2914 © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 57, 2914—2918 (1984)* [Vol. 57, No. 10

The Synthesis and Thermal Decomposition of Calcium Phosphoramidate

Makoto WATANABE,* Yoshio MORII, and Shoji SATO
Department of Industrial Chemistry, Chubu University, Matsumoto-cho, Kasugai, Aichi 487

(Received March 5, 1984)

Calcium phosphoramidate monohydrate was made by adding an aqueous calcium chloride solution to an aqueous potassium hydrogenphosphoramidate solution at pH 9.0—9.5 below 5 °C. The product was stable at room temperature, but it was decomposed by heating. When the product was heated at 150 °C in air, the phosphoramidate decomposed to produce anhydrous calcium phosphoramide and also ortho- and diphosphates. The elimination of ammonia from amino groups to form a P–N(H)–P linkage was not observed at this temperature. The phosphoramidate decomposed in air to form ortho-, imidodi-, di-, and a small amount of higher polyphosphates at a temperature higher than 150 °C. Imidodiphosphate was decomposed to diphosphate by moisture in air. β-Calcium diphosphate was formed by heating the phosphoramidate at a temperature higher than 750 °C in air. When the phosphoramidate was heated in dried N_2, it showed the same thermal reaction as that in air below 250 °C, while the amount of imidodiphosphate in the thermal product was larger than that in air at a temperature higher than 400 °C

There are so many phosphorus-nitrogen compounds which have a P–N covalent bond. In the compounds, the phosphazens are maybe the best known and most intensively investigated compounds. There are a series of phosphorus-nitrogen compounds which have amino groups on a P atom. These compounds have potential for use as a new type of chemical fertilizer with a P–N covalent bond and as flameproof materials because they produce polyphosphates containing imino and amino groups when they are heated. They can also be used as starting materials for the preparation of many organic and inorganic phosphorus compounds.[1] In our previous paper,[2,3] the thermal decomposition of calcium or magnesium bis(hydrogenphosphoramidate) was studied. The two hydrogenphosphoramidates were unstable even at room temperature and were decomposed to polyphosphates at that temperature or at higher temperatures. This unstability was concluded to be due to the presence of an OH group in the phosphoramidates. This paper will describe the synthesis and the thermal decomposition of calcium phosphoramidate in order to ascertain the difference in thermal properties between the phosphoramidate and the hydrogenphosphoramidates.

Experimental

Preparation. The potassium hydrogenphosphoramidate was made by the method described in a previous paper;[4] 0.12 mol of the phosphoramidate was dissolved in 1.2 dm³ of water. The aqueous solution of calcium chloride, which was made by dissolving 0.12 mol of calcium chloride dihydrate in 360 cm³ of water, was added to the phosphoramidate solution below 5 °C to prevent the hydrolysis of the phosphoramidate. The resulting solution was stirred for 15 min. During the treatment, the pH of the solution was kept at 9.0—9.5 with 2.7% aqueous ammonia. The white precipitate thus produced was filtered off and washed with 50-V% aqueous ethanol, ethanol, and then acetone. The product was dried under 5330 Pa at 25 °C for 2 d.

Chemical Analysis. About 0.2 g of the product was dissolved in 20 cm³ of 6-mol nitric acid, and the solution was heated on a water bath for 1 h. The orthophosphate in the solution was determined by the gravimetric method.[5] The nitrogen and calcium were estimated by, respectively, the Kjeldahl method and the EDTA (disodium dihydrogen ethylenediaminetetraacetate dihydrate) substitution-titration method with a BT indicator.

Paper Chromatography and Colorimetry of Phosphates. The paper-chromatographic separation of phosphate species in a sample and the determination of the phosphates on the chromatogram were run by the method described in our previous paper.[2]

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.

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

DTA and TG. A sample was heated at a rate of 5 °C min^{-1} in air and dried N_2 by means of a Cho Balance TRDA$_1$-H apparatus.

^{31}P NMR Measurement. About 50 mg of a powder sample was put in 1.2 cm³ of a 6% EDTA deuterated-water solution and stirred for 1—20 min, depending on the solubility of the sample, below 5 °C. The ^{31}P NMR spectrum of the solution was then measured by means of a JEOL JNM-FX-60-FT-NMR instrument.

