JOURNAL OF MATERIALS SCIENCE **21** (1986) 2623–2627

The synthesis and thermal behaviour of sodium phosphorodiamidate

MAKOTO WATANABE, SHOJI SATO
Department of Industrial Chemistry, Chubu University, Matsumoto-cho, Kasugai, Aichi 487, Japan

Sodium phosphorodiamidate pentahydrate, $NaPO_2(NH_2)_2 \cdot 5H_2O$, was made by saponifying phenyl phosphorodiamidate with a 4 mol dm^{-3} aqueous sodium hydroxide solution. The product was stable below 5° C, but it decomposed gradually to phosphoramidate and orthophosphate at 30° C. The phosphorodiamidate produced imidopolyphosphates and polyphosphates other than phosphoramidate and orthophosphate when it was heated above 30° C, and was finally converted to sodium metaphosphate above 300° C in air.

1. Introduction

Among many phosphorus–nitrogen compounds, phosphazens are maybe the most intensively studied ones. There are a series of phosphorus–nitrogen compounds which have amino groups on a phosphorus atom. These compounds are considered to have potential as a new type of chemical fertilizer having a P–N covalent bond, and also of flameproof materials because they produce polyphosphates containing imino and amino groups when they are heated. However, the available chemical and physical data for these compounds are few. We have therefore reported the syntheses and thermal decomposition and condensation reactions of several phosphoramidates [1–4]. When the phosphoramidates were heated in air, a part of each of them condensed to imidopolyphosphates with the liberation of ammonia, and the rest was converted to ortho- and polyphosphates by the action of water. In this paper, we describe the synthesis and mechanism of the thermal decomposition and condensation of sodium phosphorodiamidate.

2. Experimental procedure

2.1. Preparation of sodium phosphorodiamidate

There have been wet methods to make sodium phosphorodiamidate from phosphorodiamidic acid, but the methods are laborious. We developed the following new method for the preparation of the phosphorodiamidate. Phenyl phosphorodiamidate was made by the method described in a textbook [5], and 0.2 mol of the phosphorodiamidate was saponified in 100 cm^3 of a 4 mol dm^{-3} aqueous sodium hydroxide solution by boiling for 5 min. The resulting solution was cooled and 500 cm^3 of ethanol was added to the solution to produce a white precipitate. The precipitate was purified by dissolving it in 100 cm^3 of water and then adding 500 cm^3 of ethanol. The product was dried in air at room temperature.

2.2. Chemical analysis

Sodium, phosphorus and nitrogen in a sample were determined by, respectively, atomic absorption analysis, the colorimetric method and the Kjeldahl technique.

2.3. Paper chromatography and colorimetry of phosphates

One-dimensional paper chromatography was used for the separation of phosphate species in a sample by using solvents that were acidic (for the separation of chain phosphates) and basic (for the separation of phosphorodiamidate and ring phosphates); the A_2 and B_2 solvents in Table 3 of Ohashi [6] were used. The determination of the phosphates on a chromatogram was carried out by the method described in our previous paper [1].

2.4. X-ray diffractometry

An X-ray diffraction diagram of a powder sample was taken with nickel-filtered Cu*Kα* radiation by using a Toshiba X-ray diffractometer, ADG–102.

2.5. IR spectrophotometry

An IR spectrum of a sample was measured by a Jasco IR spectrophotometer, A–3, by means of the KBr disc method.

2.6. Differential thermal analysis (DTA) and thermogravimetric (TG) measurements.

A sample was heated at a rate of 5° C min^{-1} in air with a Cho Balance TRDA$_1$–H apparatus.

2.7. Nuclear magnetic resonance

A ^{31}P nuclear magnetic resonance (NMR) spectrum of a sample was recorded on a JNM–GX270 NMR instrument by dissolving the sample in water. As is customary, the NMR chemical shifts are reported relative to external 85% orthophosphoric acid with positive shifts being downfield.

