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Preparation and thermal decomposition of hexa-ammonium tetraphosphate dihydrate $(NH_4)_6P_4O_{13} \cdot 2H_2O$

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Hexa-ammonium tetraphosphate dihydrate, $(NH_4)_6P_4O_{13} \cdot 2H_2O$ (HATP), was prepared by the hydrolysis of sodium cyclo-tetraphosphate with sodium hydroxide solution, followed by ion-exchange with ammonium. Thermal decomposition in static air was first carried out dynamically, at a heating rate of 5 K min^{-1} as used in thermal analysis (thermogravimetry-differential thermal analysis), and also isothermally. To examine the effect of humidity on the thermal decomposition, HATP was heated isothermally in streams of dry and humid air. The products were characterized by X-ray diffraction analysis and high-performance liquid chromatography–flow injection analysis. At 100 °C, HATP was decomposed to mono- and triphosphates and to 2 mol diphosphate, and this was accelerated by humidity. Further degradation of the triphosphate to mono- and diphosphates took place slowly. The 2 mol diphosphate also decomposed slowly to 4 mol monophosphate. At temperatures above 150 °C, the form I of ammonium polyphosphate (I-APP) was produced. I-APP was further hydrolysed by humidity to shorter-chain phosphates, such as mono-, di- and triphosphates.

1. Introduction

Ammonium tetraphosphate is a member of the group of ammonium phosphates having chain anions. It is not commercially used alone. However, mixtures of the ammonium mono-, di-, tri-, tetra- and more highly condensed phosphates have been used to prepare liquid fertilizers that do not salt out at low temperatures [1]. Some ammonium phosphates, such as ammonium dihydrogen, diammonium hydrogen and triammonium monophosphates, are also applied as flame-proofing materials [2].

Regarding the properties of ammonium phosphates, although the thermal behaviour of ammonium mono- [3–7], di- [8–10] and triphosphates (e.g. [10–16]) has been studied repeatedly and widely, that of ammonium tetraphosphate has not been examined, although preparation of ammonium tetraphosphate has been carried out by several workers. Griffith reported a method for preparing hexa-ammonium tetraphosphate hexahydrate, $(NH_4)_6P_4O_{13} \cdot 6H_2O$, using the metathesis of lead tetraphosphate with ammonium disulphide [17]. Hexa-ammonium tetraphosphate dihydrate, $(NH_4)_6P_4O_{13} \cdot 2H_2O$, was prepared by Farr *et al.* by a modification of the method of Griffith [18]. X-Ray diffraction data for $(NH_4)_6P_4O_{13} \cdot 2H_2O$ are given by Waerstad and McClellan [19]. Regarding other salts of tetraphosphate, Watanabe *et al.* studied the thermal behaviour of amorphous calcium [20], strontium [21], barium [21] and magnesium tetraphosphates [22], which were prepared by hydrolysis of cyclo-tetraphosphate in sodium hydroxide solution.

In this paper, we describe a novel preparation of hexa-ammonium tetraphosphate dihydrate $(NH_4)_6P_4O_{13} \cdot 2H_2O$ (HATP) using hydrolysis of cyclo-tetraphosphate, followed by ion-exchange, and we discuss its thermal decomposition. The effect of water vapour, present in the atmosphere, on the thermal decomposition of HATP was examined and compared with previous papers [7, 23].

2. Experimental procedure

2.1. Preparation of hexa-ammonium tetraphosphate dihydrate $(NH_4)_6P_4O_{13} \cdot 2H_2O$

Sodium cyclo-tetraphosphate tetrahydrate was prepared according to the method of Bell *et al.* [24]. It was then treated with a 5 mol dm^{-3} sodium hydroxide aqueous solution at 20 °C for 4 days. After filtering, the solution was neutralized with a 1 mol dm^{-3} hydrochloric acid at a temperature below 3 °C [20–22]. The sodium tetraphosphate solution thus obtained was converted to ammonium tetraphosphate solution by passing through a column packed with NH_4-type cation exchanger [23, 25]. By addition of methanol to the effluent, hexa-ammonium tetraphospate dihydrate, $(NH_4)_6P_4O_{13} \cdot 2H_2O$, was precipitated. To avoid contamination by ammonium chloride, the precipitate was recrystallized twice using methanol. The purity of the final product was indicated by phosphorus present as $P_4O_{13}^{6-}$ more than 98.4%. The X-ray diffraction pattern of the product agreed with that of hexa-ammonium tetraphosphate dihydrate $(NH_4)_6P_4O_{13} \cdot 2H_2O$ [19].

