April, 1990] © *1990 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 63, 1243—1245 (1990)* 1243

The Hydrolytic Property of Imidodiphosphate in Solid and in an Aqueous Medium

Makoto Watanabe,* Shoji Sato, and Khosaku Wakasugi
Department of Industrial Chemistry, Chubu University, Matsumoto-cho, Kasugai, Aichi 487

(Received September 2, 1989)

Synopsis. Crystalline tetrasodium imidodiphosphate decahydrate, $Na_4P_2O_6NH \cdot 10H_2O$, was directly converted to diphosphate by heating above 200 °C in air according to the equation:

$$Na_2O_3PNHPO_3Na_2 + H_2O \longrightarrow Na_2O_3POPO_3Na_2 + NH_3$$

Amorphous tetrasodium imidodiphosphate was prepared by stirring the crystalline imidodiphosphate in excess ethanol. The substitution of an imino group of the amorphous imidodiphosphate for bridging oxygen took place much faster than that of the crystalline one. Imidodiphosphate was hydrolyzed to phosphoramidate and orthophosphate in an aqueous solution:

$$Na_2O_3PNHPO_3Na_2 + H_2O \longrightarrow Na_2PO_3NH_2 + Na_2HPO_4$$

Diphosphates are well known and well studied chemicals and have been used as detergents, food additives, materials for water treatment, and so forth. Imidodiphosphate has the structure that the bridging oxygen of diphosphate is replaced by an imino group. The polyphosphates with imino groups can be used as chemical fertilizers and flame proof materials, and are also interesting from a biochemical view point. There have been many papers about polyphosphates, but a few reports on imidopolyphosphates have been published.[1)] Several studies on the synthesis of imidodiphosphate have been made.[2–5)] We found that the synthetic method still needed some modification. This paper describes the synthesis and the decomposition of imidodiphosphate in solid and in an aqueous solution to establish a chemical basis of imidopolyphosphates.

Experimental

Preparation of Diphenyl Phosphoramidate. Phosphoryl chloride (2 mol) and phenol (4 mol) were placed in a three necked round bottom flask with a condenser and the mixture was heated at the boiling point of phosphoryl chloride for 2 h. Magnesium dichloride (2 g) was used as a catalyser for the reaction. The resulting oil was dropped in 1 dm³ of ethanol saturated with ammonia and the mixture was well stirred. The product was added to 10 dm³ of water cooled with ice. The precipitate was filtered off and recrystallized with ethanol. The reactions included in this process are as follows:

$$2Ph\text{-}OH + POCl_3 \longrightarrow Ph_2PO_3Cl + 2HCl$$

$$Ph_2PO_3Cl + 2NH_3 \longrightarrow Ph_2PO_3NH_2 + NH_4Cl$$

where Ph stands for a phenyl group.

Preparation of Diphenyl Imidodiphosphate. Diphenyl phosphoramidate (0.2 mol) and phosphorus pentachloride (0.2 mol) were reacted at room temperature (15—25 °C) for 5—6 h and the reaction was completed by heating at 50—60 °C for 30 min. The resulting product was added to 100 cm³ of water and the mixture was allowed to stand overnight and then additional water (100 cm³) was added to the product to remove the hydrochloric acid produced. The residue was filtered off and washed with water. The precipitate was recrytallized with dioxane. The reactions in this process can be written as follows:

$$Ph_2PO_3NH_2 + PCl_5 \longrightarrow Ph_2O_3P\text{-}N{=}PCl_3 + 2HCl$$

$$Ph_2O_3P\text{-}N{=}PCl_3 + 3H_2O \longrightarrow Ph_2O_3PNHPO_3H_2 + 3HCl$$

Preparation of Crystalline Imidodiphosphate. Sodium hydroxide (0.88 mol), phenol (0.4 mol), water (100 cm³), and diphenyl imidodiphosphate (0.04 mol) were placed in a four necked round bottom flask and the mixture was heated above 100 °C, and the water evaporated. When the temperature of the solution reached 135 °C, a condenser was attached to the flask. The saponification of the phenyl imidodiphosphate was achieved by heating at 135—150 °C for 30 min. The resulting reaction mixture was cooled and then 50 cm³ of water was added and stirred. The product was placed in a 1-dm³ beaker with 50 cm³ of water and 500 cm³ of ethanol was added to the mixture. The solution was allowed to stand for a while and a white substance was precipitated. The precipitate was filtered off and recrystallized by dissolving in water and adding ethanol. The following reaction can be written for the process:

$$Ph_2O_3PNHPO_3H_2 + 4NaOH \longrightarrow Na_2O_3PNHPO_3Na_2 + 2Ph\text{-}OH + 2H_2O$$

Preparation of Amorphous Imidodiphosphate. Amorphous imidodiphosphate was prepared by stirring the crystalline imidodiphosphate in excess ethanol at room temperature for 2 d and then filtrating the residue.

