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The synthesis and thermal behaviour of magnesium bis(phosphorodiamidate)

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Magnesium bis(phosphorodiamidate) hexahydrate, $Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O$, was made by the wet process. The phosphorodiamidate was stable below 5° C, but it was converted to phosphoramidate, orthophosphate, and polyphosphates above 30° C in air. When the phosphorodiamidate was heated in air or in dry nitrogen at a higher temperature, it produced phosphoramidate, ortho- and polyphosphates, and polyphosphates with imino groups. The thermal products in air and in dry nitrogen finally gave $Mg(PO_3)_2$ associated with the following reaction at a higher temperature than about 700° C

$$Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O \rightarrow Mg(PO_3)_2 + 4NH_3 + 4H_2O$$

and the product in dry nitrogen still contained 3 to 4% nitrogen.

1. Introduction

Among many phosphorus–nitrogen compounds, phosphazenes may be the best known and the most intensively studied. There is a series of phosphorus compounds with amino groups on a phosphorus atom. These compounds can be used as fertilizers, as they have a P–N covalent bond, flameproof materials, and starting materials for the preparation of many organic and inorganic phosphorus compounds [1]. We have previously reported the syntheses and thermal behaviour of phosphoramidates and sodium phosphorodiamidate [2–9]. The phosphoramidates were converted to ortho-, poly-, and imidopolyphosphates by heating to a temperature less than several hundreds degree centigrade, and finally produced polyphosphates above air temperature. Sodium phosphorodiamidate pentahydrate produced ortho-, poly-, and imidopolyphosphates as well as phosphoramidate when it was heated above 30° C. The phosphorodiamidate was converted to sodium metaphosphate above 300° C in air. This paper describes the synthesis and thermal reaction of magnesium bis(phosphorodiamidate) in air and in dry nitrogen.

2. Experimental procedure

2.1. Preparation of magnesium bis(phosphorodiamidate)

Sodium phosphorodiamidate pentahydrate was prepared by the method described in our previous paper [8]. The phosphorodiamidate (20.8 g) was dissolved in 100 cm^3 of water and 100 cm^3 of a 0.5 M dm^{-3} magnesium chloride solution was added to the solution. Acetone (450 cm^3) was put in the resulting mixed solution and a white precipitate was filtered off. The product was dissolved in 200 cm^3 of water and the residue filtered off. The product was recrystallized by adding 400 cm^3 of acetone to the solution. It was filtered and washed with 75 vol % of an aqueous solution of acetone, and then dried in a silica-gel desiccator for a few days.

2.2. Chemical analysis

The product was dissolved in water and the amounts of magnesium, phosphorus, and nitrogen in the solution were determined by, EDTA (disodium dihydrogen ethylenediaminetetraacetate dihydrate) titration with a BT indicator, colorimetric analysis, and the Kjeldahl technique, respectively.

2.3. Paper chromatography and colorimetry of phosphates

The thermal product (0.1 g) of magnesium bis(phosphorodiamidate) hexahydrate was dissolved in 10 cm^3 of a 6%-EDTA solution by adjusting the pH of the solution to 10 with aqueous ammonia. One-dimensional paper chromatographic separation was employed for the separation of phosphate species in the solution by using acidic (for the separation of chain phosphates) and basic (for the separation of phosphorodiamidate and ring polyphosphates) solvents [10]. The colorimetric determination of the phosphates on a chromatogram was carried out by the technique described in our previous paper [2].

2.4. X-ray diffractometry

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

2.5. IR spectrophotometry

An IR spectrum of a sample was recorded on a JASCO IR spectrophotometer, A-3, by means of the KBr disc method.

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2.6. ^{31}P nuclear magnetic resonance (NMR) measurement

A ^{31}P NMR spectrum of a sample was taken with a JNM-GX270 spectrograph by dissolving it in water or in a 6%-EDTA solution. The NMR chemical shifts are reported relative to external 85% orthophosphoric acid, with positive shifts being downfield.

2.7. Thermogravimetry (TG) and differential thermal analysis (DTA)

A sample was heated at a rate of $10^\circ C\,min^{-1}$ in air and in dry nitrogen by means of a Rigaku TG-DTA instrument.

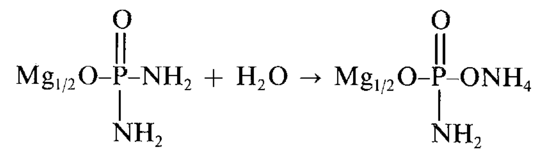
3. Results and discussion

3.1. Composition of the phosphorodiamidate

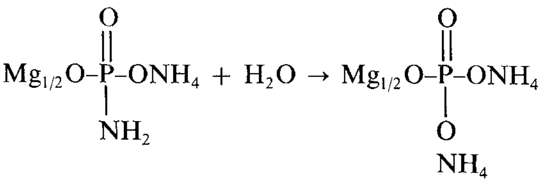
The chemical analysis of the product gave the data as follows: Mg, 7.49; P, 19.66: N, 17.52%. The calculated contents of these elements for $Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O$ are as follows: Mg, 7.54; P, 19.21; N, 17.38%. The product gave only one ^{31}P NMR peak of phosphorodiamidate at 14.3 p.p.m. Therefore, the product is magnesium bis(phosphorodiamidate) hexahydrate, $Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O$. The yield of the product was about 15 g. The phosphorodiamidate was stable below 5° C, but it decomposed gradually above room temperature.