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

Results and Discussion

Composition of the Product. The yield of the product was about 15 g. The ^{31}P NMR spectrum of the product gave only one peak of phosphoramidate at 3.4 ppm. (To get a single peak, the measuring time had to be as short as possible because the phosphoramidate was easily hydrolyzed to orthophosphate and the spectrum of the phosphoramidate solution also showed a peak of orthophosphate, depending on the experimental conditions.) Found: P, 19.9; N, 8.9; Ca, 27.1; H_2O, 12.1%. Calcd for $CaPO_3NH_2\cdot H_2O$: P, 20.2; N, 9.2; Ca, 26.2; H_2O, 11.8%. Accordingly, it was found that the product was calcium phosphoramidate monohydrate, $CaPO_3NH_2\cdot H_2O$. The product was stable at room temperature.

Thermal Reaction in Air. *(1) DTA and TG*: The DTA and TG curves of the product in air are presented in Fig. 1. The samples, numbered as in Fig. 1, were removed from the furnace, cooled in a silica-gel desiccator, and subjected to further analysis. The results are shown in Table 1 and Fig. 2. According to Table 1, the first large endothermic peak accompanying a rapid weight loss seemed to be mainly

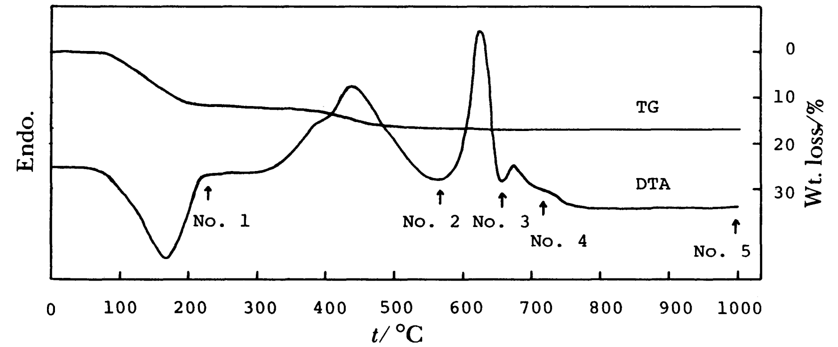


Fig. 1. DTA and TG curves of $CaPO_3NH_2 \cdot H_2O$ in air.

Table 1. Weight loss of the product, and nitrogen and water content of the thermal decomposition products in air

Sample	Total N/%	Water/%	Wt. loss/%
Product	8.9	12.1	—
No. 1	9.1	1.4	11.3
No. 2	4.0	0	16.9
No. 3	1.6	0	17.1
No. 4	1.2	0	17.2
No. 5	0	0	17.2

caused by the elimination of bound water. The weight loss of the product at this stage was very close to the one calculated according to the following reaction:

$$CaPO_3NH_2 \cdot H_2O \longrightarrow CaPO_3NH_2 + H_2O, \qquad (1)$$

but the thermal product, No. 1, still had 1.4% of water and its nitrogen content was a little less than that of $CaPO_3NH_2$. The IR spectrum of No. 1 showed a peak at 930 cm^{-1} which is considered to be due to a P–N(H)–P or a P–O–P linkage, and it was found that the endothermic reaction included condensation. The following condensation reaction is acceptable for the formation of a P–N(H)–P linkage:

$$2CaO_3P\text{-}NH_2 \longrightarrow CaO_3P\text{-}N(H)\text{-}PO_3Ca + NH_3. \qquad (2)$$

There are two ways for the formation of a P–O–P linkage. One is:

$$\begin{aligned} 2CaO_3P\text{-}NH_2 + 2H_2O &\longrightarrow 2CaO_3P\text{-}ONH_4 \\ &\longrightarrow CaO_3P\text{-}O\text{-}PO_3Ca + 2NH_3 + H_2O; \qquad (3) \end{aligned}$$

the other is:

$$\left.\begin{aligned} &CaO_3P\text{-}N(H)\text{-}PO_3Ca + 2H_2O \longrightarrow \\ &\qquad\qquad 2CaO_3P\text{-}OH + NH_3 \\ &2CaO_3P\text{-}OH \longrightarrow CaO_3P\text{-}O\text{-}PO_3Ca + H_2O. \end{aligned}\right\} \quad (4)$$

