# The Synthesis and Decomposition of Calcium Bis(hydrogenphosphoramidate)

Makoto WATANABE,* Toshihiko INAGAKI, and Shoji SATO

*Department of Industrial Chemistry, Chubu Institute of Technology, Matsumoto-cho, Kasugai, Aichi 487*

(Received June 16, 1982)

Calcium bis(hydrogenphosphoramidate)–water (2/3) was made by adding an aqueous calcium chloride solution to an aqueous potassium hydrogenphosphoramidate solution. The product decomposed slowly to diammonium calcium diphosphate monohydrate in air at room temperature. When the product was heated above 600 °C, the decomposition product was β-type calcium metaphosphate. According to the result of the isothermal decomposition of the product at 150 °C in air, no formation of P–NH–P linkages by the elimination of $NH_3$ from P–$NH_2$ linkages was observed, and it was concluded that the phosphoramidate thermally decomposed to form only polyphosphates in air.

Phosphoramidates have P–N covalent bonds and have potential of new chemical fertilizers containing phosphorus and nitrogen. Several papers concerning synthesis, decomposition, or hydrolysis of ammonium and alkali-metal salts of phosphoramidic or phosphorodiamidic acid have been published, but other salts of these phosphoramidic and phosphorodiamidic acids have not been studied. This paper describes the synthesis and decomposition of calcium bis(hydrogenphosphoramidate).

## Experimental

*Materials and Procedure.* Ethanol was purified by distillation. Other chemicals used were of reagent grade and used without further purification. Potassium hydrogenphosphoramidate was prepared by the method described in a previous paper,[1] and 0.08 mol of the phosphoramidate was dissolved in 85 $cm^{-3}$ of water. Calcium chloride was dissolved in 40 $cm^3$ of water by 0.04 mol. The calcium chloride solution was added slowly to the phosphoramidate solution below 5 °C to prevent the hydrolysis of the latter. The resulting mixture was stirred for several minutes. The pH of the solution was 6.5—6.3 during the treatment. A white precipitate was formed and was filtered off, washed with cooled water, ethanol, and then acetone. The product was dried under 5330 Pa at 25 °C for 2 d.

*Elemental Analysis.* Phosphorus in the product was determined by the gravimetric technique. About 0.2 g of the product was dissolved in 20 $cm^3$ of 6-mol nitric acid and the solution was heated on a water bath for 1 h. A few drops of concentrated hydrochloric acid was added to the solution and the solution was heated for several hours on a water bath. The orthophosphate in the solution was determined as $Mg_2P_2O_7$ by the gravimetric method.[2] Nitrogen and calcium in the product were determined by the Kjeldahl method and the EDTA (disodium dihydrogen ethylenediaminetetraacetate dihydrate) back-titration method with a calcein indicator respectively.

*Paper Chromatography.* One-dimensional paper chromatography was used for the separation of the phosphate species in a sample by using acidic (for the separation of chain phosphates) and basic (for the separation of ring phosphates) solvents.[3] About 0.1 g of a sample was dissolved in 10 $cm^3$ of a 2% EDTA aqueous solution. The pH value of the solution was adjusted to about 7 with a 0.5-mol $dm^{-3}$ aqueous sodium hydroxide solution. About 8 $mm^3$ of the solution was spotted on Toyo No. 51A filter paper (2 by 50 cm). The development was run at 5 °C for 2 d.

*Colorimetric Measurement of Phosphates.* Every individual spot on the chromatogram was cut at the demarcation line and placed in a 100-$cm^3$ beaker containing 10 $cm^3$ of a 0.1-mol $dm^{-3}$ ammonia solution. After 1 h, the solution was transferred to a 25-$cm^3$ volumetric flask, together with 10 $cm^3$ of wash water, and a 1-$cm^3$ portion of Lucena-Conde and Prat's reagent[4] was added to the flask. The flask was heated in a boiling-water bath for 1 h, subsequently cooled by placing it in a both of cold water, and diluted to the mark with water. The absorbance of the blue solution was measured with a Shimadzu Spectronic 88 spectrophotometer at 830 nm. The phosphate content (P%) was calculated from the absorbance data.