2.2. Thermal decomposition

A 0.1 g portion of HATP was heated in static air in a cylindrical electric furnace by dynamic heating at the same heating rate of $5\ \mathrm{K\,min^{-1}}$ as that used in thermogravimetry–differential thermal analysis (TG–DTA). Isothermal heating was carried out in static air also, and in streams ($50\ \mathrm{cm^3\,min^{-1}}$) of dry and humid air (relative humidity 90% at 25 °C) prepared as reported previously [7, 23]. Before heating, the furnace was purged with about twice its volume of the appropriate air stream to obtain the desired atmosphere. After heating, samples were taken out immediately and cooled in a silica-gel desiccator for analysis.

2.3. Thermal analysis

About 10 mg HATP was placed in a platinum pan. Thermal analyses were carried out in static air at $5\ \mathrm{K\,min^{-1}}$ on a MAC SCIENCE TG-DTA 2020 system.

2.4. X-ray diffractometry

X-ray diffraction (XRD) patterns were recorded on a Rigaku Denki Geigerflex X-ray diffractometer, RAD-IA, using nickel-filtered CuK_α radiation.

2.5. HPLC–flow injection analysis (HPLC–FIA)

The composition of phosphates was determined with a JASCO LC-800 Liquid Chromatograph-FIU-300N flow injection analysis unit (HPLC–FIA) system in a similar manner to that reported by Baba and Tsuhako [26].

3. Results and discussion

3.1. Thermal decomposition in static air

Fig. 1 shows TG and DTA curves of HATP measured in static air. There are several endothermic peaks at 97, 145, 180 and around 300 °C. The peaks around 300 °C probably reflect the melting of the sample, as found previously [23].

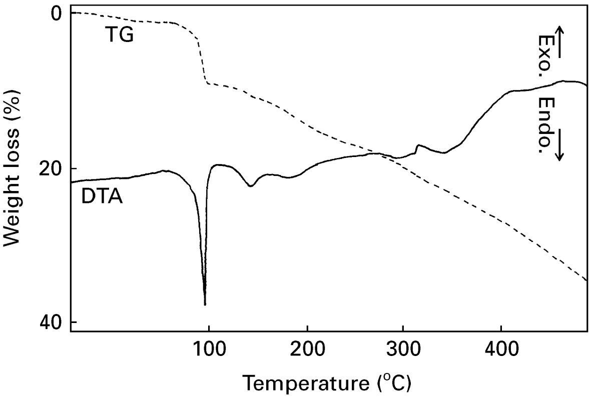

Figure 1 TG and DTA curves for $(NH_4)_6P_4O_{13} \cdot 2H_2O$ measured in static air. Heating rate $5\ \mathrm{K\,min^{-1}}$.

TABLE I Change in the percentage of phosphorus atoms (P %) present as mono-, di-, tri-, tetra-, oligo- and polyphosphates in the products obtained by heating $(NH_4)_6P_4O_{13} \cdot 2H_2O$ at $5\ \mathrm{K\,min^{-1}}$ in static air.

Temp. °C	Composition P %					
	Mono-	Di-	Tri-	Tetra-	Oligo-[a]	Poly-
100	3.1	1.3	8.9	81.7	5.1	–
150	4.9	14.4	18.1	30.3	17.2	15.1
200	13.5	18.0	11.7	5.8	3.7	47.3
250	6.4	8.6	6.8	4.8	6.3	67.2

[a] Chain length (n): 5–9.

