BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50, (1) 307—308 (1977)

Studies of Nitrogen-Phosphorus Compounds. XXVIII.[1] The Thermal Decomposition and Fireproofing Effect of Trimeric and Tetrameric Phosphorus Diamide Nitride

Etsuro KOBAYASHI and Tadao KANAYAMA
National Chemical Laboratory for Industry, Hon-machi, Shibuya-ku, Tokyo 151

(Received June 25, 1976)

Synopsis. The thermal decomposition of $N_3P_3(NH_2)_6 \cdot H_2O$ and $N_4P_4(NH_2)_8 \cdot H_2O$ and their fireproofing effects for cellulose have been investigated by means of DTA and TG. These compounds dehydrated at 113 and 124 °C and deammonated at 265 and 271 °C. The activation energies of the dehydration and deammonation were 27 and 42 kcal/mol in the trimer, and 37 and 40 kcal/mol in the tetramer. The cellulose impregnated with either of these compounds flamed up at lower temperatures than did the pure cellulose, but its carbonized product remakably resisted combustion.

The amidated derivatives of the lower polymers of phosphorus dichloride nitride have drawn interest as fireproof materials.[2,3] The present authors had prepared $N_3P_3(NH_2)_6$[4] and $N_4P_4(NH_2)_8$[5] and investigated their hydrolysis behaviors under various conditions.[5-7] In this study, the thermal decomposition of $N_3P_3(NH_2)_6 \cdot H_2O$ and $N_4P_4(NH_2)_8 \cdot H_2O$ was investigated by means of the differential thermal analysis (DTA) and thermogravimetric (TG) measurements; the incombustibility of the cellulose impregnated with either of these compounds was also examined and compared with that of the pure cellulose.

Experimental

$N_3P_3(NH_2)_6 \cdot H_2O$ and $N_4P_4(NH_2)_8 \cdot H_2O$ for the DTA and TG measurements were prepared by the procedures reported previously.[4,5] DTA and TG were performed simultaneously by the use of macro-type and micro-type thermal analysers. The conditions of the thermal analysis are indicated along with Figs. 1 and 3. The cellulose impregnated with $N_nP_n(NH_2)_{2n}$ (n=3,4) was formed as follows: a filter paper (Toyo Roshi Co., Ltd. No. 5B) was immersed in an aqueous solution of $N_nP_n(NH_2)_{2n}$ (n=3,4). It was drawn up, pressed, and dryed. The incombustibility was also examined by using the microthermal analyser.

Results and Discussion

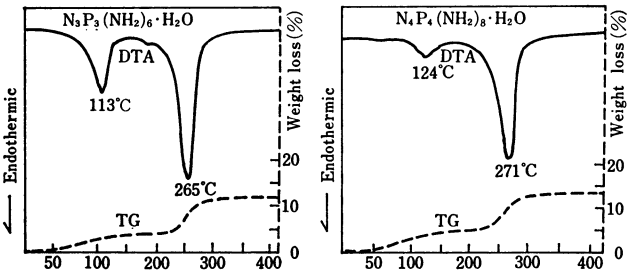

Fig. 1. DTA and TG curves for trimeric and tetrameric phosphorus diamide nitride.
Sample: 100 mg, heating rate: 5 °C/min, DTA: ±250 μV, current gas: N_2 gas 0.3 l/min.

The DTA and TG curves for trimeric and tetrameric phosphorus diamide nitride are shown in Fig. 1. In the DTA curve for $N_3P_3(NH_2)_6 \cdot H_2O$, endothermic peaks appeared at 113 and 265 °C: these seemed to be due to the dehydration of the water of crystallization and the deammonation from the amido-groups. In the DTA curve for $N_4P_4(NH_2)_8 \cdot H_2O$, two endothermic peaks also appeared. The height of the first peak was lower than that of the trimer variety, and was shifted to the higher temperature side. Therefore, it may be expected that the water of crystallization of the tetramer is bound more strongly than in the case of the trimer. On the other hand, the weight losses in two steps, which proved the dehydration and deammonation, were recognizable on each TG curve. The activation energies in these reactions were calculated in accordance with Kissinger's method.[8] The peak temperatures ($T_{\max}$) related to the reactions were measured at the heating rates (ϕ) of 5, 10, 20, and 40 °C/min. The activation energies, which were obtained from the relation between the reciprocal of the $T_{\max}$ and the log $\phi/T^2_{\max}$ shown in Fig. 2, were 27 and 37 kcal/mol for the dehydrations in $N_3P_3(NH_2)_6 \cdot H_2O$ and $N_4P_4(NH_2)_8 \cdot H_2O$, and 42 and 40 kcal/mol for their deammonations. It had already been known that the lower polymers of phosphorus diamide nitride decomposed at the elevated temperatures, and then were converted into phospham $(PN_2H)_n$.[4] In this study, it was confirmed by the use of the thermal analyser that a heating product of $N_nP_n(NH_2)_{2n} \cdot H_2O$ (n=3, 4) lost weight quickly at 800 °C, melted at about 900 °C, and immediately sublimed in nitrogen gas, although it burned in air.

