of humidity on the thermal decomposition. The humid air streams were prepared by the use of an Ace Constant-humidity Generator Model AHC-1 (Ace Scientific Laboratory Co., Ltd.), as reported by Nariai et al.[15] The humidity of the streams was controlled by changing the pressure of the air introduced into the apparatus, which was kept at the required temperature. One of the humid air streams, thus prepared, supplied ca. 1.0 mg of water vapor per minute, and the other ca. 1.9 mg min^{-1}. Thermal decomposition was studied mainly by the use of a dynamic heating method (heating rate: 2.5 K min^{-1}). Isothermal experiments were also carried out at a fixed reaction time (5 h). The other experimental procedures were essentially the same as those described in the literature.[12–14]

Results and Discussion

Figure 1 shows an example of thermal analyses (TG-DTA) measured in air. The weight loss was ca. 2.1% at 120 °C. Isothermal products heated at 120 °C in a N_2 gas stream did not produce a weight loss as much as that of ca. 4.7%, which was smaller than that calculated for the following equation (6.12%):

$$(NH_4)ZnH_3(PO_4)_2 \cdot H_2O \rightarrow (NH_4)ZnH_3(PO_4)_2 + H_2O.$$

Since the isothermal products at 120 °C contained a small amount of diphosphates, it is probably impossible to obtain anhydrous $(NH_4)ZnH_3(PO_4)_2$ by a thermal treatment. Even the isothermal products hardly lost ammonia; thus, the endothermic peaks at 80 and 110 °C can be attributed to the liberation of a part of the hydrated water of NZHP.

The notches of the DTA curve observed between 150 and 450 °C changed for each measurement, which must be due to the tendency of NZHP to sputter. A weight loss of up to 600 °C was ca. 23.7%, which was close to that calculated according to the following equation (24.15%).

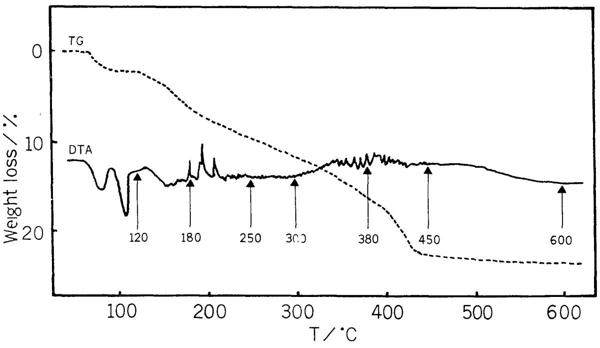

Fig. 1. Thermal analysis of $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$ measured in air. Heating rate: 2.5 K min^{-1}.

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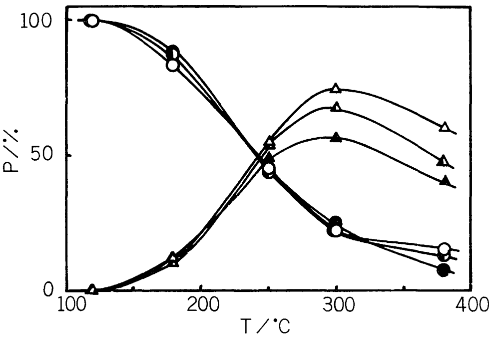

Fig. 2. Effect of humidity on the changes in the amounts of mono- (P_1) and diphosphates (P_2) in the decomposition products of $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$. ○ and △: P_1 and P_2 in dry N_2 gas, ◐ and ◭: P_1 and P_2 in ca. 1.0 mg-H_2O, ● and ▲: P_1 and P_2 in ca. 1.9 mg-H_2O.

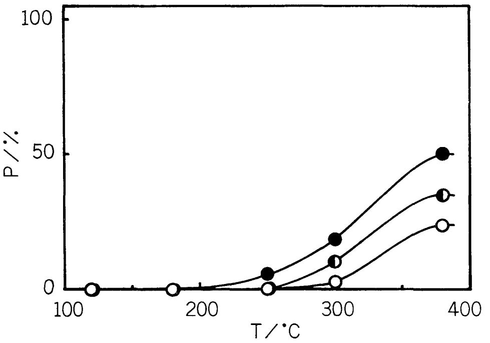

Fig. 3. Effect of humidity on the changes in the amounts of oligophosphates (n=3—9) in the decomposition products of $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$. ○: dry N_2 gas, ◐: ca. 1.0 mg-H_2O, ●: ca. 1.9 mg-H_2.

$$(NH_4)ZnH_3(PO_4)_2 \cdot H_2O \rightarrow Zn(PO_3)_2 + NH_3 + 3H_2O.$$

Figures 2 and 3 represent the percentage of phosphorus atoms present as mono- (P_1), di- (P_2) and oligophosphates (chain length n=3—9: P_{oligo}) in the products, obtained by heating up to the temperatures indicated by the arrows in Fig. 1. The products heated up to temperatures below 380 °C were dissolved well in a 0.1 mol dm^{-3} Na_2H_2edta (disodium dihydrogen ethylenediaminetetraacetate dihydrate) solution used for HPLC-FIA, while those heated up to 450 and 600 °C were not dissolved completely in the Na_2H_2edta solution. Therefore, since the HPLC-FIA data of the products above 450 °C were not thought to show accurate percentages of phosphates in the products, the results are not illustrated in Figs. 2 and 3. There were X-ray diffraction lines only due to zinc polyphosphate β-$Zn(PO_3)_2$[16] in the products heated up to 450 and 600 °C. Preliminary isothermal experiments in air gave the formation of β-$Zn(PO_3)_2$, even at 350 °C; thus, β-$Zn(PO_3)_2$ was formed above 350 °C.