*X-Ray Diffractometry.* An X-ray diffraction diagram of a testing material was taken with nickel-filtered Cu *Kα* radiation by using a Toshiba X-ray diffractometer, ADG-102.

*IR Measurement.* IR spectra of samples were measured with a JASCO IR spectrophotometer, model A-3, using a KBr disk method.

*DTA and TG.* A sample was heated at the heating rate of 5 °C $min^{-1}$ in air by using a Cho Balance $TRDA_1$-H-type apparatus.

*$^{31}P$ NMR.* About 50 mg of a sample was put in 1.2 $cm^3$ of a 6% EDTA deuterated-water solution and stirred for several minutes. The $^{31}P$ NMR spectrum of the solution was recorded on a JEOL JNM-FX-60-FT-NMR instrument.

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

*Decomposition in Air.* The decomposition of the product at room temperature and 150 °C in air was studied by paper chromatography, X-ray diffractometry, IR spectrophotometry, and $^{31}P$ NMR as described above.

## Results and Discussion

*Composition of the Product.* The yield of the product thus obtained was about 10 g. Found: P, 23.1; N, 10.4; Ca, 16.5; $H_2O$, 11.0%. Calcd for $Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$: P, 23.9; N, 10.8; Ca, 15.5; $H_2O$, 10.4%. So the product is calcium bis(hydrogenphosphoramidate)–water (2/3). The product was only slightly soluble in water but soluble in an aqueous solution of EDTA.

*Decomposition at Room Temperature.* The stability of the product was checked at room temperature in air. The distribution of phosphate species in the decomposition product at several reaction times are listed in Table 1. The phosphoramidate decomposed to form polyphosphates. The main decomposition product was diphosphate. The IR spectra of the decomposition products

Table 1. Distribution of phosphate species in the decomposition product of $Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$ at room temperature in air

| Reaction time/d | Phosphate/P(%) | | | |
|---|---|---|---|---|
| | Amide and Ortho | Di | Tri | Higher |
| 0 | 100 | — | — | — |
| 15 | 85 | 15 | — | — |
| 55 | 66 | 26 | 5 | 3 |
| 176 | 18 | 70 | 10 | 2 |
| 220 | 14 | 75 | 9 | 2 |

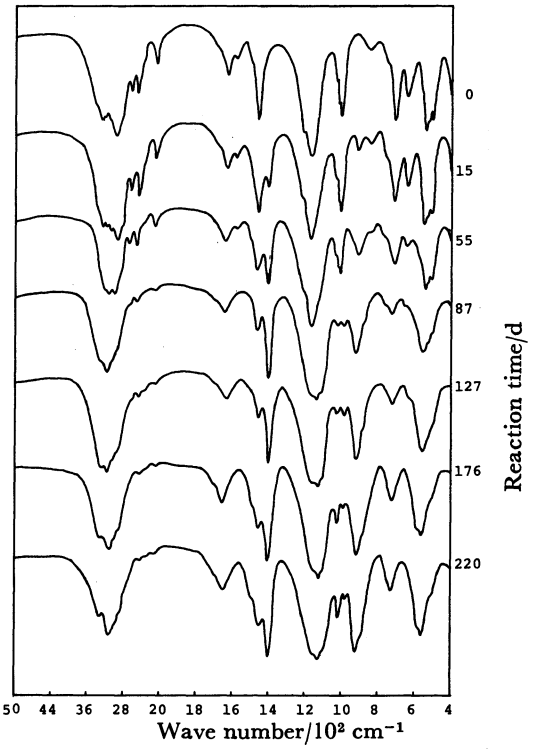



Fig. 1. IR spectra of the decomposition products of $Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$ at room temperature.

