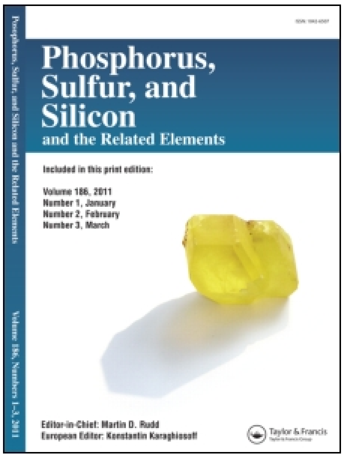

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CONDENSATION AND DECOMPOSITION OF HYDRATED ALKALINE EARTH BIS(HYDROGENPHOSPHORAMIDATES) WITH ACIDS

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CONDENSATION AND DECOMPOSITION OF HYDRATED ALKALINE EARTH BIS(HYDROGENPHOSPHORAMIDATES) WITH ACIDS

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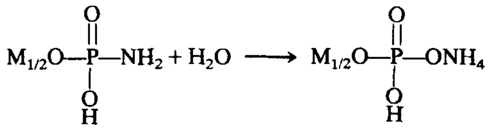
Alkaline earth bis(hydrogenphosphoramidates) were made by the wet process. The phosphoramidates reacted with hydrogen chloride, acetic acid, and oxalic acid to form ortho- and polyphosphates without producing imidopolyphosphates. For the degradation and polymerization, water was considered to play a very important role and the following reaction seemed to be the first step:



$$M_{1/2}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\underset{\displaystyle O}{|}}}{P}}{-}NH_2 + H_2O \longrightarrow M_{1/2}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\underset{\displaystyle O}{|}}}{P}}{-}ONH_4$$

where *M* stands for an alkaline earth cation.

Key words: Phosphoramidate, Condensation, Decomposition, Hydrolysis Phosphorus-Nitrogen Compound, Alkaline Earth, Polyphosphate.

INTRODUCTION

Among the many phosphorus-nitrogen compounds, phosphazenes may be the best known. Many papers about these compounds have been published. There are various types of phosphorus-nitrogen compounds other than phosphazenes, but many of them have not been well established yet or have not been thoroughly studied. The present authors have investigated the syntheses and thermal behavior of phosphates containing amino groups.[1–6] Such phosphorus-nitrogen compounds can be used as a new type of chemical fertilizer having a P–N covalent bond and as flameproofing agents. They can also be employed as starting materials for the preparation of many organic and inorganic phosphorus compounds. This paper describes the chemical reactions of alkaline earth bis(hydrogenphosphoramidates) with hydrogen chloride, acetic acid, and oxalic acid to elucidate the reactivity of the phosphoramidates with acids.

EXPERIMENTAL

Preparation of Hydrogenphosphoramidates

Alkaline earth bis(hydrogenphosphoramidates) other than the strontium salt were made by the methods described in our previous papers.[1,2,6] Strontium bis(hydrogenphosphoramidate),

$Sr(HPO_3NH_2)_2$, was prepared by the following method. Strontium dichloride hexahydrate (10.7 g) was dissolved in 40 cm^3 of water and potassium hydrogenphosphoramidate (10.8 g) was dissolved in 85 cm^3 of water. The solutions were mixed at 5°C to prevent the hydrolysis of the phosphoramidate and the resulting mixture was stirred for about 20 min. During the treatment, the pH of the solution was 6.0–6.5. A white precipitate was filtered off, washed with cold water and ethanol, and then dried at 50°C for 1 day under reduced pressure. The chemical compositions of the phosphoramidates used were $Mg(HPO_3NH_2)_2 \cdot 4H_2O$, $Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$, $Sr(HPO_3NH_2)_2$, and $Ba(HPO_3NH_2)_2 \cdot H_2O$. All the phosphoramidates were crystalline.