3.2. Thermal reaction at 30° C in air

The isothermal reaction of magnesium bis(phosphorodiamidate) hexahydrate was run at 30° C in air to study the thermal stability. When the phosphorodiamidate was heated at 30° C in air, the products exhibited IR spectra shown in Fig. 1. An absorption peak at 1400 cm^{-1} is due to an NH_4^+ ion and the height of the peak increased with the passage of time. This means that the amino group of the phosphorodiamidate changes to an ammonium ion. The ^{31}P NMR spectra of the thermal products are shown in Fig. 2. The products indicated peaks of phosphoramidate, orthophosphate, an end-PO_4 group, and a middle-PO_4 group other than that of phosphorodiamidate. The chemical analysis of the thermal products showed the result in Table I. The result showed that the amino group of the phosphorodiamidate was converted to an ammonium ion and the phosphorodiamidate changed to phosphoramidate, orthophosphate, and polyphosphates at the same time. The result is in good agreement with those in Figs 1 and 2. From the above results, one can write the following reaction for the decomposition of the phosphorodiamidate to phosphoramidate and orthophosphate:

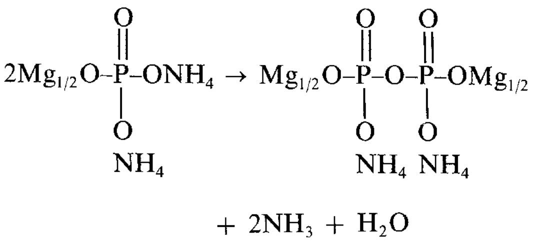


$$Mg_{1/2}O{-}\underset{\displaystyle NH_2}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}NH_2 + H_2O \rightarrow Mg_{1/2}O{-}\underset{\displaystyle NH_2}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}ONH_4 \qquad (1)$$



$$Mg_{1/2}O{-}\underset{\displaystyle NH_2}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}ONH_4 + H_2O \rightarrow Mg_{1/2}O{-}\underset{\displaystyle \underset{\displaystyle NH_4}{O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}ONH_4 \qquad (2)$$

Condensation of the orthophosphate to polyphosphates can be written as follows



$$2Mg_{1/2}O{-}\underset{\displaystyle \underset{\displaystyle NH_4}{O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}ONH_4 \rightarrow Mg_{1/2}O{-}\underset{\displaystyle \underset{\displaystyle NH_4}{O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}O{-}\underset{\displaystyle \underset{\displaystyle NH_4}{O}}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}{-}OMg_{1/2} + 2NH_3 + H_2O \qquad (3)$$

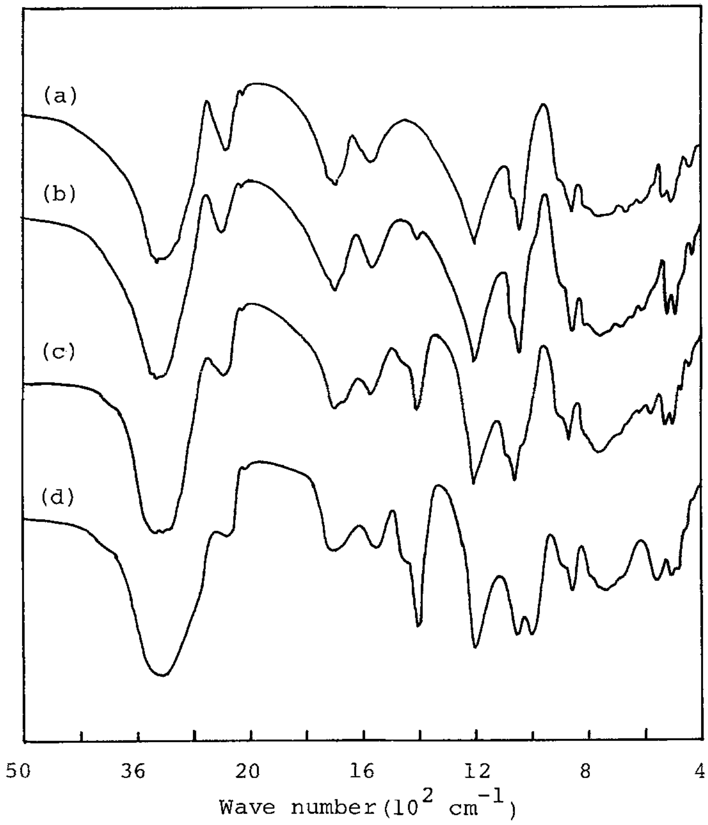
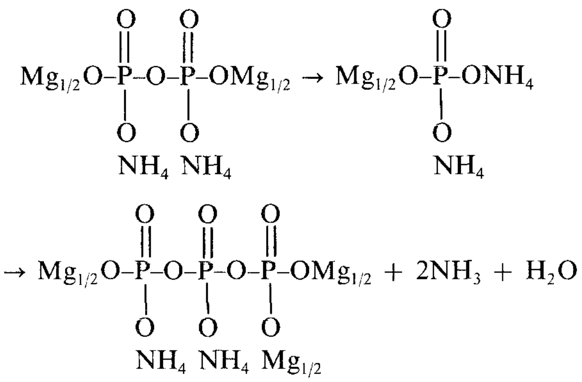


Figure 1 IR spectra of the decomposition products of $Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O$ at 30°C after (a) 0, (b) 6, (c) 11, and (d) 19 days.