are shown in Fig. 1. The assignment of the absorptions is listed in Table 2. The absorption due to a P–O–P linkage appeared and the intensity of the absorption increased with the elapse of the reaction time. The peaks of a $(PO_3)^{2-}$ group were strong even at 220 d. So the degree of polymerization of phosphates seemed to be very low. This means that most of the phosphates contained in the decomposition products are di- and triphosphates. This conclusion agrees well with that shown in Table 1. The absorption due to an ammonium ion appeared and grew with the passage of time, while the height of the absorptions associated with P–O–H and P–N–H linkages decreased with an increase in the reaction time. As Table 3 shows, the total nitrogen content in the decomposition product decreased and that of nitrogen as an ammonium ion increased with tiem. This means that an amido group is converted to an ammonium ion and the ammonia escapes gradually into the air. The discussion explains well the change in the IR spectra. Phosphoramidate having an OH-group is considered to be connected with zwitterion formation as follows:[7]

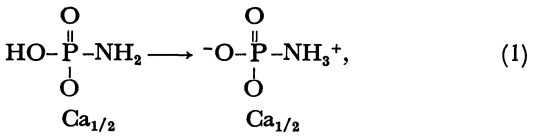
Table 2. Assignment of thf spectra of thf products

| Position of absorption maxima $\tilde{\nu}/cm^{-1}$ | Assignment[a] |
|---|---|
| 3450 | $\nu$O–H of bound water |
| 3300—2950 | $\nu$(P)–N–H and N–H of $NH_4^+$ |
| 2630—2100 | $\nu$(P)–O–H |
| 1635 | $\delta$(P)–N–H and/or $\delta$H–O–H of bound water |
| 1580 | $\delta$(P)–N–H |
| 1460 | $\delta$(P)–O–H |
| 1400 | $\delta NH_4^+$ |
| 1280 | $\nu_{as}(PO_2)^-$ |
| 1150 | $\nu_{as}(PO_3)^{2-}$ |
| 1100 | $\nu_s(PO_2)^-$ |
| 1020—980 | $\nu$P–O–(H) and/or $\nu_s(PO_3)^{2-}$ |
| 910 | $\nu_{as}$P–O–P |
| 840[b] | (P–N–H or P–O–H) |
| 780—730 | $\nu$P–O–P |
| 720—640 | $\nu$P–N–(H) |
| 580—560 | $\delta(PO_2)^-$ and/or $\delta(PO_3)^{2-}$ |
| 530—500 | $\delta$P–O–(H) |

a) The assignment was made on the basis of Refs. 5 and 6. b) The absorption could not be assigned, but seemed to be associated with a P–N–H or a P–O–H linkage since the absorption decreased with the passage of reaction time and finally disappeared.

Table 3. Content of nitrogen in the decomposition products of $Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$ at room temperature in air

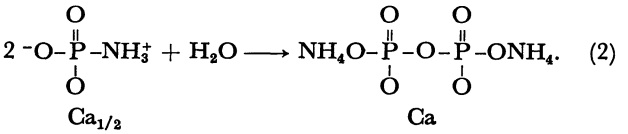
| Reaction time/d | Total N(%) | N(%) as $NH_4^+$ |
|---|---|---|
| 0 | 10.4 | 0 |
| 15 | 10.2 | 1.2 |
| 55 | 9.9 | 3.0 |
| 176 | 8.3 | 7.5 |
| 220 | 8.2 | 7.6 |



$$HO\text{–}P(=O)(O)\text{–}NH_2 \longrightarrow {}^-O\text{–}P(=O)(O)\text{–}NH_3^+, \quad (1)$$

$Ca_{1/2}$ $Ca_{1/2}$

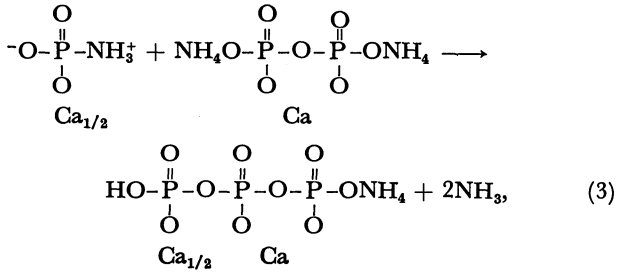
The zwitterion seems to be unstable and to decompose to diphosphate with water,



$$2\ {}^-O\text{–}P(=O)(O)\text{–}NH_3^+ + H_2O \longrightarrow NH_4O\text{–}P(=O)(O)\text{–}O\text{–}P(=O)(O)\text{–}ONH_4. \quad (2)$$