It was, however, impossible to distinguish between the P–N(H)–P and the the P–O–P linkages according to the IR spectrum. There appeared a broad exothermic peak accompanying weight loss at 320—560 °C. After the reaction, the nitrogen content in the product decreased from 9.1 to 4.0, so the reaction includes the elimination of ammonia. As has been mentioned above, Reactions 2, 3, and 4 can be presented for the elimination of ammonia. As Fig. 2 shows, the No. 1 thermal product has a very weak peak of NH_4^+ at 1400 cm^{-1}. It is still difficult to say that Reaction 3 does not take place much, because the overall-reaction rate of Reaction 3 in that temperature range is obscure in these data. No detailed information about Reaction 4 could be obtained by the above data, either. The exothermic reaction may, however, be thought to include all these reactions at this stage. The formation of an ammonium ion in the thermal product will be discussed in the next section. The No. 1 sample showed an unkown X-ray diffraction pattern, while No. 2 was X-ray diffractometrically amorphous. The unknown pattern may be thought to be due to $CaPO_3NH_2$, because Reaction 1 may be predominant at this step. The IR spectrum of No. 2 showed a weak absorption of a $(PO_2)^-$ group at 1300 cm^{-1}, a strong absorption of a $(PO_3)^{2-}$ group at 1150 cm^{-1}, and absorptions of a P–N(H)–P or a P–O–P linkage at 930 and 730 cm^{-1}. The sample did not show any absorptions of an amino group in its spectrum. Accordingly, the main thermal product involved in No. 2 may be calcium diphosphate, $CaO_3P\text{-}O\text{-}PO_3Ca$, or calcium imidodi-

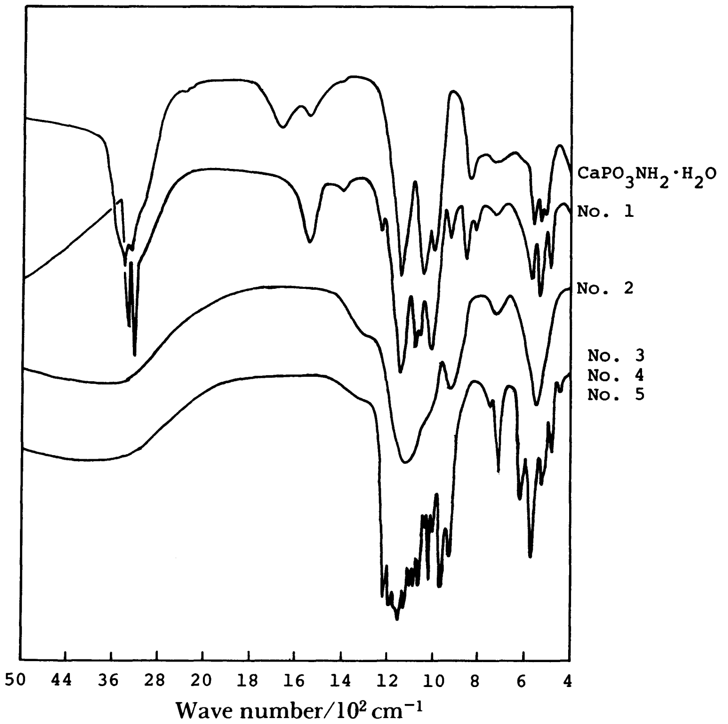
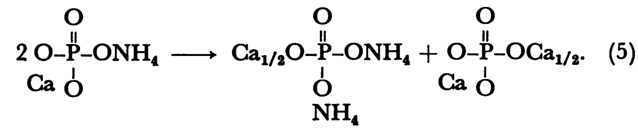