TABLE I Decomposition of $\mathrm{Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O}$ at 30° C

Reaction time (days)	Total nitrogen (%)	% N as $\mathrm{NH_4^+}$	Phosphates (% P)		
			Diamido	Ortho and Monoamido	Higher
0	17.5	-	100	-	-
3	19.6	0.4	93.7	6.3	-
6	19.6	0.9	90.9	9.1	-
11	19.2	4.0	62.7	28.8	8.5
15	18.7	4.1	39.6	50.9	9.5
19	18.0	6.0	27.5	60.9	11.6



$$\mathrm{Mg_{1/2}O\!-\!\underset{\substack{|\\ O\\ NH_4}}{\overset{\substack{O\\ \|}}{P}}\!-\!O\!-\!\underset{\substack{|\\ O\\ NH_4}}{\overset{\substack{O\\ \|}}{P}}\!-\!OMg_{1/2} \rightarrow Mg_{1/2}O\!-\!\underset{\substack{|\\ O\\ NH_4}}{\overset{\substack{O\\ \|}}{P}}\!-\!ONH_4 \rightarrow Mg_{1/2}O\!-\!\underset{\substack{|\\ O\\ NH_4}}{\overset{\substack{O\\ \|}}{P}}\!-\!O\!-\!\underset{\substack{|\\ O\\ NH_4}}{\overset{\substack{O\\ \|}}{P}}\!-\!O\!-\!\underset{\substack{|\\ O\\ Mg_{1/2}}}{\overset{\substack{O\\ \|}}{P}}\!-\!OMg_{1/2} + 2NH_3 + H_2O} \quad (4)$$

The condensation of ortho- and polyphosphates to polyphosphates with longer chain lengths has not been observed at this low temperature. The elimination of ammonia seems to occur according to the reaction at this temperature

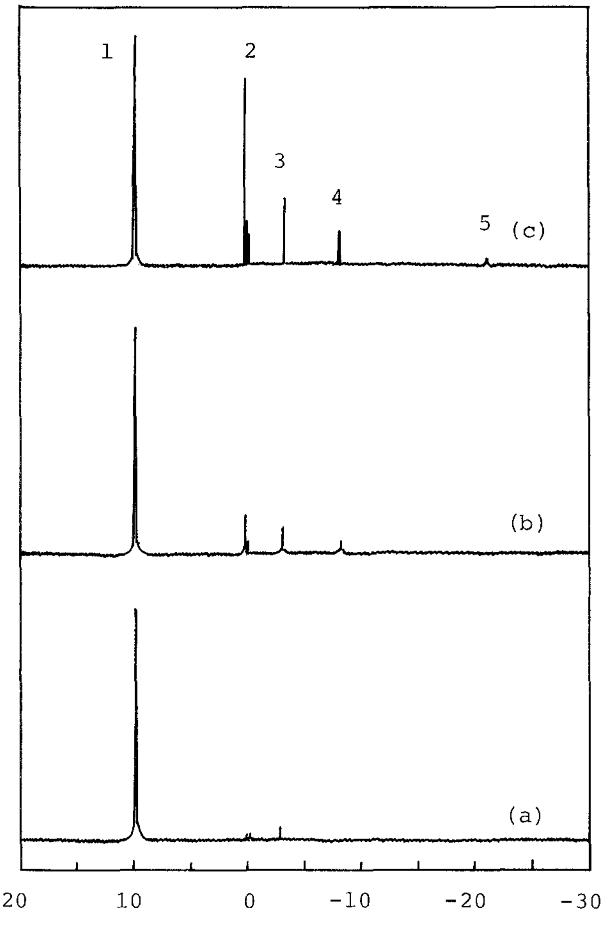
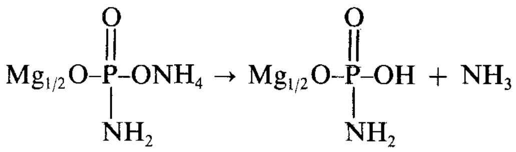
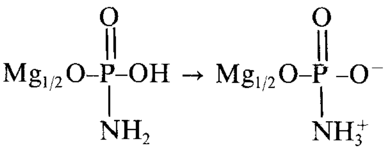


Figure 2 ^{31}P NMR spectra of the decomposition products of $\mathrm{Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O}$ at 30° C after (a) 6, (b) 11, and (c) 19 days. 1: Phosphorodiamidate, 2: orthophosphate, 3: phosphoramidate, 4: end-$\mathrm{PO_4}$ group, 5: middle-$\mathrm{PO_4}$ group.