Reaction with acids

Hydrogen chloride. Gaseous hydrogen chloride made by adding concentrated hydrochloric acid to concentrated sulphuric acid was dried by passing through concentrated sulphuric acid. The dried HCl gas was introduced to the glass reaction tube containing about 5 g of the hydrogenphosphoramidate. The product was washed quickly with ethanol to remove adsorbed HCl gas on the product. The reaction was run at room temperature.

Acetic acid. About 2 g of the phosphoramidate was put in a mixed solution of 5 cm^3 of acetic acid and 20 cm^3 of chloroform. The mixture was stirred at 25 and 60°C. The solid product was filtered off and washed with ethanol.

Oxalic acid. Oxalic acid (3 g) was dissolved in 10 cm^3 of ethanol and then about 2 g of the phosphoramidate was added in the solution. The mixture was heated at 25 and 60°C with stirring. The solid product was filtered off and washed with ethanol.

Paper Chromatography and Colorimetry of Phosphates

A sample (0.1 g) was dissolved in 10 cm^3 of an aqueous 6%-EDTA(disodium dihydrogen ethylenediaminetetraacetate) solution. The pH of the EDTA solution was adjusted to 9–10, if necessary, with aqueous ammonia. The one-dimensional paper-chromatographic separation and the colorimetric determination of phosphate species in the solution were run by the method described in our previous paper.[1]

Quantitative Analysis of Nitrogen

The amount of total nitrogen and that of an ammonium ion in a sample were measured by the Kjeldahl technique.

X-Ray Diffractometry

An X-ray diffraction pattern of a sample was taken with nickel-filtered Cu Kα radiation using a Rigaku X-ray diffractometer, RAD-1B.

IR Spectrophotometry

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

^{31}P NMR Measurement

A sample was dissolved in an aqueous 6%-EDTA solution (pH 4–6) and the ^{31}P NMR spectrum of the solution was taken by a JNM-GX270 spectrograph. The pH of the sample solution was adjusted to 9–10 with aqueous ammonia and the ^{31}P NMR of the solution was also measured to study the influence of pH on the chemical shift. The solubility of the reaction products of the alkaline earth salts in basic media was higher than that in acidic media. The NMR chemical shifts are reported relative to external 85%-orthophosphoric acid with positive shifts being downfield.

RESULTS AND DISCUSSION

Reaction with Hydrogen Chloride

The observed chemical compositions and X-ray diffraction data of the reaction products are shown in Table I. Phosphoramidate and orthophosphate were not separated by the developing solvents used here. The result shows that the hydrogenphosphoramidates react with hydrogen chloride to produce

TABLE I

Compositions of the reaction products of phosphoramidates with HCl gas

Phosphoramidates	Reaction time (min)	Total N(%)	N(%) as NH_4^+	X-Ray dif.	Phosphates (P%) Amido & Ortho	Di	Tri	Higher
$Mg(HPO_3NH_2)_2 \cdot 4H_2O$	60	9.2	4.6	SM, NH_4Cl	27.6	28.8	16.6	27.0
	180	9.1	5.1	SM, NH_4Cl	27.2	29.7	17.2	25.9
	300	8.9	5.1	SM, NH_4Cl	31.0	30.5	17.0	21.5
$Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$	60	8.9	7.1	NH_4Cl	34.8	37.3	12.4	15.5
	180	8.7	7.1	NH_4Cl	41.1	34.1	13.3	11.5
	300	8.6	7.4	NH_4Cl	45.2	31.3	13.1	10.4
$Sr(HPO_3NH_2)_2$	60	11.0	1.0	SM	77.6	13.7	5.1	3.6
	180	10.1	1.1	SM	81.2	12.1	3.8	2.9
	300	9.7	1.6	SM	82.8	10.4	2.5	4.3
$Ba(HPO_3NH_2)_2 \cdot H_2O$	60	6.9	5.7	NH_4Cl	20.7	48.6	10.9	19.8
	180	7.1	6.1	NH_4Cl	22.9	45.8	13.9	17.4
	300	6.9	6.4	NH_4Cl	23.8	37.2	17.9	21.1