$Ca_{1/2}$ Ca

The formation of polyphosphates higher than diphosphate can be represented as follows:



$$^-O\text{–}P(=O)(O)\text{–}NH_3^+ + NH_4O\text{–}P(=O)(O)\text{–}O\text{–}P(=O)(O)\text{–}ONH_4 \longrightarrow$$

$Ca_{1/2}$ Ca

$$HO\text{–}P(=O)(O)\text{–}O\text{–}P(=O)(O)\text{–}O\text{–}P(=O)(O)\text{–}ONH_4 + 2NH_3, \quad (3)$$

$Ca_{1/2}$ Ca

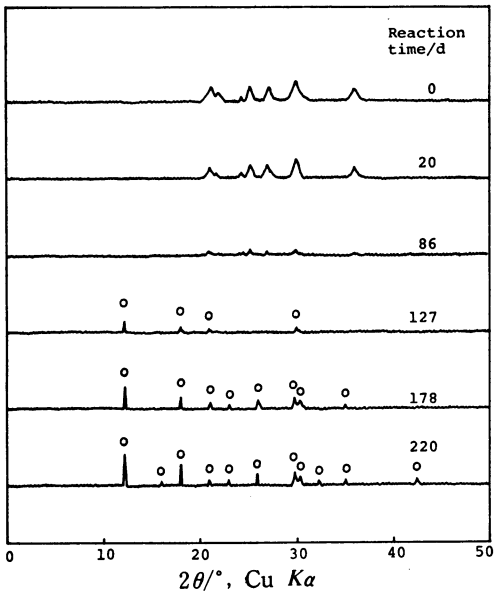



Fig. 2. X-Ray diffraction diagrams of the decomposition products of $Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$ at room temperature.
○: Peaks due to $(NH_4)_2CaP_2O_7 \cdot H_2O$ (ASTM card, No. 22-38).

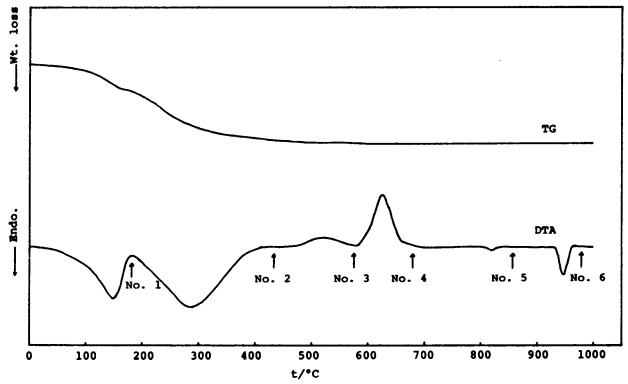



Fig. 3. DTA and TG curves of $Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$.

TABLE 4. WEIGHT LOSS OF THE PRODUCT AND NITROGEN AND WATER CONTENT OF THE THERMAL DECOMPOSITION PRODUCTS

| Sample | Total N(%) | Water(%) | Wt. loss/% |
|---|---|---|---|
| Product | 10.4 | 11.0 | 0 |
| No. 1 | 7.5 | 1.2 | 10.8 |
| No. 2 | 0.8 | — | 23.0 |
| No. 3 | 0.3 | — | 23.4 |
| No. 4 | — | — | 23.7 |

and so on. The X-ray diffraction patterns of the decomposition products are shown in Fig. 2. The intensity of the diffraction peaks decreased with the passage of reaction time and the decomposition product gave very weak peaks at 86 d. Then new peaks appeared and the intensity of the peaks increased with the elapse of time. These new peaks were assigned to diammonium calcium diphosphate monohydrate, $(NH_4)_2CaP_2O_7 \cdot H_2O$ (ASTM card, No. 22-38). The result