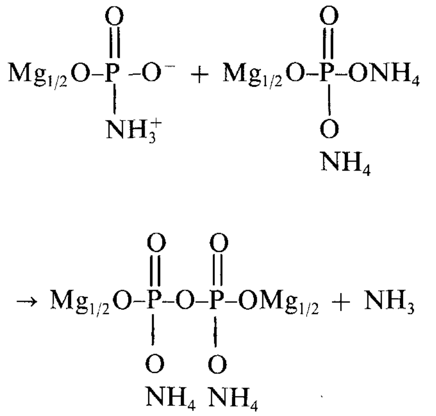
$$\mathrm{Mg_{1/2}O\!-\!\underset{\substack{|\\ NH_2}}{\overset{\substack{O\\ \|}}{P}}\!-\!ONH_4 \rightarrow Mg_{1/2}O\!-\!\underset{\substack{|\\ NH_2}}{\overset{\substack{O\\ \|}}{P}}\!-\!OH + NH_3} \quad (5)$$

The phosphoramidate with an OH group is considered to form a zwitterion [1]

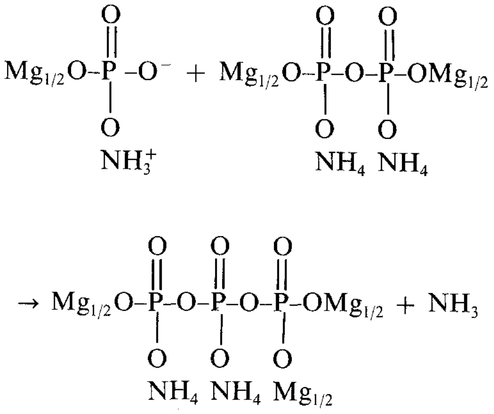


$$\mathrm{Mg_{1/2}O\!-\!\underset{\substack{|\\ NH_2}}{\overset{\substack{O\\ \|}}{P}}\!-\!OH \rightarrow Mg_{1/2}O\!-\!\underset{\substack{|\\ NH_3^+}}{\overset{\substack{O\\ \|}}{P}}\!-\!O^-} \quad (6)$$

The zwitterion is active and can react with ortho- and polyphosphates to make polyphosphates with longer chain lengths

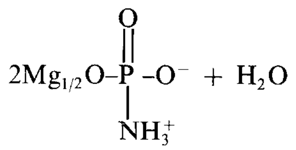


$$\mathrm{Mg_{1/2}O\!-\!\underset{\substack{|\\ NH_3^+}}{\overset{\substack{O\\ \|}}{P}}\!-\!O^- + Mg_{1/2}O\!-\!\underset{\substack{|\\ O\\ NH_4}}{\overset{\substack{O\\ \|}}{P}}\!-\!ONH_4 \rightarrow Mg_{1/2}O\!-\!\underset{\substack{|\\ O\\ NH_4}}{\overset{\substack{O\\ \|}}{P}}\!-\!O\!-\!\underset{\substack{|\\ O\\ NH_4}}{\overset{\substack{O\\ \|}}{P}}\!-\!OMg_{1/2} + NH_3} \quad (7)$$



$$\mathrm{Mg_{1/2}O\!-\!\underset{\substack{|\\ O\\ NH_3^+}}{\overset{\substack{O\\ \|}}{P}}\!-\!O^- + Mg_{1/2}O\!-\!\underset{\substack{|\\ O\\ NH_4}}{\overset{\substack{O\\ \|}}{P}}\!-\!O\!-\!\underset{\substack{|\\ O\\ NH_4}}{\overset{\substack{O\\ \|}}{P}}\!-\!OMg_{1/2} \rightarrow Mg_{1/2}O\!-\!\underset{\substack{|\\ O\\ NH_4}}{\overset{\substack{O\\ \|}}{P}}\!-\!O\!-\!\underset{\substack{|\\ O\\ NH_4}}{\overset{\substack{O\\ \|}}{P}}\!-\!O\!-\!\underset{\substack{|\\ O\\ Mg_{1/2}}}{\overset{\substack{O\\ \|}}{P}}\!-\!OMg_{1/2} + NH_3} \quad (8)$$

or the following polymerization can also be written



$$\mathrm{2Mg_{1/2}O\!-\!\underset{\substack{|\\ NH_3^+}}{\overset{\substack{O\\ \|}}{P}}\!-\!O^- + H_2O}$$