3. Results and discussion

3.1. Composition of the product

The yield of the product was about 80%. The product

0022–2461/86 $03.00 + .12

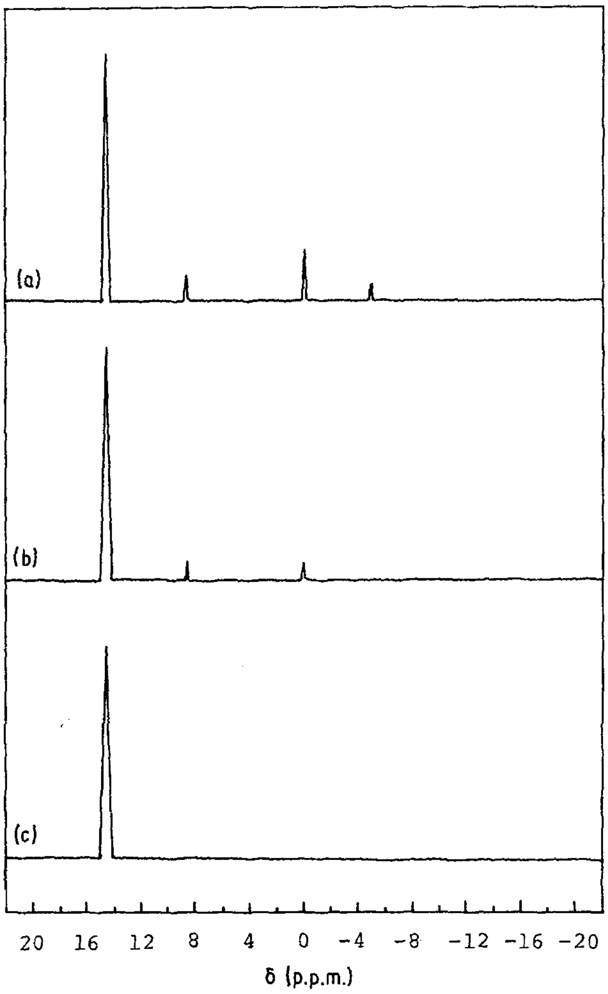


Figure 1 ^{31}P NMR spectra of the thermal products of $NaPO_2(NH_2)_2 \cdot 5H_2O$ after 30 days at (a) 40 and (b) 30° C in air, with (c) spectrum of untreated material.

gave only one ^{31}P NMR peak of phosphorodiamidate at 14.5 p.p.m. The elemental analysis of the product gave the data as follows: Na, 11.3; P, 14.7; N, 13.1%. The calculated contents of the elements for $NaPO_2(NH_2)_2 \cdot 5H_2O$ gave the following values: Na, 11.1; P, 14.9; N, 13.5%. Accordingly, it was concluded that the product was sodium phosphorodiamidate pentahydrate, $NaPO_2(NH_2)_2 \cdot 5H_2O$. The product was stable at a temperature lower than 5° C, but it decomposed gradually above 30° C. When the product was heated at 80° C under 2670 Pa for 2 days, anhydrous sodium phosphorodiamidate was obtained.

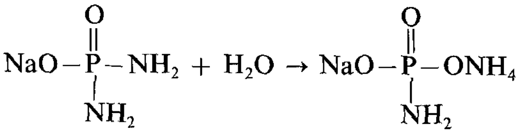
TABLE I Composition of the thermal products at 40° C in air

Reaction time (days)	Phosphate (% P)*		
	DA	1P + MA	2P
3	92.1	7.9	–
9	88.1	11.9	–
17	82.8	15.9	1.3
30	69.6	26.5	3.9

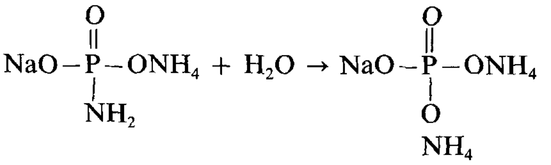
*DA, 1P, MA and 2P stand for phosphorodiamidate, orthophosphate, phosphoramidate and diphosphate, respectively.

3.2. Thermal reactions at 30 and 40° C

The isothermal reaction of $NaPO_2(NH_2)_2 \cdot 5H_2O$ at 30° C was studied with the result shown in Fig. 1. When the phosphorodiamidate was heated at 30° C in air, the thermal product showed two small NMR peaks after about two weeks. The one at 8.7 p.p.m. is assigned to phosphoramidate and the other at 0 p.p.m. is due to orthophosphate [7]. The intensity of these peaks increased with the passage of time. When the phosphorodiamidate was heated at 40° C in air, the product showed these two small peaks after a few days, and also exhibited a new peak of diphosphate at about −5 p.p.m. after two weeks. Table I shows the composition of the thermal product at 40° C. The phosphorodiamidate decomposed gradually to phosphoramidate, ortho- and/or diphosphates at these temperatures. The following reaction processes can be written for the termal decomposition of the phosphorodiamide to phosphoramide and orthophosphate:

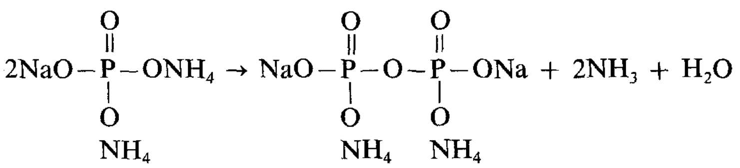


$$\mathrm{NaO{-}\underset{\displaystyle NH_2}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}NH_2 + H_2O \rightarrow NaO{-}\underset{\displaystyle NH_2}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}ONH_4} \qquad (1)$$



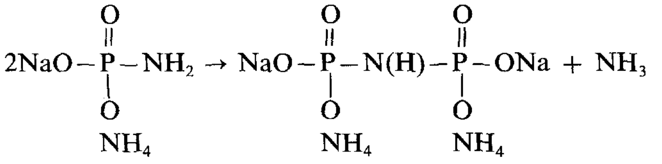
$$\mathrm{NaO{-}\underset{\displaystyle NH_2}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}ONH_4 + H_2O \rightarrow NaO{-}\underset{\underset{\displaystyle NH_4}{\displaystyle O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}ONH_4} \qquad (2)$$

One can write the following thermal condensation reactions for the formation of diphosphate:

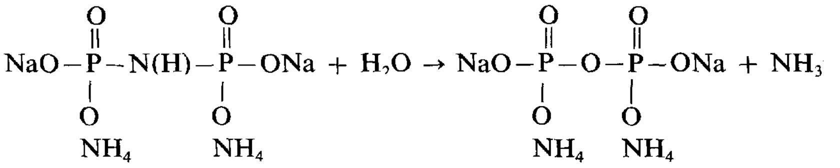


$$\mathrm{2NaO{-}\underset{\underset{\displaystyle NH_4}{\displaystyle O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}ONH_4 \rightarrow NaO{-}\underset{\underset{\displaystyle NH_4}{\displaystyle O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}O{-}\underset{\underset{\displaystyle NH_4}{\displaystyle O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}ONa + 2NH_3 + H_2O} \qquad (3)$$

and/or



$$\mathrm{2NaO{-}\underset{\underset{\displaystyle NH_4}{\displaystyle O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}NH_2 \rightarrow NaO{-}\underset{\underset{\displaystyle NH_4}{\displaystyle O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}N(H){-}\underset{\underset{\displaystyle NH_4}{\displaystyle O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}ONa + NH_3} \qquad (4)$$



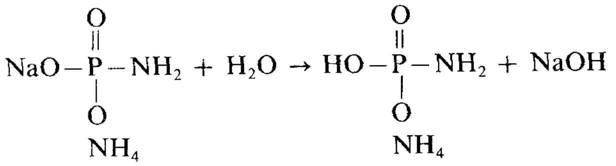
$$\mathrm{NaO{-}\underset{\underset{\displaystyle NH_4}{\displaystyle O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}N(H){-}\underset{\underset{\displaystyle NH_4}{\displaystyle O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}ONa + H_2O \rightarrow NaO{-}\underset{\underset{\displaystyle NH_4}{\displaystyle O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}O{-}\underset{\underset{\displaystyle NH_4}{\displaystyle O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}ONa + NH_3} \qquad (5)$$

TABLE II Weight loss and composition of the thermal products of $NaPO_2(NH_2)_2 \cdot 5H_2O$

Sample No.	Total nitrogen (%)	% N as NH_4^+	Weight loss (%)	X-ray diffraction	Phosphate (% P)*			
					DA	IP + MA	HP + IP	TM
1	–	–	3.5	Melt	100	–	–	–
2	16.4	0.3	33.0	Melt	97.8	2.2	–	–
3	16.2	0.2	45.5	Amorphous	63.3	9.0	27.7	–
4	12.2	0.6	47.3	Amorphous	1.4	9.9	88.7	–
5	2.7	0.2	50.8	$NaPO_3$-III	–	–	48.2	51.8

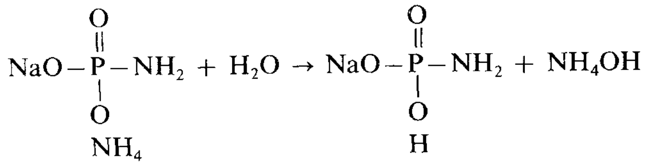
*DA, IP, MA, HP, IP and TM stand for phosphorodiamidate, orthophosphate, phosphoramidate, polyphosphate, imidopolyphosphate and cyclo-triphosphate, respectively.