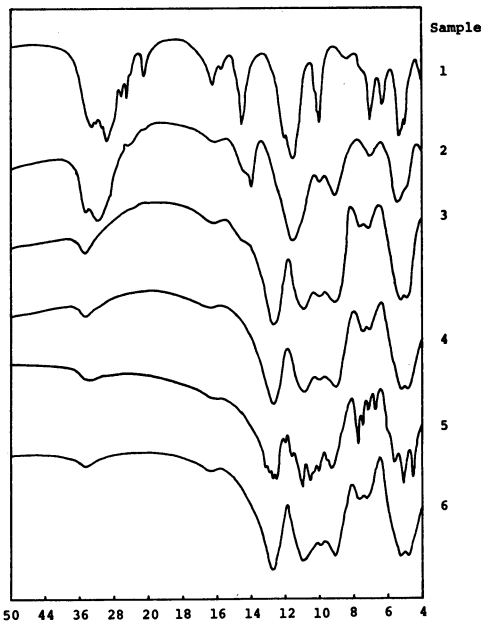



Fig. 4. IR spectra of the thermal decomposition products of $Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$.
1: $Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$, 2: No. 1, 3: No. 2, 4: No. 3, 5: Nos. 4 and 5, 6: No. 6.

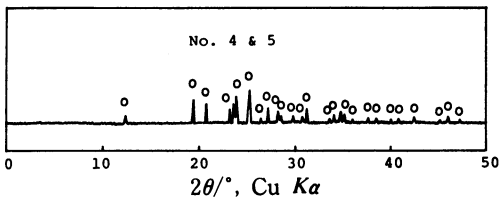



Fig. 5. X-Ray diffraction diagrams of the thermal decomposition products of $Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$.
○: Peaks due to $\beta$-$Ca(PO_3)_2$ (ASTM card, No. 17-500).

agrees with that of Table 1. According to the above results, one can write a decomposition process for calcium bis(hydrogenphosphoramidate)–water (2/3) to diammonium calcium diphosphate monohydrate as follows:

$$Ca(HPO_3NH_2)_2 \cdot 1.5H_2O + 0.5H_2O \longrightarrow (NH_4)_2CaP_2O_7 \cdot H_2O. \quad (4)$$

*DTA and TG.* To study the thermal decomposition of the product, DTA and TG measurements of the product were made with the result shown in Fig. 3. The product decomposes at room temperature, as described above. So the product was used for the analysis immediately after synthesis to prevent the contamination by the decomposition products. The samples as numbered on Fig. 3 were removed from a furnace, cooled in a silica-gel desiccator, and subjected to further analysis. The results are presented in Table 4, and Figs. 4 and 5. As Table 4 shows, the endothermic reaction accompanying weight loss below 170 °C seemed mainly to be due to loss of bound water; the elimination of ammonia from the product was also observed in this