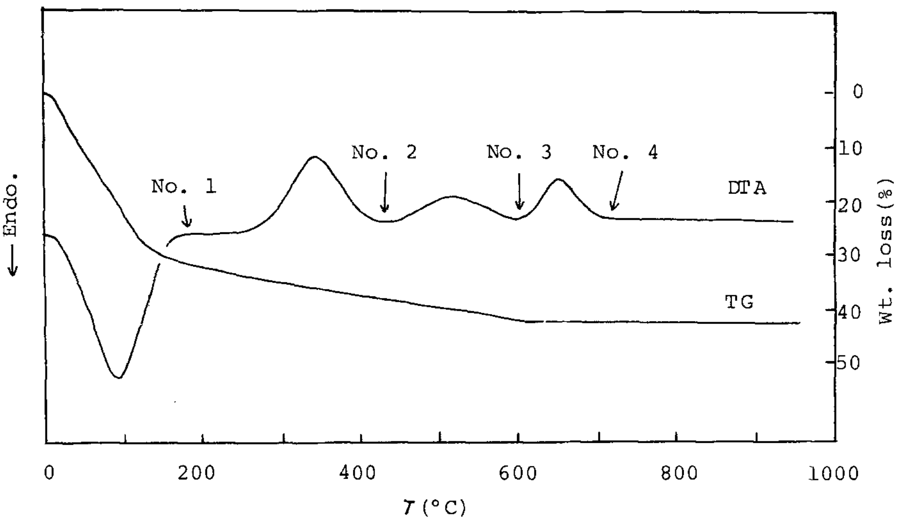
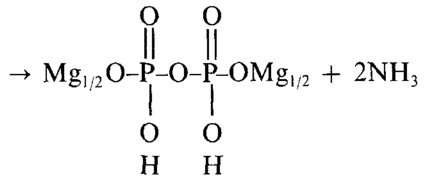
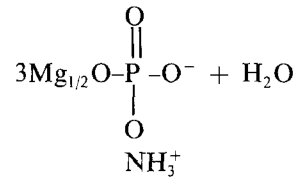


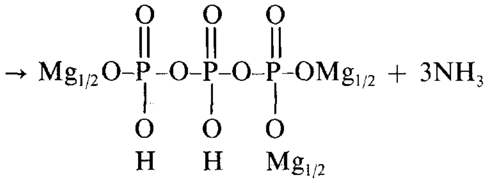
Figure 3 TG and DTA curves of $\mathrm{Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O}$ in air.



$$\rightarrow \mathrm{Mg_{1/2}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle \overset{\displaystyle O}{H}}{|}}{P}}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle \overset{\displaystyle O}{H}}{|}}{P}}{-}OMg_{1/2}} + 2\mathrm{NH_3} \qquad (9)$$



$$3\mathrm{Mg_{1/2}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle \overset{\displaystyle O}{NH_3^+}}{|}}{P}}{-}O^-} + \mathrm{H_2O}$$



$$\rightarrow \mathrm{Mg_{1/2}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle \overset{\displaystyle O}{H}}{|}}{P}}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle \overset{\displaystyle O}{H}}{|}}{P}}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle \overset{\displaystyle O}{Mg_{1/2}}}{|}}{P}}{-}OMg_{1/2}} + 3\mathrm{NH_3} \qquad (10)$$

There is no technique available to detect the presence of the zwitterion at present, so it is impossible to decide which process is more reasonable. The water represented in the equations can come from the crystal water and/or the adsorbed water of the phosphorodiamidate.

3.3. TG and DTA in air

TG and DTA curves of the phosphorodiamidate were taken together with the result in Fig. 3 to study the thermal behaviour at a higher temperature. The thermal products as numbered in Fig. 3 were removed from the furnace and subjected to further analysis. The analytical data are shown in Table II and Figs 4 and 5. The first large endothermic reaction accompanied by large weight loss seemed to be due to elimination of crystal water

$$\mathrm{Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O}$$
$$\rightarrow \mathrm{Mg[PO_2(NH_2)_2 \cdot (6-\mathit{n})H_2O} + n\mathrm{H_2O} \quad (11)$$

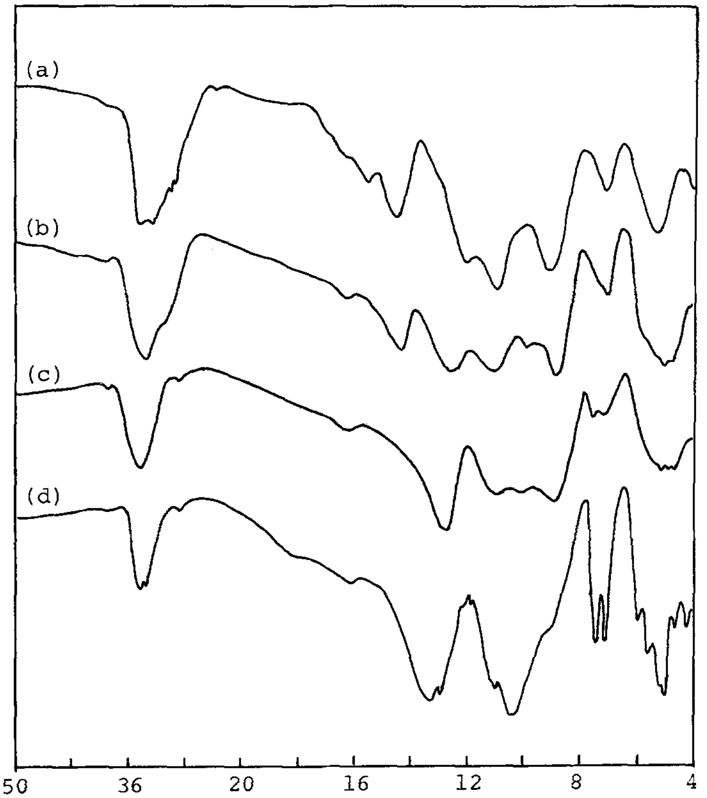
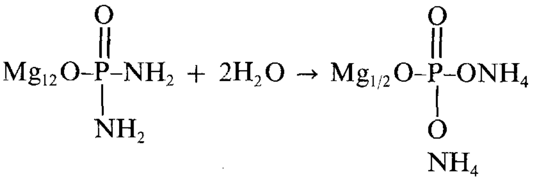


Figure 4 IR spectra of the thermal products of $\mathrm{Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O}$ in air: (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4.