Table I shows the percentage of phosphorus atoms, P (%), present as mono-, di-, tri-, tetra-, oligo- (chain length 5–9) and polyphosphates in the products obtained by heating HATP at $5\ \mathrm{K\,min^{-1}}$ in static air. Because more than 80% phosphorus atoms remained undecomposed in the product heated to 100 °C, the endothermic peak at 97 °C was considered to be caused by the release of water of crystallization from HATP. However, the release of water would give a loss in weight of only 7.57%, while the TG loss observed to 100 °C was larger, ~9.0%. The endothermic peak at 97 °C, largely attributable to the elimination of the water of crystallization, may also indicate slight loss of ammonia.

Table II shows the percentage of phosphorus atoms, P (%), present as mono-, di-, tri-, tetra-, oligo- (chain length 5–9) and polyphosphates in the products obtained by heating HATP at 100, 150 and 200 °C for 10, 30 and 60 min. At 100 °C, HATP was decomposed to mono-, di- and triphosphates. As the reaction time is increased, the P (%) of diphosphate became larger, while the ratio of the P (%) of triphosphate to the P (%) of monophosphate stays unchanged at about three. The triphosphate at first produced from HATP must therefore be decomposed slowly to mono- and diphosphates. The decomposition rate of 2 mol diphosphate to 4 mol monophosphate is also slow. It is dependent on the cleavage of P–O–P linkages of HATP. The decomposition process can be written as follows

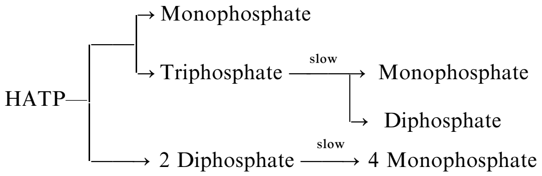

TABLE II Change in the percentage of phosphorus atoms (P %) present as mono-, di-, tri-, tetra-, oligo- and polyphosphates in the products obtained by heating $(NH_4)_6P_4O_{13} \cdot 2H_2O$ at 100, 150 and 200 °C for 10, 30 and 60 min in static air.

Temp. °C	Time (min)	Composition P %					
		Mono-	Di-	Tri-	Tetra-	Oligo-[a]	Poly-
100	10	2.9	2.7	8.2	80.8	5.5	–
	30	4.4	8.2	12.3	67.5	7.7	–
	60	5.6	16.3	16.9	52.6	8.6	–
150	10	7.0	16.6	16.4	23.1	15.8	21.2
	30	26.0	27.9	10.7	3.1	1.7	30.6
	60	27.2	30.5	11.6	3.9	1.3	25.6
200	10	11.6	18.4	10.9	5.5	4.9	48.6
	30	2.9	4.6	2.9	1.6	1.8	86.2
	60	3.4	6.0	4.3	2.5	2.7	81.1

[a] Chain length (n): 5–9.

Watanabe *et al.* proposed a similar process for the decomposition of amorphous calcium tetraphosphate at room temperature [20].

Since the P (%) of oligophosphates (chain length 5–9) hardly increased from 10–60 min, little condensation of the shorter-chain phosphates took place at 100 °C.

At temperatures above 150 °C, the ratio of the P (%) triphosphate to the P (%) monophosphate decreases, e.g. to 0.41 at 150 °C for 30 min. Polyphosphates with long-chain anions were produced simultaneously. The decomposition of di- and triphosphates to monophosphate is thus not negligible, and the condensation of the shorter-chain mono-, di- and triphosphates takes place appreciably. Therefore, one can not systematically describe the thermal reaction of HATP above 150 °C, in contrast to that at 100 °C.

Fig. 2 shows X-ray diffraction patterns of HATP and of the products obtained by heating at 100, 150 and 200 °C for 30 min. The X-ray diffraction patterns did not essentially alter with reaction time, although the variation in the intensity of diffraction lines was found.

Shen *et al.* reported five different forms of crystalline ammonium polyphosphates [27]. Although the unit cell dimensions of form I of ammonium polyphosphate (I-APP) were not determined because of a lack of crystals large enough for single-crystal X-ray studies, the X-ray diffraction data for I-APP were given. The formation of I-APP in the samples of HATP decomposed at 150 and 200 °C was indicated by X-ray diffractometry, as shown in Fig. 2 [27]. The presence of I-APP corresponds to the formation of polyphosphate above 150 °C (see Table II); therefore, the polyphosphate must be the I-APP.