reaction. The sample No. 1 was amorphous and exhibited an IR absorption due to an ammonium ion and a P–O–P linkage. Polyphosphates seemed to be formed in the sample No. 1, but the strong absorption of the antisymmetric stretching of a $(PO_3)^{2-}$ group was also observed at about 1150 $cm^{-1}$ and the absorptions of a $(PO_2)^-$ group ($\nu_{as}$; about 1280 $cm^{-1}$, $\nu_s$; about 1100 $cm^{-1}$) were not observed. Accordingly, the main decomposition product at this point may be diphosphate and the paper-chromatographic data concerning the distribution of phosphates in the decomposition product supported the conclusion. There appeared a broad endothermic peak and a corresponding weight loss between 170 and 430 °C. According to Table 4, the elimination of ammonia caused the weight loss. A broad exothermic peak accompanying a slight amount of weight loss was observed between 470 and 570 °C. IR spectra of Nos. 2 and 3 were very similar to each other and they involved a very small amount of nitrogen. The strong absorptions due to a $(PO_2)^-$ group and a P–O–P linkage appeared, while no obvious absorption of a $(PO_3)^{2-}$ group was observed for these samples. So the decomposition products could be highly polymerized phosphates. The samples of Nos. 2 and 3 were X-ray diffractometrically amorphous. A large exothermic peak was observed between 580 and 660 °C. The sample No. 4 gave X-ray diffraction peaks and these were all assigned to those of β-calcium metaphosphate (ASTM card, No. 17-500). Each IR peak of No. 3 split into a few peaks in the spectra of Nos. 4 and 5. According to Table 4, small difference of chemical composition was observed between the samples of Nos. 3 and 4. Therefore, the exothermic reaction may be due to the crystallization of amorphous calcium metaphosphate to the β-form. A small endothermic peak at around 820 °C may be caused by the melting of a small part of the sample because the sample after the thermal reaction was sintered. The melting of the β-form of calcium metaphosphate gave the last endothermic peak at around 950 °C. According to the above results, the following equation can be written for the overall-thermal decomposition reaction of calcium bis(hydrogenphosphoramidate)–water (2/3):

$$Ca(HPO_3NH_2)_2 \cdot 1.5H_2O \xrightarrow{(heat)} Ca(PO_3)_2 + 2NH_3 + 1.5H_2O. \quad (5)$$

The final weight loss of the product was also very close to the calculated value for the above condensation reaction.

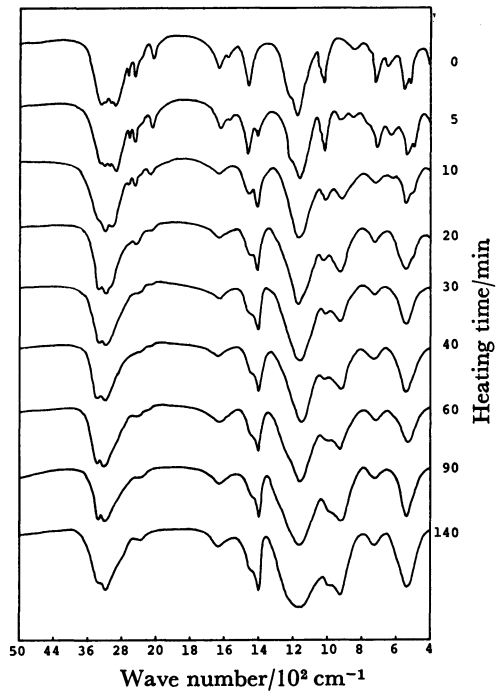



Fig. 6. IR spectra of the thermal decomposition products of $Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$ at 150 °C.

Table 5. Weight loss of the product and nitrogen and water content of the thermal decomposition products at 150 °C in air

| Reaction time/min | Total N(%) | N(%) as $NH_4^+$ | Water (%) | Wt. loss/% |
|---|---|---|---|---|
| 0 | 10.4 | — | 11.0 | — |
| 10 | 8.7 | 4.5 | 3.0 | 7.4 |
| 20 | 7.2 | 4.5 | 1.5 | 9.6 |
| 30 | 6.7 | 4.8 | 1.5 | 10.1 |
| 60 | 5.8 | 4.8 | 1.5 | 11.2 |
| 140 | 5.0 | 4.4 | 1.5 | 12.6 |

Table 6. Distribution of phosphate species in the decomposition products at 150 °C in air

| Reaction time/min | Phosphate/P(%) | | | |
|---|---|---|---|---|
| | Amido and Ortho | Di | Tri | Higher |
| 0 | 100 | — | — | — |
| 5 | 80.1 | 12.8 | 4.4 | 2.7 |
| 10 | 56.6 | 29.5 | 9.3 | 4.6 |
| 20 | 34.3 | 41.9 | 15.4 | 8.3 |
| 30 | 27.1 | 41.4 | 17.8 | 13.7 |
| 60 | 19.9 | 44.6 | 23.0 | 12.5 |
| 140 | 18.3 | 42.4 | 24.7 | 14.6 |