TABLE II Weight loss and composition of the thermal products of $Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O$ in air

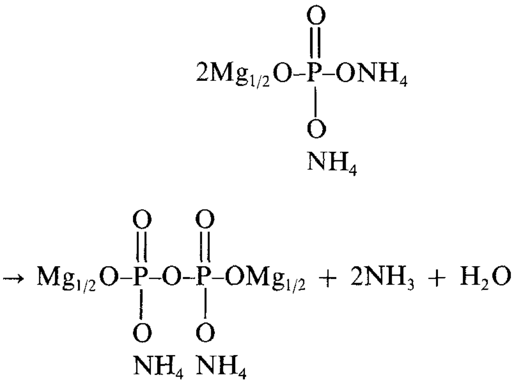
Sample	Total nitrogen (%)	% N as NH_4^+	Weight loss (%)	X-ray diffraction	Phosphates (% P)		
					Diamido	Ortho and Monoamido	Higher
1	15.0	8.0	31.8	amorphous	10.0	52.9	37.1
2	6.0	4.4	38.7	amorphous	–	–	–
3	1.1	0.7	43.3	amorphous	–	–	–
4	–	–	43.9	$Mg(PO_3)_2$ (JCPDS 27-1273)	–	–	–

The nitrogen content analysis indicated that the amino group in the phosphorodiamidate was converted to an ammonium ion at the same time through the thermal reaction



$$\mathrm{Mg_{12}O{-}\overset{O}{\overset{\|}{\underset{\underset{NH_2}{|}}{P}}}{-}NH_2 + 2H_2O \rightarrow Mg_{1/2}O{-}\overset{O}{\overset{\|}{\underset{\underset{\underset{NH_4}{O}}{|}}{P}}}{-}ONH_4} \qquad (12)$$

IR absorption of sample 1 at 1100 cm^{-1} is assigned to that of a PO_3^{2-} group and the result agrees well with the above one. Sample 1 also showed peaks at 900 and 720 cm^{-1}. These peaks can be attributed to a P–O–P linkage, and the following condensation can be concluded



$$\mathrm{2Mg_{1/2}O{-}\overset{O}{\overset{\|}{\underset{\underset{\underset{NH_4}{O}}{|}}{P}}}{-}ONH_4}$$
$$\rightarrow \mathrm{Mg_{1/2}O{-}\overset{O}{\overset{\|}{\underset{\underset{\underset{NH_4}{O}}{|}}{P}}}{-}O{-}\overset{O}{\overset{\|}{\underset{\underset{\underset{NH_4}{O}}{|}}{P}}}{-}OMg_{1/2} + 2NH_3 + H_2O} \qquad (13)$$

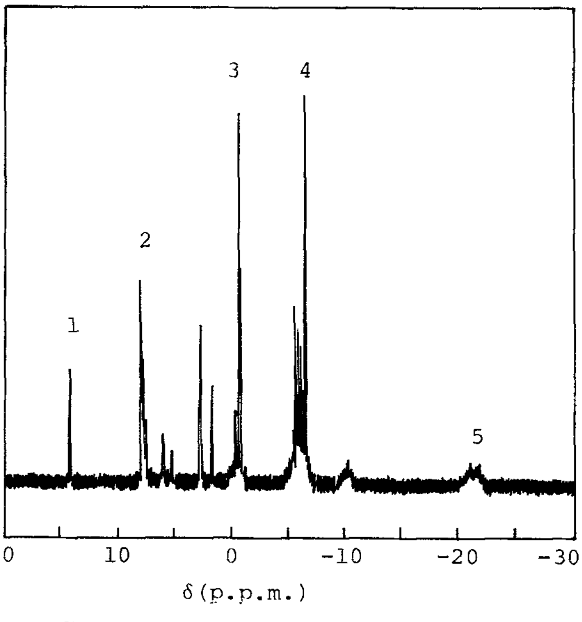
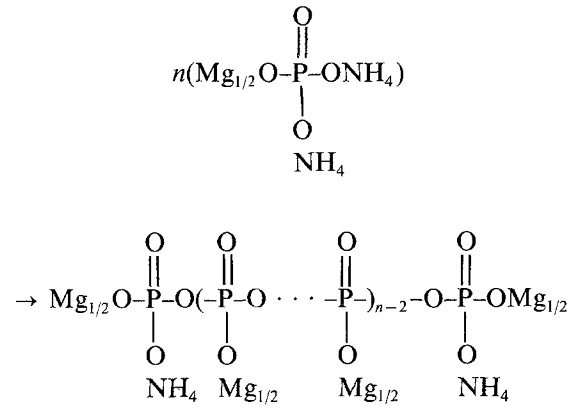
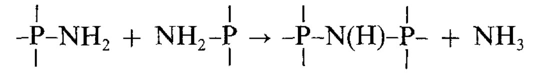


Figure 5 ^{31}P NMR spectrum of the thermal product (sample 1). 1: Phosphorodiamidate, 2: phosphoramidate, 3: orthophosphate, 4: end-PO_4 group, 5: middle-PO_4 group.