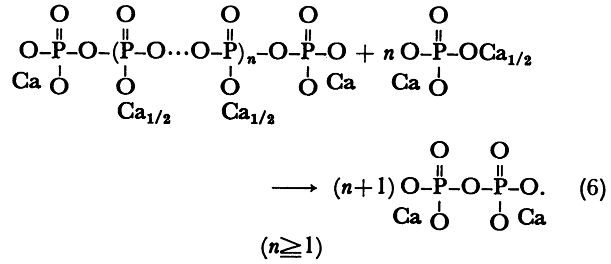
Fig. 2. IR spectra of the thermal decomposition products of $CaPO_3NH_2 \cdot H_2O$ in air.

phosphate, $CaO_3P\text{-}N(H)\text{-}PO_3Ca$. If the sample is the imidodiphosphate, its nitrogen content should be 5.5%. Therefore, the sample No. 2 may be a mixture of the two diphosphates. To obtain proof of this, the ^{31}P NMR spectrum of No. 2 was taken; it is shown in Fig. 3. The peaks at about 0.9 and 10—11 ppm may be due to imidodiphosphate and diphosphate respectively. As has been described above, the sample No. 2 showed a weak IR absorption of a $(PO_2)^-$ group at 1300 cm^{-1}. This means that the thermal product contains polyphosphates or imidopolyphosphates with chain lengths longer than that of the dimer (diphosphate and imidodiphosphate). According to Reactions 2—4, the formation of such polyphosphates with a $(PO_2)^-$ group seems to be impossible at a relatively low-temperature range. The problem can be solved by assuming that the following disproportionation is taking place in the amorphous thermal decomposition products:



$$2\,\text{O-}\underset{\text{Ca}\,\text{O}}{\overset{\overset{\text{O}}{\|}}{\text{P}}}\text{-ONH}_4 \longrightarrow \text{Ca}_{1/2}\text{O-}\underset{\underset{\text{NH}_4}{\text{O}}}{\overset{\overset{\text{O}}{\|}}{\text{P}}}\text{-ONH}_4 + \text{O-}\underset{\text{Ca}\,\text{O}}{\overset{\overset{\text{O}}{\|}}{\text{P}}}\text{-OCa}_{1/2}. \qquad (5)$$

The $Ca_{1/2}(NH_4)_2PO_4$ species is bifunctional for thermal condensation in this temperature range and can produce tri- and higher polyphosphates. The sample No. 2 did not show any ^{31}P NMR peak of a $(PO_2)^-$ group. The sample contained an insoluble part, and so it could be concluded that the polyphosphates with a $(PO_2)^-$ group has a very low solubility. The NMR spectrum of No. 2 also exhibited a peak of phosphoramidate. It is found that the thermal product No. 2 is composed of these compounds. After the sharp large exothermic peak at around 630 °C, the sample showed an X-ray diffraction diagram of β-$Ca_2P_2O_7$ (ASTM cards, Nos. 9—346 and 20—24). It is clear that the thermal reaction is caused by the crystallization of amorphous calcium diphosphate to the β-form. It was difficult to understand the next small exothermic peak at about 670 °C because no definitive change in the IR spectrum or in the X-ray diffraction diagram of the sample after the exothermic peak was observed. As Table 1 shows, however, nitrogen was released from the sample during the crystallization, so it might be said that the amorphous calcium diphosphate produced according to Reactions 3 and/or 4 in this temperature range crystallizes at around 670 °C. The weight loss of the product was observed until about 620 °C; this seems to support the above discussion. The samples Nos. 3—5 did not indicate any IR absorption of a $(PO_2)^-$ group. The disappearance of the absorption may be explained by the following reorganization or degradation of amorphous phosphates to β-$Ca_2P_2O_7$;



$$\text{O-}\underset{\text{Ca}\,\text{O}}{\overset{\overset{\text{O}}{\|}}{\text{P}}}\text{-O-(}\underset{\underset{\text{Ca}_{1/2}}{\text{O}}}{\overset{\overset{\text{O}}{\|}}{\text{P}}}\text{-O}\cdots\text{O-}\underset{\underset{\text{Ca}_{1/2}}{\text{O}}}{\overset{\overset{\text{O}}{\|}}{\text{P}}}\text{)}_n\text{-O-}\underset{\text{O}\,\text{Ca}}{\overset{\overset{\text{O}}{\|}}{\text{P}}}\text{-O} + n\,\text{O-}\underset{\text{Ca}\,\text{O}}{\overset{\overset{\text{O}}{\|}}{\text{P}}}\text{-OCa}_{1/2}$$