SM stands for starting material.

ortho- and polyphosphates, and at the same time, the amino group is converted to the ammonium ion. The IR spectra of the products in Figure 1 indicate the same result. All the reaction products gave an absorption of NH_4^+ at 1400 cm^{-1} and absorptions due to a P–O–P or a P–N(H)–P linkage at about 900 and 700 cm^{-1}. These data do not give evidence for the existence of a P–N(H)–P linkage in the reaction products. However, information concerning a P–N(H)–P linkage in the products may be obtained from a ^{31}P NMR measurement. The NMR data are presented in Figure 2. The measurements on the magnesium and barium salts were made in basic solution and those on calcium and strontium were performed in acidic solution. A peak for the phosphoramidate appeared at about −3 to −4 ppm in acidic media(pH 4–6) and shifted to +5 to +8 ppm in basic media (pH 9–10). An end-PO_4 group in the acidic solution exhibited peaks at about −9 to −10 ppm, and these peaks shifted to −6 to −8 ppm in the basic solution. A peak for orthophosphate in the acidic solution (about 0 ppm)

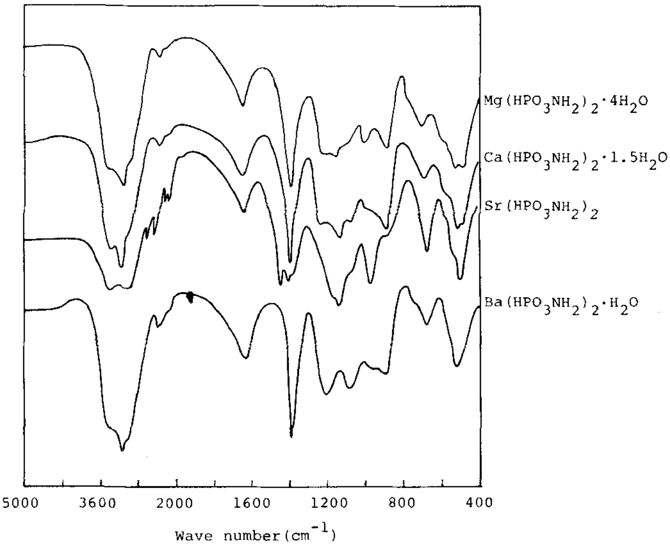


FIGURE 1 IR spectra of the reaction products of phosphoramidates with HCl gas for 1 hr.

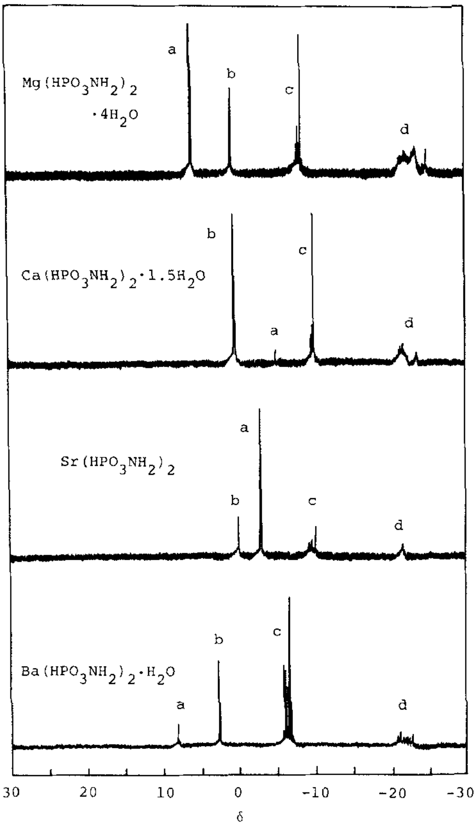
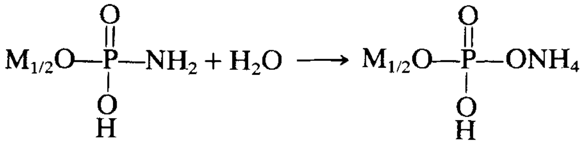


FIGURE 2 ^{31}P NMR spectra of the reaction products of phosphoramidates with HCl gas at room temperature for 1 hr. a: Phosphoramidate, b: orthophosphate, c: end-PO$_4$ group, d: middle-PO$_4$ group.