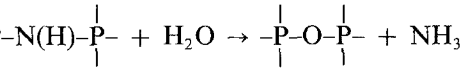
$$\mathrm{n(Mg_{1/2}O{-}\overset{O}{\overset{\|}{\underset{\underset{\underset{NH_4}{O}}{|}}{P}}}{-}ONH_4)}$$
$$\rightarrow \mathrm{Mg_{1/2}O{-}\overset{O}{\overset{\|}{\underset{\underset{\underset{NH_4}{O}}{|}}{P}}}{-}O({-}\overset{O}{\overset{\|}{\underset{\underset{\underset{Mg_{1/2}}{O}}{|}}{P}}}{-}O \cdots {-}\overset{O}{\overset{\|}{\underset{\underset{\underset{Mg_{1/2}}{O}}{|}}{P}}}{-})_{n-2}{-}O{-}\overset{O}{\overset{\|}{\underset{\underset{\underset{NH_4}{O}}{|}}{P}}}{-}OMg_{1/2}}$$
$$+ 2(n-1)\mathrm{NH_3} + (n-1)\mathrm{H_2O} \qquad (14)$$

The paper chromatographic analysis and the ^{31}P NMR spectrum of sample 1 support the conclusion. (The NMR peaks of phosphorodiamidate, phosphoramidate, and an end PO_4 group at +14 to +15, +7 to +8, and −5 to −6 p.p.m. in a basic solution shifted, respectively, to +7 to +10, −2 to −3, and −8 to −10 p.p.m. in an acidic solution.) The peaks of the ^{31}P NMR spectrum between +1.7 and +6.0 are considered to be due to short chain and/or small ring imidopolyphosphates, because the phosphates with imino groups usually show chemical shifts lower fields than that of orthophosphoric acid in an acidic solution. Therefore, the following reaction can result at the same time



$$\mathrm{{-}\overset{|}{\underset{|}{P}}{-}NH_2 + NH_2{-}\overset{|}{\underset{|}{P}} \rightarrow {-}\overset{|}{\underset{|}{P}}{-}N(H){-}\overset{|}{\underset{|}{P}}{-} + NH_3} \qquad (15)$$

The next two exothermic reactions accompany weight loss and, after the reaction, nitrogen content decreased. Accordingly, the thermal reactions of 12 to 15 and the reaction may take place at the temperature range



$$\mathrm{{-}\overset{|}{\underset{|}{P}}{-}N(H){-}\overset{|}{\underset{|}{P}}{-} + H_2O \rightarrow {-}\overset{|}{\underset{|}{P}}{-}O{-}\overset{|}{\underset{|}{P}}{-} + NH_3} \qquad (16)$$

The IR spectra of samples 2 and 3 exhibited absorptions due to a PO_2^- group (1260 to 1300 cm^{-1}), a PO_3^{2-} group (1100 cm^{-1}), and a P–O–P linkage (900 and 780 to 720 cm^{-1}). The spectra also explain well the progress of the thermal reactions of 12 to 16. The weight loss of sample 3 agrees with the thermal reaction

$$\mathrm{Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O}$$
$$\rightarrow \mathrm{Mg(PO_3)_2 + 4NH_3 + 4H_2O} \qquad (17)$$

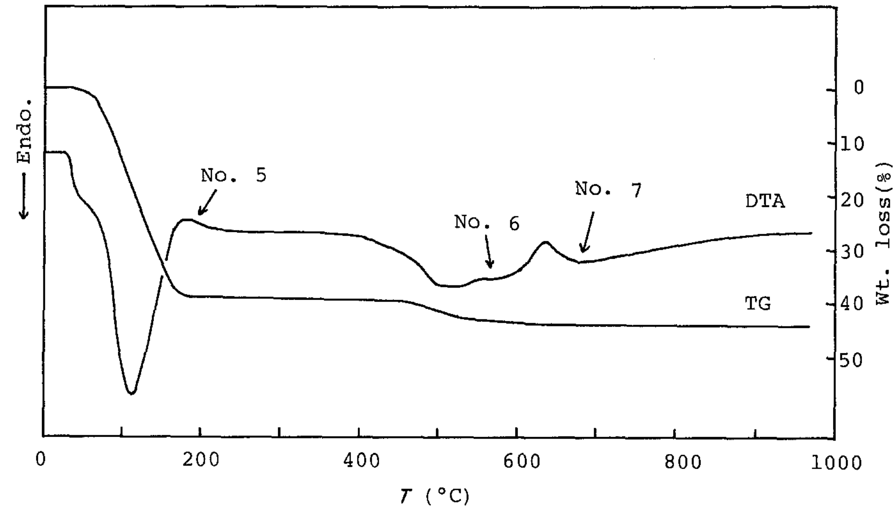


Figure 6 TG and DTA curves of $Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O$ in dry nitrogen.