Figures 2 and 3 show that the humidity decreased the amounts of diphosphates (P_2) between 250 and 380 °C, while it increased those of oligophosphates (P_{oligo}); thus, the formation of P_{oligo} probably involved a partial hydrolysis of –P–O–P– linkages of P_2. McGilvery and Scott reported such a hydrolytic effect of water vapor.[17] The hydrolysis of P_2 produces acidic monophosphates (P_1). In other words, it results in an increase in the hydroxyl groups. Reasonably, as indicated by Thilo and Seemann,[18] the increase causes more chances that the hydroxyl groups of the P_1 encounter those of other phosphates ($n \geqslant 2$). It is certainly favorable for a heterogeneous solid-state reaction through which P_{oligo} is formed, i.e., condensation. Since some of ammonia was evolved until 300 °C (ca. 20% against its content of NZHP), the phosphates ($n \geqslant 2$) must also have –OH groups to perform the condensation. As shown in Fig. 2, the humidity hardly made any apparent differences in the disappearance of monophosphates (P_1), which implies that the condensation of the acidic P_1 with the phosphates ($n \geqslant 2$) took place immediately, independent of the humidity. Therefore, in the temperature range (250—380 °C), humidity is thought to be more effective for the hydrolysis of the –P–O–P– linkages than for the retardation of liberation of the water vapor produced by condensation.

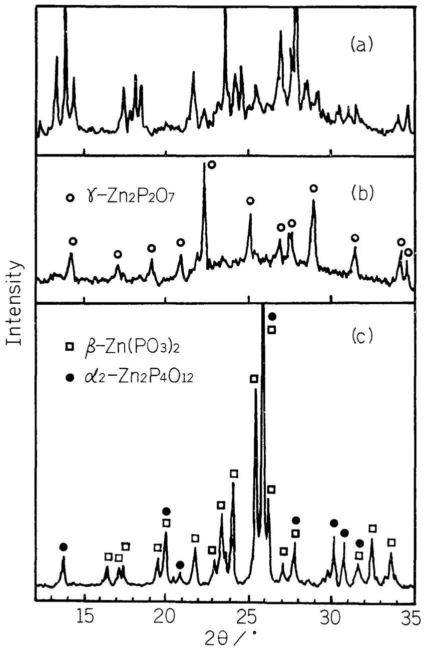

Fig. 4. X-Ray diffraction patterns of the isothermal products under dry conditions. (a): at 250 °C for 5 h, (b): at 300 °C for 5 h, (c): at 500 °C for 5 h. Cu$K\alpha$ radiation was used.

Figure 4 shows X-ray diffraction patterns of the isothermal products heated at 250, 300, and 500 °C under dry conditions. The products at 170 °C were amorphous, while those at 250 °C could not be characterized. The diffraction patterns of these products were not changed by the humidity. The diffraction lines of the samples heated at 300 °C under dry conditions, agreed with those due to γ-$Zn_2P_2O_7$ (Fig. 4(b)).[7] Although humid conditions gave some lines, except for those of γ-$Zn_2P_2O_7$, these lines could not be characterized in the present work. Anyway, γ-$Zn_2P_2O_7$ was obviously formed through disproportionation. Isothermal experiments (reaction time: 5 h) hardly showed any effect of humidity on the composition of phosphate ions of the products, which must be attributed to the attainment of equilibrium. Perhaps the only formation of γ-$Zn_2P_2O_7$ under dry conditions might result from a larger quantity of P_2 before the attainment of equilibrium (Fig. 2).

X-Ray diffraction patterns showed isothermal products at 500 °C to consist of long-chain β-$Zn(PO_3)_2$ and *cyclo*-tetraphosphate α_2-$Zn_2P_4O_{12}$.[19] The humidity did not cause any difference in the patterns. Beucher and Grenier[19] reported that α_2-$Zn_2P_4O_{12}$ had strong diffraction lines at 13.8, 19.9 and 30.7° (d(A) reported are converted to $2\theta(°)$:Cu $K\alpha$ radiation). Comparing the corresponding lines in Fig. 4 with the strongest line of β-$Zn(PO_3)_2$ at 25.8°,[16] α_2-$Zn_2P_4O_{12}$ was thought to be a minor component. The products were allowed to stand in a 0.1 mol dm^{-3} Na_2H_2edta solution for three days at room temperature. They were apparently fairly dissolved in the Na_2H_2edta solution. If the solubility of α_2-$Zn_2P_4O_{12}$ was the same as that of β-$Zn(PO_3)_2$, and if these phosphate ions were not hydrolyzed, the HPLC-FIA for the supernatant solution showed that ca. 90% and ca. 5% of phosphorus atoms in the products were present as polyphosphate ions and *cyclo*-tetraphosphate ions, respectively. And HPLC-FIA by the use of a rapid metathesis for 5 min, with a 10% (w/w) sodium sulfide aqueous solution, also gave results that there were hardly any *cyclo*-tetraphosphate ions. Therefore, we should like to conclude that the $Zn(PO_3)_2$ formed was not zinc *cyclo*-tetraphosphate $Zn_2P_4O_{12}$, but zinc polyphosphate β-$Zn(PO_3)_2$.

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