Although the X-ray diffraction pattern of the product obtained at 100 °C was similar to that of HATP, several diffraction lines attributable to HATP such as 0.749, 0.649 and 0.554 (d/nm) are absent. At the reaction time of 30 min, tetraphosphate remained undecomposed with more than 67.5% as phosphorus atoms. The product obtained at 100 °C may contain a kind of ammonium tetraphosphate resulting from the dehydration and deammoniation of HATP.

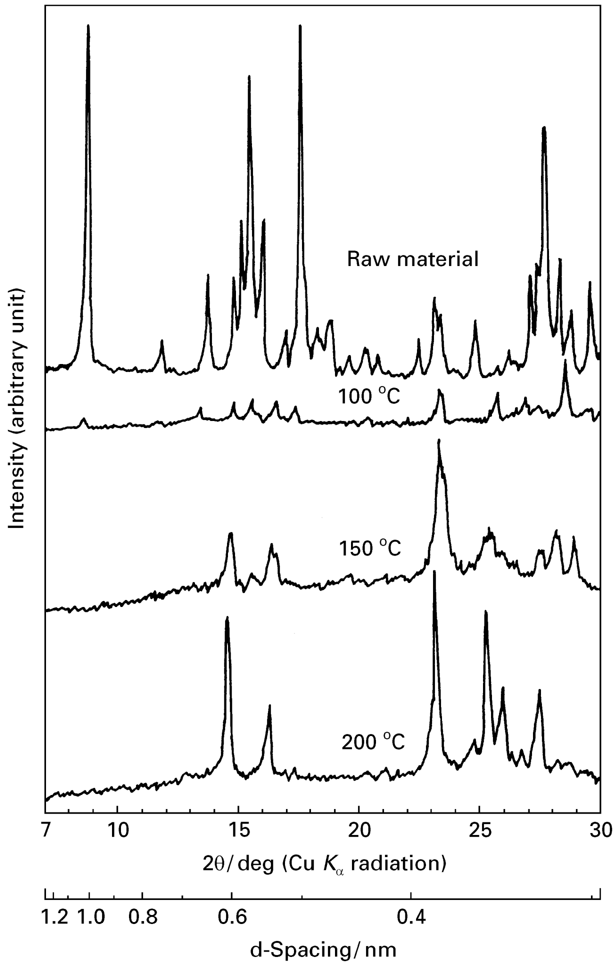

Figure 2 X-ray diffraction patterns of the products obtained by heating $(NH_4)_6P_4O_{13} \cdot 2H_2O$ at 100, 150 and 200 °C for 30 min in static air. The X-ray diffraction pattern obtained at 100 °C was that of an unknown material. At temperatures above 150 °C, form I of ammonium polyphosphate was produced as the only crystal component (see text).

3.2. Effect of humidity present in the atmosphere on the thermal decomposition

Figs 3 and 4 show the percentage of phosphorus atoms, P (%), present as mono-, di- and triphosphates, tetraphosphate and the phosphates with chain length