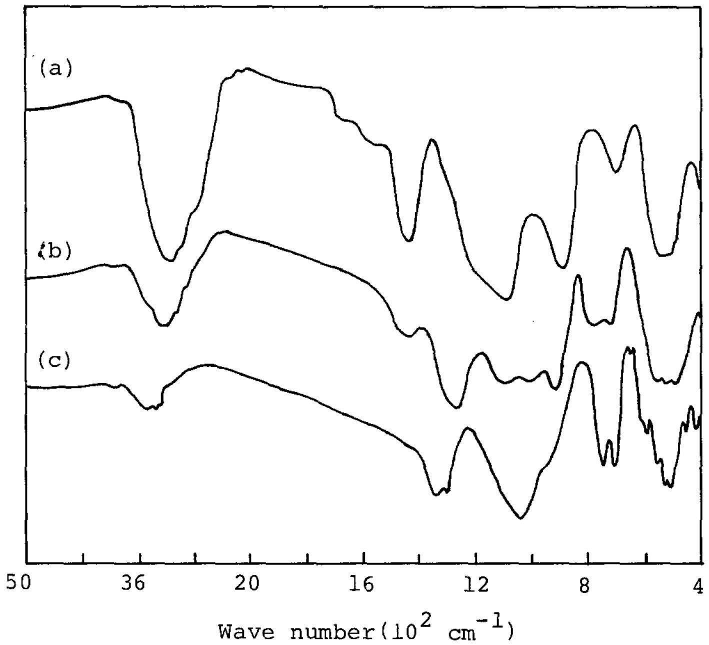


Figure 7 IR spectra of the thermal products of $Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O$ in dry N_2: (a) sample 5, (b) sample 6, (c) sample 7.

After the last exothermic reaction at about 720° C, sample 4 exhibited an X-ray pattern of crystalline $Mg(PO_3)_2$. The exothermic peak can be attributed to crystallization of amorphous magnesium metaphosphate.

3.4. TG and DTA in dry nitrogen

TG and DTA curves of the phosphorodiamidate in dry nitrogen are shown in Fig. 6. The thermal products as numbered in Fig. 6 were removed from the furnace and subjected to further analysis to study the difference of the thermal reaction between in air and in dry nitrogen. The nitrogen content and distribution of phosphate species of the thermal products in Table III show that an amino group of the phosphorodiamidate was converted to an ammonium ion and the amidates and the phosphates were polymerized to phosphates with longer chain lengths. As Figs 7 and 8 show, the IR and ^{31}P NMR spectra of the thermal products gave the same results. Therefore, the reactions of 11 to 15 also take place in dry nitrogen. The exothermic peaks which appeared in the thermal reaction in air at about 400 and 600° C were not observed in the thermal process in dry nitrogen. Sample 6 still contained 4.0% nitrogen. The thermal reaction 12 may take place in dry nitrogen more slowly than in air.

TABLE III Weight loss and composition of the thermal products of $Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O$ in dry nitrogen

Sample	Total nitrogen (%)	% N as NH_4^+	Weight loss (%)	X-ray diffraction	Phosphates (% P)		
					Diamido	Ortho and Monoamido	Higher
5	19.8	8.1	38.9	amorphous	12.6	38.2	49.2
6	4.0	0.5	42.9	amorphous	–	–	–
7	3.4	–	44.0	$Mg(PO_3)_2$ (JCPDS 27-1273)	–	–	–

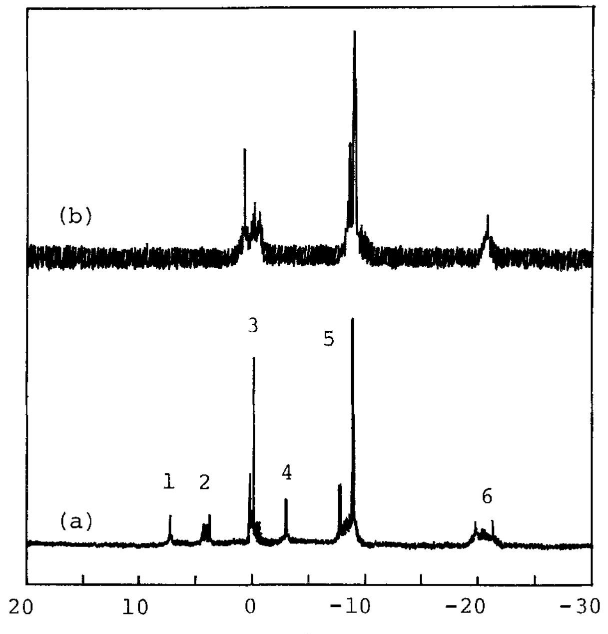


Figure 8 ^{31}P NMR spectra of the thermal products of $Mg[PO_2(NH_2)_2]_2 \cdot 6H_2O$ in dry nitrogen: (a) sample 5, (b) sample 6. 1: Phosphorodiamidate, 2: imidophosphate, 3: orthophosphate, 4: phosphoramidate, 5: end-PO_4 group, 6: middle-PO_4 group.

This could be responsible for the absence of the exothermic peak at about 400° C. The thermal process of Equation 16 does not occur in dry nitrogen, and disappearance of the peak at about 600° C could be caused by this. The last exothermic peak at about 620° C is due to crystallization of amorphous magnesium metaphosphate, because, after the thermal reaction, the product gave an X-ray diffraction pattern of crystalline magnesium metaphosphate (JCPDS card, No. 27-1273).

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