$$\longrightarrow (n+1)\,\text{O-}\underset{\text{Ca}\,\text{O}}{\overset{\overset{\text{O}}{\|}}{\text{P}}}\text{-O-}\underset{\text{O}\,\text{Ca}}{\overset{\overset{\text{O}}{\|}}{\text{P}}}\text{-O}. \qquad (6)$$

$$(n \geqq 1)$$

The sample No. 5 did not contain nitrogen. The nitrogen as an imino group in the thermal product may be converted to oxygen according to Reaction 4. Since the weight change associated with the reaction is very small, no increase in the weigh of the thermal product could be observed by the TG.

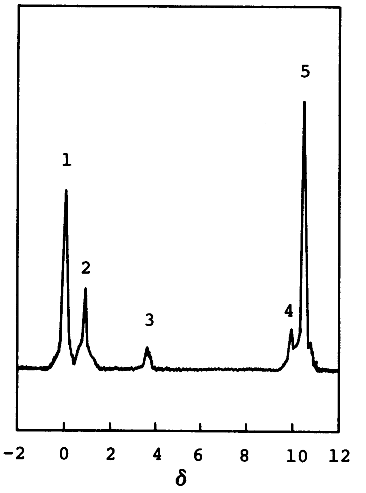


Fig. 3. ^{31}P NMR spectrum of the thermal product, No. 2.

1: Orthophosphate, 2: imidodiphosphate, 3: phosphoramidate, 4: and 5: diphosphate.[6]

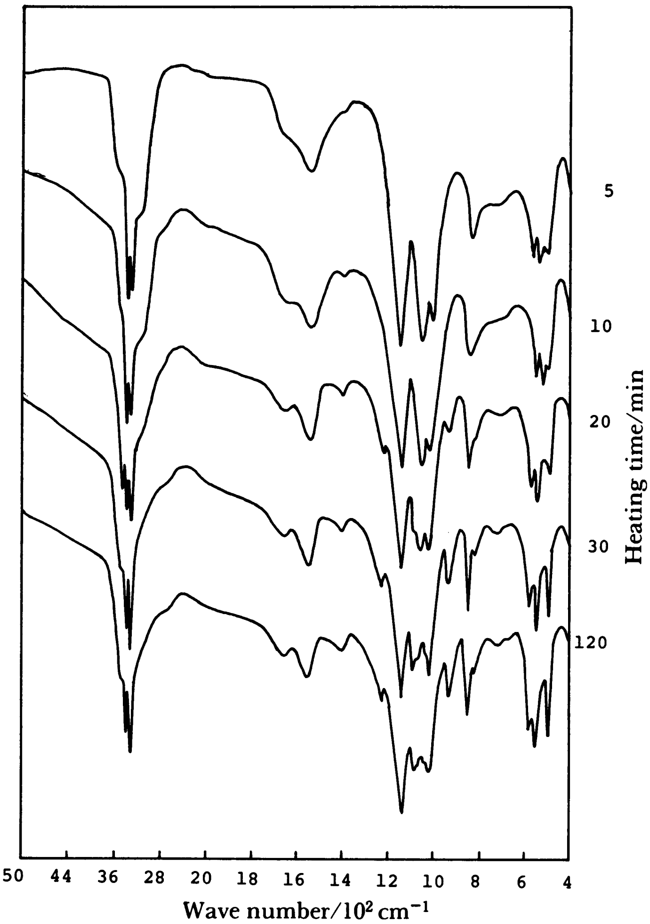


Fig. 4. IR spectra of the isothermal decomposition products in air at 150 °C.