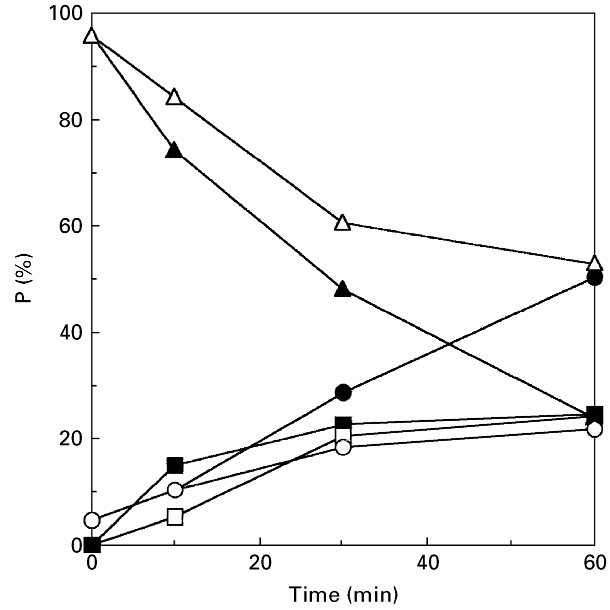

Figure 3 Changes in the percentage of phosphorus atoms, P (%), present as mono-, di- and triphosphates, tetraphosphate and the phosphates with a chain length of more than 5 in the products obtained by heating $(NH_4)_6P_4O_{13} \cdot 2H_2O$ at 100 °C in streams of dry and humid air. (○, ●) mono-, di- and triphosphates in dry and humid air, respectively; (△, ▲) tetraphosphate in dry and humid air, respectively; (□, ■) the phosphates with a chain length of more than 5 in dry and humid air, respectively.

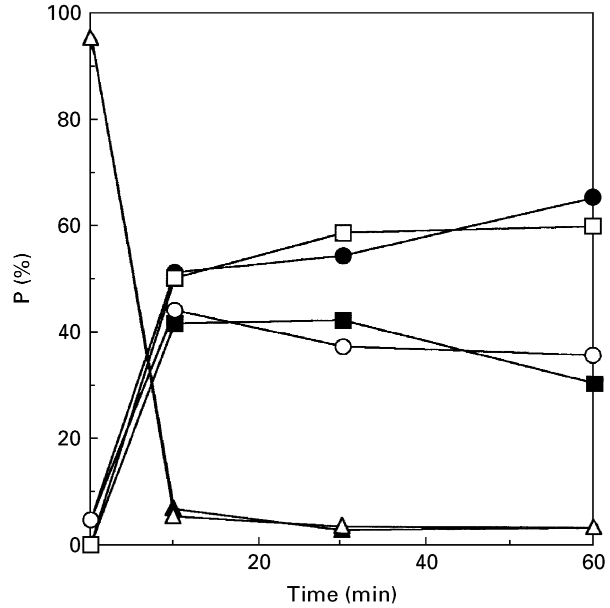

Figure 4 Changes in the percentage of phosphorus atoms, P (%), present as mono-, di- and triphosphates, tetraphosphate and the phosphates having a chain length of more than 5 in the products obtained by heating $(NH_4)_6P_4O_{13} \cdot 2H_2O$ at 150 °C in streams of dry and humid air. (○, ●) mono-, di- and triphosphates in dry and humid air, respectively; (△, ▲) tetraphosphate in dry and humid air, respectively; (□, ■) the phosphates having a chain length of more than 5 in dry and humid air, respectively.

more than five in the products obtained by heating HATP in streams of dry and humid air at 100 and 150 °C, respectively. Because mono-, di- and triphosphate are hydrolytic products of HATP, the total amount of them are plotted in Figs 3 and 4 to demonstrate the hydrolytic effect of humidity on the decomposition of HATP. The P (%) of the phosphates with chain length more than 5 is also summarized to show the inhibiting effect of humidity on the condensation of phosphates with chain length less than 4.

Fig. 3 shows that at 100 °C humidity in the atmosphere accelerates the decomposition of tetraphosphate to mono-, di- and triphosphates, while it does not inhibit the condensation of mono-, di-, tri- and tetraphosphates, resulting in the formation of phosphates having a chain length more than 5. A relative humidity of 90% at 25 °C, as used in these experiments, corresponds to a relative humidity of about 3% at 100 °C, and this may be too small to affect the condensation.

At 150 °C, the P (%) of tetraphosphate decreases apparently independently of the humidity between 10 and 60 min. Therefore, the mono-, di- and triphosphates shown in Fig. 4 do not directly result from hydrolysis of HATP. Because the P (%) present as mono-, di-, and triphosphates is larger and that the P(%) present as phosphates having chain length more than 5 is smaller in the products obtained in the humid atmosphere, compared to those obtained in the dry atmosphere, then the hydrolysis of phosphates having a chain length of more than 5 must give the mono-, di- and triphosphates. The phosphates having a chain length of more than 5 are secondary condensation products of mono-, di-, tri- and tetraphosphates. The initial fall in tetraphosphate may, perhaps, indicate an accelerating effect of humidity on hydrolysis of tetraphosphate.