These reactions are usually impossible at low temperatures like these. The phosphorodiamidate melted when it was heated at these temperatures for a long time. The following substitution of cations can take place in the melt:



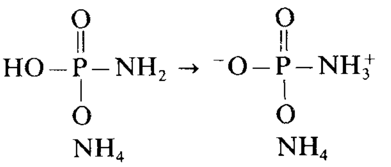
$$\mathrm{NaO-\underset{\underset{NH_4}{O}}{\overset{\overset{O}{\|}}{P}}-NH_2 + H_2O \rightarrow HO-\underset{\underset{NH_4}{O}}{\overset{\overset{O}{\|}}{P}}-NH_2 + NaOH} \qquad (6)$$

and/or



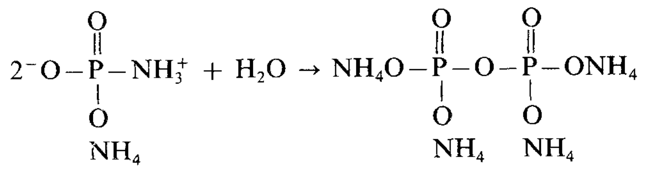
$$\mathrm{NaO-\underset{\underset{NH_4}{O}}{\overset{\overset{O}{\|}}{P}}-NH_2 + H_2O \rightarrow NaO-\underset{\underset{H}{O}}{\overset{\overset{O}{\|}}{P}}-NH_2 + NH_4OH} \qquad (7)$$

Phosphoramidate with an OH group is thought to form a zwitterion as follows [8]:



$$\mathrm{HO-\underset{\underset{NH_4}{O}}{\overset{\overset{O}{\|}}{P}}-NH_2 \rightarrow {}^-O-\underset{\underset{NH_4}{O}}{\overset{\overset{O}{\|}}{P}}-NH_3^+} \qquad (8)$$

The zwitterion is unstable and decomposes to diphosphate with water.



$$\mathrm{2\,{}^-O-\underset{\underset{NH_4}{O}}{\overset{\overset{O}{\|}}{P}}-NH_3^+ + H_2O \rightarrow NH_4O-\underset{\underset{NH_4}{O}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{NH_4}{O}}{\overset{\overset{O}{\|}}{P}}-ONH_4} \qquad (9)$$

3.3. DTA and TG

To study the thermal behaviour of $NaPO_2(NH_2)_2 \cdot 5H_2O$ at a higher temperature, DTA and TG curves of the product were taken and are shown in Fig. 2. The samples as numbered in Fig. 2 were removed from the furnace and subjected to further analysis. The results are presented in Table II and Figs 3 and 4. Sample No. 1 did not show any ^{31}P NMR peak other than that of the phosphorodiamidate. Weight loss from the sample was very small and the thermal product was liquid. The first endothermic reaction is therefore due to melting of the phosphorodiamidate. After the second endothermic peak, the weight loss of the product was large and, as Table II and Fig. 3 show, a small amount of the phosphorodiamidate decomposed to phosphoramidate and orthophosphate. The second endothermic reaction is mainly caused by removal of bound water. The measured weight loss of No. 3 is close to the calculated value according to the following reaction:

$$NaPO_2(NH_2)_2 \cdot 5H_2O \rightarrow NaPO_2(NH_2)_2 + 5H_2O \qquad (10)$$

The third endothermic reaction is considered to be mainly responsible for removal of the rest of the bound water, but, as Table II and Figs 3 and 4 show, the thermal product (No. 3) contained several phosphate species other than the phosphorodiamidate. The nitrogen content of the thermal product was smaller than that of $NaPO_2(NH_2)_2$. The ^{31}P NMR peaks of No. 3 other than phosphorodiamidate

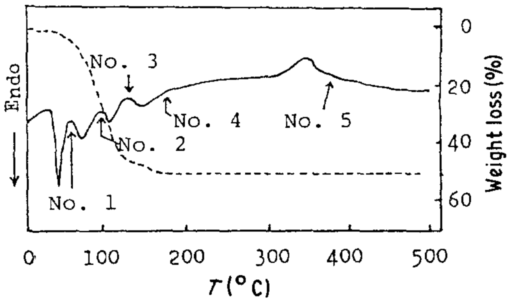


Figure 2 (—) DTA and (---) TG curves of $NaPO_2(NH_2)_2 \cdot 5H_2O$ in air.