*Decomposition at 150 °C.* To gain further detailed data about the thermal decomposition of the product, an isothermal decomposition at 150 °C was run. As Table 5 shows, an amido group was converted rapidly to an ammonium ion and elimination of the ammonia from the product also took place rapidly. Bound water in the product could not be removed completely at this temperature. The IR spectra of the decomposition products are shown in Fig. 6. The peaks of P–N–H and P–O–H linkages disappeared gradually, and those due to an ammonium ion and a P–O–P linkage appeared with the elapse of reaction time. The absorptions due to a $(PO_2)^-$ group were equivocal, so the amount of phosphates having a P–O–P linkage longer than triphosphate seemed to be small in the decomposition product. As Table 6 shows, the determination of the phosphates contained in the decomposition products supported this conclusion. The main decomposition product was diphosphate. The decomposition products associated with a heating time longer than 20 min were X-ray diffractometrically amorphous. According to the above results, it is not apparent if the formation of a

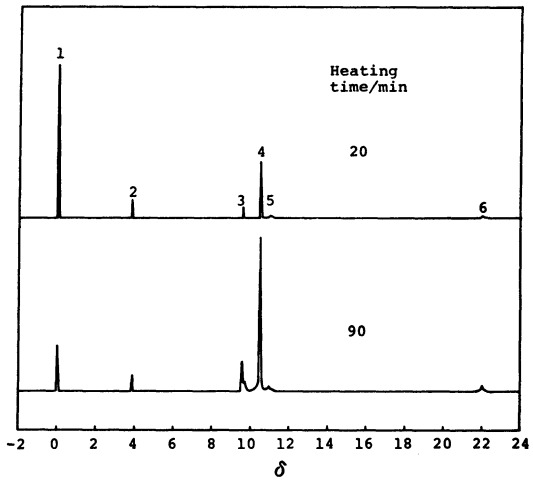



Fig. 7. $^{31}P$ NMR spectra of the decomposition products at 150°C.
1: Orthophosphate, 2: phosphoramidate, 3 and 4: diphosphate, 5: end $PO_4$ group of triphosphate, 6: middle $PO_4$ group of triphosphate.

P–NH–P linkage is proceeded by the elimination of ammonia between P–$NH_2$ linkages as follows:

$$-\overset{|}{\underset{|}{P}}-NH_2 + NH_2-\overset{|}{\underset{|}{P}}- \longrightarrow -\overset{|}{\underset{|}{P}}-NH-\overset{|}{\underset{|}{P}}- + NH_3. \quad (6)$$

The $^{31}P$ NMR spectra of the decomposition products at 20 and 90 min are shown in Fig. 7. No peak of any phosphorus compounds having a P–NH–P linkage was observed in the spectra. It was concluded that calcium bis(hydrogenphosphoramidate)–water (2/3) did not decompose thermally to form imidophosphates. The same decomposition processes as Reactions 1, 2, and 3 may be responsible for the thermal decomposition of the product.

## References

1) "Shin Gitsuken Kagaku Koza," ed by the Chemical Society of Japan, Maruzen, Tokyo (1976), Vol. 8, p. 354.
2) "Bunseki Kagaku Binran," ed by the Japan Society for Analitical Chemistry, Maruzen, Tokyo (1971), pp. 205 and 1492.
3) S. Ohashi, *Kagaku To Kogyo*, **21**, 878 (1968). The $A_2$ and $B_2$ solvents in Table 3 were used.
4) F. Lucena-Conde and L. Prat, *Anal. Chim. Acta*, **16**, 473 (1957).
5) M. Grayson and E. J. Griffith, "Topics in Phosphorus Chemistry," John Wiley and Sons, New York (1969), Vol. 6, p. 235.
6) K. Nakanishi, "Sekigai Kyushu Supekutoru," Nankodo, Tokyo (1960).
7) D. E. C. Corbridge, "Phosphorus," Elsevier, Amsterdam (1980), p. 222.