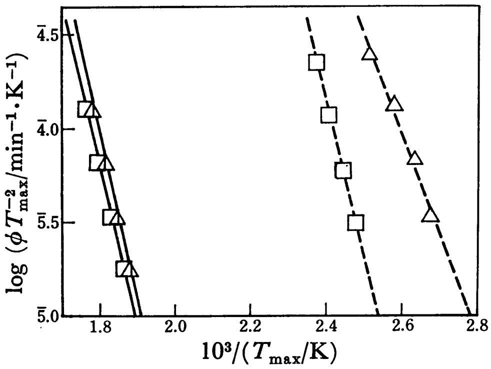

Fig. 2. Relation between $1/T_{\max} \cdot 10^3$ and log ($\phi \cdot T^{-2}_{\max}$).
△: $N_3P_3(NH_2)_6 \cdot H_2O$, □: $N_4P_4(NH_2)_8 \cdot H_2O$.
-----: Dehydration, ——: deammonation.

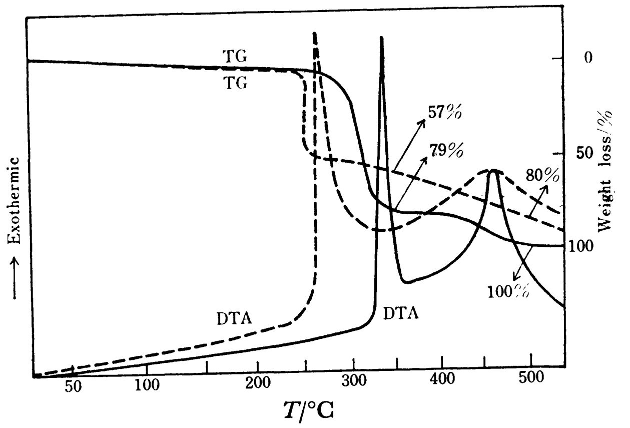

Fig. 3. DTA and TG curves for cellulose and cellulose including $N_4P_4(NH_2)_8$.
Sample: 20 mg, heating rate: 10 °C/min, DTA: ±100 μV, current gas: air 150 ml/min, ——: cellulose, ----: cellulose impregnated with $N_4P_4(NH_2)_8$ (P: 2.9%).

The DTA and TG curves for the filter paper of pure cellulose and that treated with the aqueous solution of $N_4P_4(NH_2)_8$ are shown in Fig. 3. In the DTA curve for the pure cellulose, exothermic peaks appeared at 333 and 461 °C. The cellulose flamed up at the temperature of the first peak. The weight loss reached 79% at 350 °C, and a carbonized product was incinerated completely at 500 °C. In the DTA curve for the cellulose including $N_4P_4(NH_2)_8$, two exothermic peaks also appeared at 261 and 461 °C. The first peak shifted to the lower temperature side compared with that of the pure cellulose. In this case, the weight of the carbonized residue increased with the increase of the content of phosphorus in it. When the samples of cellulose including 2.0, 2.9, and 3.7% P were heated at 500 °C, the weight % of the residues were 11, 20, and 25%, respectively. The fireproofing effects of the trimer and tetramer varieties were almost the same. From the present results, it may be concluded that these compounds effectively retard the combustion of the cellulose.

References

1) Presented at the 34th National Meeting of the Chemical Society of Japan, Tokyo, April 1976.

2) C. A. Redfarn and H. Coates (Albright and Wilson Ltd.), Brit. Patent 788 785 (1958).

3) Erik R. Nielsen and William L. Stepp (I I T Research Institute), U. S. Patent 3 348 926 (1967).

4) E. Kobayashi, *Nippon Kagaku Kaishi*, **1972**, 38, *J. Nat. Chem. Lab. Ind.*, **68**, 19 (1973).

5) E. Kobayashi, *Bull. Chem. Soc. Jpn.*, **49**, 3524 (1976).

6) E. Kobayashi, *Chem. Lett.* **1976**, 479.

7) E. Kobayashi, *Nippon Kagaku Kaishi*, **1973**, 1437; *J. Nat. Chem. Lab. Ind.*, **67**, 470 (1974).

8) H. E. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).