(14.5 p.p.m.), phosphoramidate (8.7 p.p.m.), orthophosphate (0 p.p.m.) and an end-PO_4 group (−8.6 p.p.m.) seem to be due to polyphosphates containing imino groups [7]. The IR spectrum of No. 3 shows absorptions due to a $(PO_2)^-$ group at 1320, 1200 and/or 1080 cm^{-1}, and also due to a P−O−P or a P−N(H)−P linkage at 900 and 720 cm^{-1}. The results supports the above conclusion. Accordingly, the third endothermic reaction includes also the decomposition of the phosphorodiamidate to phosphoramidate and orthophosphate and the condensation of these phosphates to imidopoly- and polyphosphates with the release of ammonia and component water.

As Table II and Fig. 3 show, Sample No. 4 contained a very small amount of the phosphorodiamidate, while the contents of ortho-, poly- and imidopolyphosphates increased after the fourth endothermic reaction. The endothermic reaction is therefore responsible for further decomposition and condensation of the phosphorodiamidate and its thermal products. Since the nitrogen content of No. 4 is close to that of $NaPO_2NH$, the chain of the thermal products consists mainly of a P−N(H)−P linkage. The ^{31}P NMR and IR spectra of No. 4 support this conclusion. The thermal product showed an exothermic peak at about 340° C. The samples before the

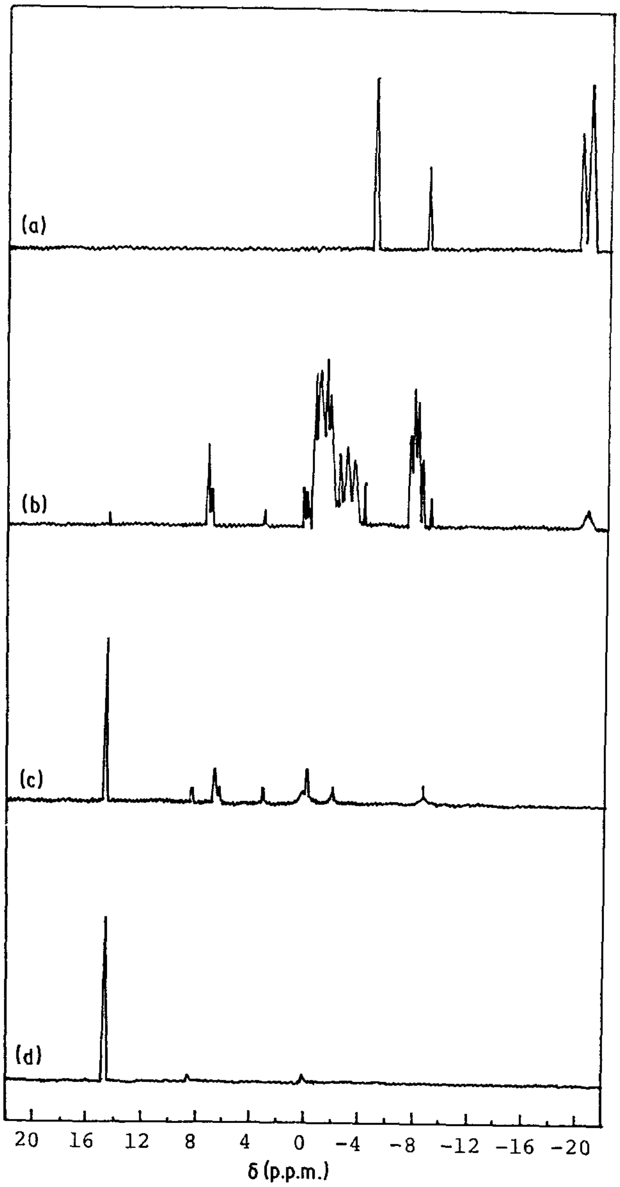


Figure 3 ^{31}P NMR spectra of the thermal products of $NaPO_2(NH_2)_2 \cdot 5H_2O$: (a) No. 5, (b) No. 4, (c) No. 3, (d) No. 2.