Elemental Analysis. Phosphorus, nitrogen, and sodium were determined, respectively, by Molybdenum Blue colorimetric analysis, Kjeldahl analysis, and atomic absorption spectrophotometric measurements.

Determination of Bound Water. The amount of bound water in a solid sample was estimated by the Karl Fisher method with an MK-AII instrument made by Kyoto Denshi.

HPLC Technique. Separation and determination of phosphate species in a sample was performed by the HPLC technique using a separation column (6 mm×150 mm) with TSK-GEL (SAX-F0011) and 0.2 and 0.4 mol dm⁻³ aqueous potassium chloride solutions as an eluent.

^{31}P NMR Measurement. A sample was dissolved in water and the ^{31}P NMR spectrum of the solution was taken by means of a JNM- GX270 spectrograph. The NMR chemical shifts are reported relative to external 85% orthophosphoric acid, with the positive shifts being downfield.

X-Ray Diffractometry. An X-ray diffraction diagram of a sample was taken with nickel-filtered Cu $K\alpha$ radiation using a Rigaku X-ray diffractometer, RAD-1B.

Hydrolysis of Imidodiphosphate in an Aqueous Solution. Tetrasodium imidodiphosphate decahydrate (0.2 g) was dissolved in 50 cm³ of water and the pH of the solution was adjusted to 5, 9, or 11 with hydrochloric acid and aqueous tetramethylammonium hydroxide. The hydrolysis of the imidophosphate was carried out at 40 °C for 30 min.

Results and Discussion

Crystalline Imidodiphosphate. Found for the crystalline imidodiphosphate: Na, 20.9; P, 14.0; N, 2.9; H_2O, 41.2%. Calcd for $Na_4P_2O_6NH \cdot 10H_2O$: Na, 20.7; P, 13.9; N, 3.1; H_2O, 40.4%. The X-ray diffraction diagram of the product was almost the same as that listed in JCPDS card (13—24) for $Na_2P_2O_6NH \cdot 10H_2O$. Therefore, the crystalline product is tetrasodium imidodiphosphate decahydrate. The imidophosphate was stable at room temperature.

Amorphous Imidodiphosphate. The amorphous imidodiphosphate showed only the ^{31}P NMR and HPLC peaks of imidodiphosphate. This indicates that the decomposition of an imino group of the imidodiphosphate decahydrate does not occur during the dehydration with ethanol. Chemical composition of the amorphous imidophosphate was as follows: Na, 30.3; P, 19.8; N, 4.4; H_2O, 12.3%. The amorphous imidodiphosphate was stable at room temperature.

TG and DTA of Crystalline Imidodiphosphate. TG and DTA curves of the crystalline imidodiphosphate are shown in Fig. 1. The thermal products as numbered in Fig. 1 were removed from a furnace and subjected to further analysis to study the thermal reactions. The results of chemical analysis are shown in Table 1. The first large endothermic reaction accompanying a large amount of weight loss seemed to be caused by elimination of the water of crystallization. The weight loss at this stage was near to the following dehydration process:

$$Na_4P_2O_6NH \cdot 10H_2O \longrightarrow Na_4P_2O_6NH \cdot 2H_2O + 8H_2O \quad (1)$$

The measured nitrogen content of the thermal product **1** was also near to that calculated for $Na_4P_2O_6NH \cdot 2H_2O$. While the phosphate composition in Table 1 indicates that a small part of the imidodiphosphate converted to phosphoramidate and orthophosphate. The formations of phosphoramidate and orthophosphate can be written by the following equations:

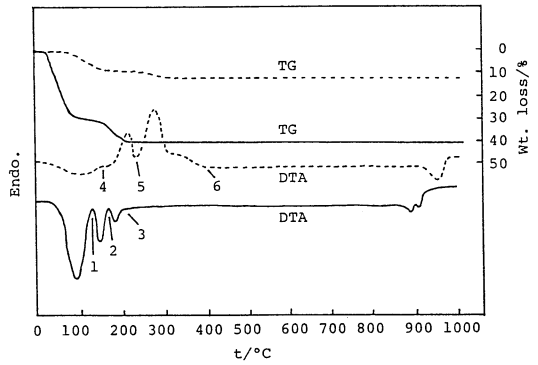

Fig. 1. TG and DTA curves of the imidodiphosphates. ——: $Na_4P_2O_6NH \cdot 10H_2O$, ----: amorphous imidodiphosphate.

$$Na_2O_3PNHPO_3Na_2 + H_2O \longrightarrow Na_2HPO_4 + Na_2PO_3NH_2 \quad (2)$$

$$Na_2PO_3NH_2 + H_2O \longrightarrow Na_2HPO_4 + NH_3 \quad (3)$$

The second and third endothermic peaks may also be due to elimination of the rest of the water of crystallization. The result in Table 1 shows that a small amount of diphosphate is formed other than phosphoramidate and orthophosphate at these steps. For the formation of diphosphate, one can write the equations:

$$Na_2O_3PNHPO_3Na_2 + H_2O \longrightarrow Na_2O_3POPO_3Na_2 + NH_3 \quad (4)$$

$$2Na_2HPO_4 \longrightarrow Na_2O_3POPO_3Na_2 + H_2O \quad (5)$$

$$2Na_2PO_3NH_2 + H_2O \longrightarrow Na_2O_3POPO_3Na_2 + 2NH_3 \quad (6)$$

The condensation reactions 5 and 6 can not occur at the second endothermic stage because the temperature (about 150 °C) is too low. Accordingly, the substitution of an imino group of the imidodiphosphate for bridging oxygen may take place at the step. The diphosphate in the product **3** can be produced through the reactions 4, 5, and 6. The melting of the sample was responsible for the last endothermic peaks at about 900 °C. The product gave the HPLC peak and X-ray diffraction pattern of $Na_4P_2O_7$. The thermal products obtained between the third and the last endothermic peaks contained only imidodiphosphate and diphosphate, and phosphoramidate and orthophosphate were not included. Therefore, the imidodiphosphate gradually converted to diphosphate according to reaction 4 after the third endothermic reaction. The water may come from the moisture in the air.

TG and DTA of Amorphous Imidodiphosphate. TG and DTA curves of the amorphous imidodiphosphate are shown in Fig. 1 together with the chemical compositions (in Table 1) of the thermal products. The amorphous imidodiphsophate showed a broad endothermic peak accompanying weight loss below 200 °C. The weight loss seemed to be due to the removal of the adsorbed water. The data in Table 1 show that a large amount of the imidodiphosphate converts to diphosphate at this stage. The formation

Table 1. Chemical Composition and Weight Loss of the Thermal Products of the Imidodiphosphates

Thermal product	Wt. loss /%	Total N/%	XRD	Phosphates/P%			
				Amido	Ortho	Imidodi	Di
1	31.9	4.1	UK	1.1	3.0	95.9	—
2	35.9	4.6	UK	0.3	4.0	94.9	0.8
3	41.1	4.3	UK	0.1	0.5	93.5	5.9
4	9.8	4.5	AM	4.8	4.1	61.0	30.1
5	10.2	0.8	$Na_4P_2O_7$	1.0	3.3	31.0	64.7
6	13.0	0.1	$Na_4P_2O_7$	0.1	1.2	3.5	95.2

UK and AM stand for unknown crystalline and amorphous substances respectively.