(2) *Isothermal Reaction at 150°C*: As has been mentioned above, it was difficult to get clear information about the formation of an ammonium ion according to Reaction 3 by means of the DTA–TG instrument. Therefore, $CaPO_3NH_2 \cdot H_2O$ was isothermally heated at 150 °C. This temperature seemed to be suitable for the analysis, because the thermal reaction was active and the elimination of ammonia from the product was very slow at this temperature. The IR spectra of the isothermal decomposition products in Fig. 4 indicate a very small peak due to NH_4^+ at 1400 cm^{-1}. This means that the amount of nitrogen present as NH_4^+ is very small. If only the dehydration of bound water from the product is taking place at this temperature according to Reaction 1, the nitrogen content in the thermal product should be 10.4%. As Table 2 shows, however, the nitrogen content was less than 10.4%. Therefore, ammonia must be released from the product. The ^{31}P NMR spectrum shows that the thermal product is composed of orthophosphate, phosphoramidate, and diphosphate. Reactions 2—4 can be responsible for the reaction. Imidophosphates were not made at all at this temperature. Therefore, Reactions 1 and 3 occur at 150 °C. By the way, the thermal product heated at 150 °C showed very small IR absorption of NH_4^+, while it had a large ^{31}P NMR peak of orthophosphate. The orthophosphate without NH_4^+ can be made by the elimination of ammonia as follows:

$$CaO_3PONH_4 \longrightarrow CaO_3POH + NH_3. \qquad (7)$$

As has been mentioned above, phosphoramidate is hydrolyzed easily to orthophosphate in water. It is difficult to ascertain which reaction is responsible for the appearance of the large NMR peak of orthophosphate, but it seems reasonable that both reactions contribute to it. The other reactions do not occur at this temperature; they may take place at a temperature higher than 150 °C.

Thermal Reaction in Dried N_2. According to Reactions 3 and 4, the presence of water causes the decomposition of the $P{-}NH_2$ and $P{-}N(H){-}P$ linkages. The water which brings about the decomposition comes from bound water and from moisture in the air. After the release of the bound water, the moisture in the air may give an important effect on the decomposition. To avoid its influence, the DTA and TG measurements of $CaPO_3NH_2 \cdot H_2O$ were made in dried N_2; the results are shown in Fig. 5. According to the results shown in Table 3, the first endothermic reaction, accompanied by a rapid weight loss, seemed to be mainly caused by the release of bound water. The weight loss of the product exhibited a value very close to the one calculated with Reaction 1, but the sample No. 6 still contained 1.5% of water and its nitrogen content was less than that of $CaPO_3NH_2$. Therefore, the elimination of ammonia seemed to take place at the same time. The IR spectrum of No. 6 had absorptions at 930 and 720 cm^{-1}. These absorptions were considered to be due to a $P{-}N(H){-}P$ or a $P{-}O{-}P$ linkage. The ^{31}P NMR spectrum of No. 6 in Fig. 6 shows that the thermal product contains ortho- and diphosphates other than phosphoramidate. The sample also indicated a small IR peak of NH_4^+ at 1400 cm^{-1}. Accordingly, the thermal reactions taking place here are Reactions 1, 3, and 7. The other reactions may not occur at this stage. The X-ray diffraction pattern of No. 6 was the same as that of No. 1 and is concluded to be the pattern of $CaPO_3NH_2$. The sample No. 7 had the same X-ray diffraction diagram and IR spectrum as those of No. 6, while No. 7 indicated the loss of nitrogen and a ^{31}P NMR peak at 0.9 ppm which seemed to be due to imidodiphosphate. Therefore, reaction 2 may be taking place at this stage. The sample showed a small endothermic peak, accompanied by a fast weight loss, at around 450 °C. The sample No. 8 was X-ray diffractometrically amorphous and had a small NMR peak of phosphoramidate and a large

TABLE 2. WEIGHT LOSS OF THE PRODUCT, AND NITROGEN AND WATER CONTENT OF THE ISOTHERMAL DECOMPOSITION PRODUCTS AT 150 °C IN AIR

Reaction time/min	Total N/%	Water/%	Wt. loss/%
5	8.9	11.4	0.6
10	8.8	10.1	2.2
20	8.8	4.5	7.9
30	8.7	1.3	11.0
60	8.7	1.2	11.4
120	8.5	1.1	11.6