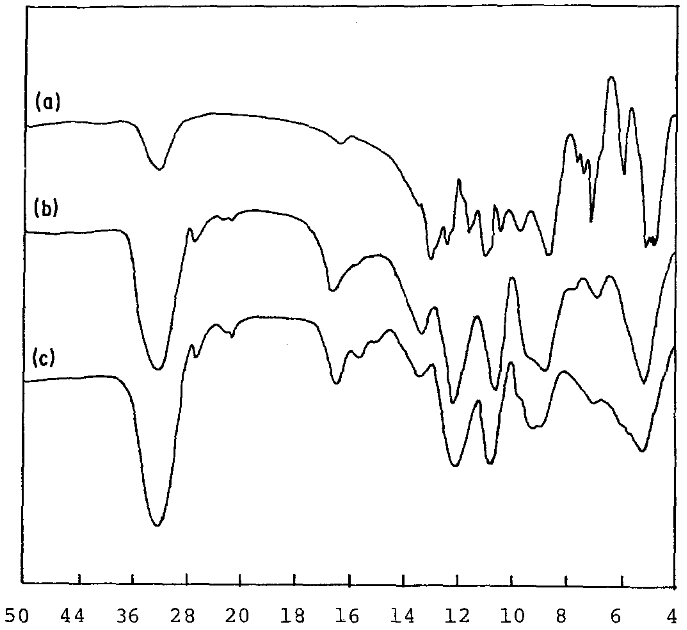
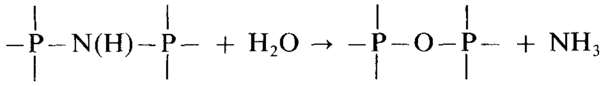


Figure 4 IR spectra of the thermal products of $NaPO_2(NH_2)_2 \cdot 5H_2O$: (a) No. 5, (b) No. 4, (c) No. 3.

exothermic reaction were amorphous by X-ray diffractometry, while Sample No. 5 exhibited an X-ray diffraction pattern of $NaPO_3$-III (JCPDS card No. 2–826). The amount of nitrogen in the product was very small. It can be concluded that the following substitution of an NH group in the imidopolyphosphates for an oxygen atom by the action of water in air takes place slowly in the temperature range used:



$$-P-N(H)-P- + H_2O \rightarrow -P-O-P- + NH_3 \qquad (11)$$

The ^{31}P NMR study of No. 5 supports this interpretation because the NMR spectrum showed peaks due to end-PO_4 groups of diphosphate (−4.8 p.p.m.) and polyphosphates with a chain length longer than that of diphosphate (−8.7 p.p.m.) and a middle-PO_4 group (−19 to −21 p.p.m.). The amorphous polyphosphate with *meta* composition thus produced can be crystallized to the sodium metaphosphate at about 340° C, and this crystallization is thought to cause the exothermic peak.

References

1. M. WATANABE, T. INAGAKI and S. SATO, *Bull. Chem. Soc. Jpn* **56** (1983) 458.
2. M. WATANABE, T. INAGAKI, Y. MORII and T. YAMADA, *Stsuko To Setsukai* No. 184 (1983) 111.
3. M. WATANABE, Y. MORII and S. SATO, *Bull. Chem. Soc. Jpn* **57** (1984) 2087.
4. *Idem, ibid.* **57** (1984) 2914.
5. "Sin Zitsuken Kagaku Koza," Vol. 8-[I] (Chemical Society of Japan, Maruzen, Tokyo, 1976) p. 354.
6. S. OHASHI, *Kagaku To Kogyo* **21** (1968) 878.
7. M. M. CRUTCHFIELD, C. H. DUNGAN, J. H. LETCHER, V. MARK and J. R. VAN WAZER, "Topics in Phosphorus Chemistry", Vol. 5 (Interscience, New York, 1967) p. 227.
8. D. E. C. CORBRIDGE, "Phosphorus" (Elsevier, Amsterdam, 1980) p. 222.

Received 15 July
and accepted 12 August 1985