A similar effect of humidity on the conversion of HATP to mono-, di- and triphosphates and the phosphates with chain length more than 5 is found at 200 °C. In the dry atmosphere the P (%) of phosphates with a chain length of more than 5 amounted to values more than 80%.

References

1. T. D. FARR and J. W. WILLIARD, *J. Chem. Eng. Data* **17** (1972) 317.
2. E. KOBAYASHI, *Phosphorus Lett.* **5** (1988) 3.
3. M. N. NABIEV, M. T. SAIBOVA, I. A. BORUKHOV and N. A. PARPIEV, *Zh. Neorg. Khim.* **14** (1969) 2950.
4. D. BOHUSLAV, K. FRANTISEK and J. FRANTISEK, *Sb. Vys. Sk. Chem.-Technol. Praze, Anorg. Chem. Technol.* **B15** (1972) 31.
5. L. G. BEREZKINA and S. I. BORISOVA, *Zh. Prikl. Khim. (Leningrad)* **57** (1984) 1372.
6. M. MACIEJEWSKI and R. RUDNICKI, *Thermochim. Acta* **113** (1987) 305.
7. A. TAKENAKA, O. TAKEO, N. MORIYAMA, I. MOTOOKA and H. NARIAI, *Chem. Express* **8** (1993) 213.
8. E. KOBAYASHI, *Nippon Kagaku Zasshi* **83** (1962) 132.
9. R. P. RILO, E. P. SAMOKHVALOV and I. M. KAGANSKII, *Zh. Prikl. Khim. (Leningrad)* **56** (1983) 879.
10. A. W. FRAZIER, J. P. SMITH and J. R. LEHR, *J. Agr. Food Chem.* **13** (1965) 317.
11. V. A. SOTNIKOVA-YUZHIK, M. M. PAVLYUCHENKO and E. A. PRODAN, *Vestsi Akad. Navuk B. Ser. Khim. Navuk* **5** (1975) 32.
12. E. A. PRODAN, L. I. PETROVSKAYA, M. M. PAVLYUCHENKO and N. A. AKULICH, *ibid.* **2** (1976) 11.
13. A. MENLIBAEV, D. Z. SERAZETDINOV, M. Kh. KIM and Zh. K. SHAIDARBEKOVA, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* **27** (1977) 1.

14. L. I. PETROVSKAYA, E. A. PRODAN, N. G. RAFAL'SKII and N. V. KHARITONCHIK, *Vestsi Akad. Navuk B SSR, Ser. Khim. Navuk* **4** (1980) 44.
15. E. A. PRODAN and V. I. KORZHUEV, *Zh. Neorg. Khim.* **28** (1983) 24.
16. E. A. PRODAN, V. N. KORZHUEV and L. I. PETROVSKAYA, *ibid.* **29** (1984) 1679.
17. E. J. GRIFFITH, *J. Inorg. Nucl. Chem.* **26** (1964) 138.
18. T. D. FARR, J. W. WILLIARD and J. D. HATFIELD, *J. Chem. Eng. Data* **17** (1972) 313.
19. K. R. WAERSTAD and G. H. McCLELLAN, *J. Appl. Crystallogr.* **7** (1974) 404.
20. M. WATANABE, H. SUZUMORI, M. MAEDA and T. YAMADA, *Bull. Chem. Soc. Jpn.* **53** (1980) 2663.
21. M. WATANABE, M. MAEDA and T. YAMADA, *ibid.* **56** (1983) 3430.
22. M. WATANABE, H. SUZUMORI, M. MAEDA and T. YAMADA, *Gypsum and Lime* **178** (1982) 3.
23. A. TAKENAKA, I. MOTOOKA and H. NARIAI, *Bull. Chem. Soc. Jpn.* **60** (1987) 4299.
24. R. N. BELL, L. F. AUDRIETH and F. HILL, *Ind. Eng. Chem.* **44** (1952) 568.
25. R. V. COATES and G. D. WOODARD, *J. Chem. Soc.* (1964) 1780.
26. Y. BABA and M. TSUHAKO, *Jasco Report* **23** (1988) 7.
27. C. Y. SHEN, N. E. STAHLHEBER and D. R. DYROFF, *J. Am. Chem. Soc.* **91** (1969) 62.

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