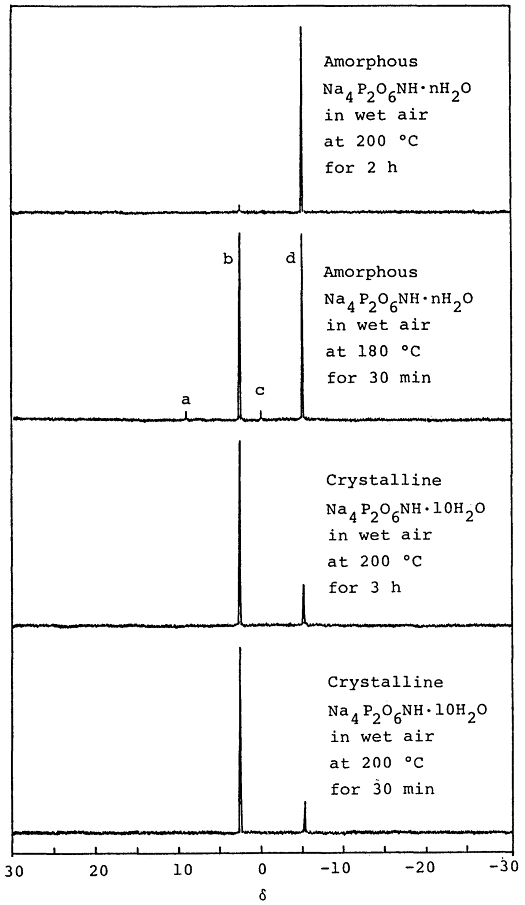

Fig. 2. ^{31}P NMR spectra of the isothermally heated products of imidodiphosphates. a: Phosphoramidate, b: imidodiphosphate, c: orthophosphate, d: diphosphate.

Table 2. Hydrolysis of Imidodiphosphate in an Aqueous Solution at 40 °C for 30 min

pH	Phosphates/P%			
	Amido	Ortho	Imidodi	Di
5	23.6	40.0	36.4	—
9	8.0	12.3	79.7	—
11	1.7	2.1	96.2	—

of diphosphate may be made through equation 4 because the amount of phosphoramidate and orthophosphate at this step is small. The thermal product **4** was amorphous by X-ray diffraction. Since the thermal product **5** showed the X-ray diffraction diagram of $Na_4P_2O_7$, the exothermic peak at about 220 °C may be due to the crystallization of amorphous $Na_4P_2O_7$. The replacement of the imino group by bridging oxygen also proceeded at this step. After the second exothermic peak at about 300 °C, almost all the imidodiphosphate was converted to crystalline tetrasodium diphosphate. The weight loss of these two steps may be caused by the loss of the rest of the adsorbed water. From the results obtained for the thermal products **1** to **6**, it can be concluded that the rate of the substitution of an imino group of the amorphous imidodiphosphate for bridging oxygen is much faster than that of the crystalline imidodiphosphate. To make sure of this, the substitution of imino groups of the amorphous and crystalline imidodiphosphates for bridging oxygen was studied isothermally in moist air.

Substitution of an Imino Group for Bridging Oxygen in Moist Air. The crystalline and amorphous imidodiphosphates were heated at 180 or 200 °C in moist air. The moist air was made by passing air through water and was introduced to a reaction glass tube which was placed in an electric furnace. The ^{31}P NMR spectra of the thermal products are shown in Fig. 2. A large amount of the crystalline imidodiphosphate was still unreacted when it was heated at 200 °C for 0.5 and 3 h. While the majority of the amorphous imidodiphosphate was converted to diphosphate by heating at 200 °C for 2 h, and nearly half portions of the amorphous imidodiphosphate was converted to diphosphate by eating at 180 °C for only 30 min. Accordingly, the NMR data indicate that the replacement of an imino group of the amorphous imidodiphosphate by bridging oxygen takes place much faster than that of the crystalline one.

From the above results, it can be concluded that the hydrolysis of the crystalline and amorphous imidodiphosphates takes place substantially according to the reaction 4. The faster replacement of an imino group in the amorphous imidodiphosphate by bridging oxygen can be explained that an amorphous phase is usually more active than a crystalline one.

Hydrolysis of Imidodiphosphate in an Aqueous Solution. The result of the hydrolysis of imidodiphosphate is shown in Table 2. In an aqueous solution, imidodiphosphate produced only phosphoramidate and orthophosphate, and it was not hydrolyzed at all to make diphosphate. It can be concluded that only the reactions 2 and 3 take place in an aqueous solution. The rate of the hydrolysis decreased with an increase in the pH of the solution.

References

1) D. E. C. Corbridge, "Phosphorus," Elsevier, Amsterdum (1980), p. 268.

2) M. N, Stokes, *Am. Chem. J.*, **15**, 198 (1893).

3) A. V. Kirsanov and T. N. Zhmurnova, *Zh. Obshch. Khim.*, **28**, 2428 (1958).

4) M. L. Nielsen, R. R. Fregson, and W. S. Coakley, *J. Am. Chem. Soc.*, **83**, 99 (1961).

5) D. E. C. Corbridge and F. R. Tromans, *Anal. Chem.*, **30**, 1101 (1958).

6) N. Yoza, Y. Sagara, H. Morioka, T. Handa, H. Hirano, Y. Baba, and S. Ohashi, *J. Flow Injection Anal.*, **3**, 37 (1986).