TABLE 3. WEIGHT LOSS OF THE PRODUCT, AND NITROGEN AND WATER CONTENT OF THE THERMAL DECOMPOSITION PRODUCTS IN DRIED N_2

Sample	Total N/%	Water/%	Wt. loss/%
No. 6	9.4	1.5	11.8
No. 7	8.3	0	13.2
No. 8	6.1	0	16.2
No. 9	4.0	0	17.1
No. 10	3.6	0	17.2

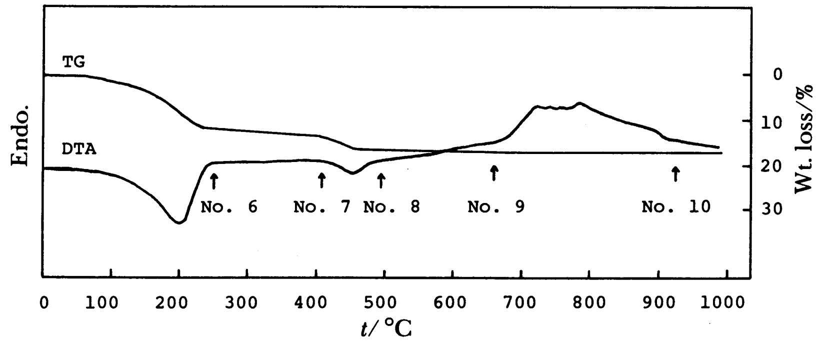


Fig. 5. DTA and TG curves of $CaPO_3NH_2 \cdot H_2O$ in dried N_2.

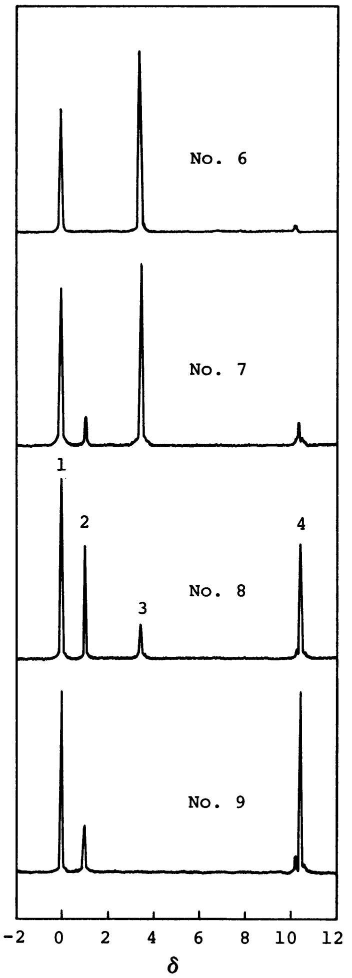
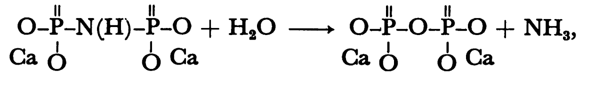
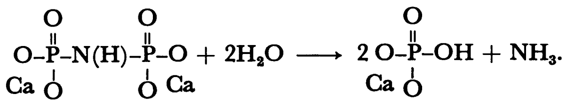


Fig. 6. ^{31}P NMR spectra of the thermal decomposition products in dried N_2.
1: Orthophosphate, 2: imidodiphosphate, 3: phosphoramidate, 4: diphosphate.

NMR peak of imidodiphosphate. The sample No.7 had a very small peak of NH_4^+. Therefore, reaction 2 may be taking place rapidly at this stage. According to the above discussion and the result that the DTA curve did not show any exothermic peak of the crystallization of calcium diphosphate at around 630 °C, the main thermal decomposition product in No. 8 is concluded to be calcium imidodiphosphate, but the sample also indicated large NMR peaks of ortho- and diphosphates. The appearance of the two large ^{31}P NMR peaks can be explained by the hydrolysis of imidodiphosphate to ortho- and diphosphates as follows:



$$\underset{\mathrm{Ca\,O}}{\overset{\mathrm{O}}{\mathrm{O\text{-}P}}}\text{-N(H)-}\underset{\mathrm{O\,Ca}}{\overset{\mathrm{O}}{\mathrm{P\text{-}O}}} + \mathrm{H_2O} \longrightarrow \underset{\mathrm{Ca\,O}}{\overset{\mathrm{O}}{\mathrm{O\text{-}P}}}\text{-O-}\underset{\mathrm{O\,Ca}}{\overset{\mathrm{O}}{\mathrm{P\text{-}O}}} + \mathrm{NH_3}, \qquad (8)$$



$$\underset{\mathrm{Ca\,O}}{\overset{\mathrm{O}}{\mathrm{O\text{-}P}}}\text{-N(H)-}\underset{\mathrm{O\,Ca}}{\overset{\mathrm{O}}{\mathrm{P\text{-}O}}} + \mathrm{2H_2O} \longrightarrow 2\,\underset{\mathrm{Ca\,O}}{\overset{\mathrm{O}}{\mathrm{O\text{-}P}}}\text{-OH} + \mathrm{NH_3}. \qquad (9)$$

The samples Nos. 7 and 8 also had a weak IR absorption at 1300 cm^{-1} which seemed to be the absorption of a $(PO_2)^-$ group. The small amount of ammonium calcium orthophosphate which was produced by Reaction 3 may disproportionate according to Reaction 5 and then produce polyphosphates with chain lengths longer than that of diphosphate in this temperature range. As has been discussed above, the calcium polyphosphates seemed to have a very low solubility, for samples Nos. 7 and 8 did not exhibit any NMR peak of a $(PO_2)^-$ group. After the small endothermic peak at about 450 °C, the weight loss of the product lasted until about 650 °C. During the reaction, the nitrogen content of the thermal product decreased from 6.1 to 4.0. The sample No. 9 did not have any ^{31}P NMR peak of phosphoramidate at all. Therefore, the loss of nitrogen content at this stage may be mainly caused by Reaction 2. The sample No. 9 did not show any IR absorption of a $(PO_2)^-$ group. The reorganization of Reaction 6 may also be taking place at this stage. The sample No. 9 showed several complex exothermic reactions in the temperature range of 700—1000 °C. The sample No. 9 was X-ray diffractometrically amorphous, while No. 10 showed an X-ray diffraction diagram of β-$Ca_2P_2O_7$ and the nitrogen content decreased a little after the exothermic reaction. It could be concluded, from the presence of slight amounts of water in the DTA-TG instrument, that the conversion of an imino group to oxygen seems to occur according to Reaction 4 at this stage. It was difficult to prevent such decomposition in the instrument used here.

Difference of Thermal Reaction Between Phosphoramidate and Hydrogenphosphoramidate. The calcium and magnesium bis (hydrogenphosphoramidate)[2,3] were unstable and decomposed to polyphosphates at room temperature. They also decomposed to polyphosphates and did not form a P-N(H)-P linkage at all upon the elimination of ammonia at a temperature higher than room temperature. On the other hand, the calcium phosphoramidate made in this study was stable at room temperature, and quite a bit of the phosphoramidate, especially in dried N_2, produced a P-N(H)-P linkage upon thermal condensation at a temperature higher than 150 °C.

References

1) For example, D. E. C. Corbridge, "Phosphorus," Elsevier, Amsterdam (1980), p. 219.

2) M. Watanabe, T. Inagaki, and S. Sato, *Bull. Chem. Soc. Jpn.*, **56**, 458 (1983).

3) M. Watanabe, T. Inagaki, Y. Morii, and T. Yamada, *Setsuko To Setsukai*, No. 184, 111 (1983).

4) "Shin Zitsuken Kagaku Koza," ed by the Chemical Society of Japan, Maruzen, Tokyo (1976), Vol. 8-[I], p. 354.

5) "Bunseki Kagaku Binran," ed by the Chemical Society of Japan, Maruzen, Tokyo (1971), pp. 204 and 1492.

6) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, "Topics in Phosphorus Chemistry," Interscience Publishers, New York (1967), Vol. 5, p. 227, and the references cited there in.