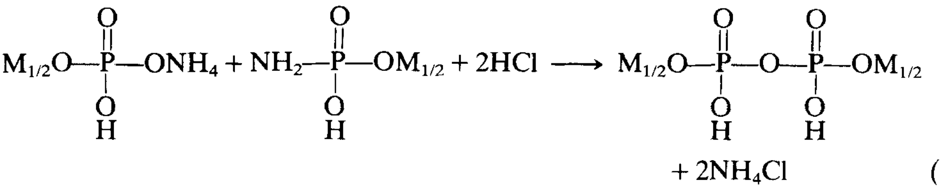
shifted downfield (about +3 ppm) in basic solution. The NMR data of the products did not give evidence that a P-N(H)-P linkage was formed in the reaction. Accordingly, the formation of this linkage with elimination of ammonia by the following reaction was not found to occur in these reaction systems:

$$-\overset{|}{\underset{|}{\mathrm{P}}}-\mathrm{NH_2} + \mathrm{NH_2}-\overset{|}{\underset{|}{\mathrm{P}}}- + \mathrm{HCl} \longrightarrow -\overset{|}{\underset{|}{\mathrm{P}}}-\mathrm{N(H)}-\overset{|}{\underset{|}{\mathrm{P}}}- + \mathrm{NH_4Cl} \qquad (1)$$

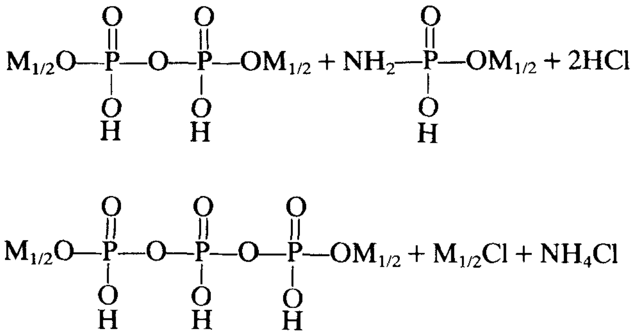
Instead, one can write the processes for the reaction systems:



$$\mathrm{M_{1/2}O}-\overset{\mathrm{O}}{\overset{\|}{\underset{\mathrm{OH}}{\underset{|}{\mathrm{P}}}}}-\mathrm{NH_2} + \mathrm{H_2O} \longrightarrow \mathrm{M_{1/2}O}-\overset{\mathrm{O}}{\overset{\|}{\underset{\mathrm{OH}}{\underset{|}{\mathrm{P}}}}}-\mathrm{ONH_4} \qquad (2)$$

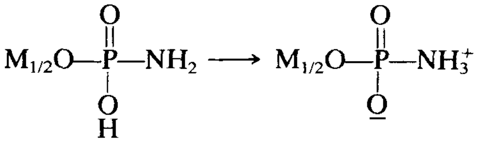


$$\mathrm{M_{1/2}O}-\overset{\mathrm{O}}{\overset{\|}{\underset{\mathrm{OH}}{\underset{|}{\mathrm{P}}}}}-\mathrm{ONH_4} + \mathrm{NH_2}-\overset{\mathrm{O}}{\overset{\|}{\underset{\mathrm{OH}}{\underset{|}{\mathrm{P}}}}}-\mathrm{OM_{1/2}} + 2\mathrm{HCl} \longrightarrow \mathrm{M_{1/2}O}-\overset{\mathrm{O}}{\overset{\|}{\underset{\mathrm{OH}}{\underset{|}{\mathrm{P}}}}}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\underset{\mathrm{OH}}{\underset{|}{\mathrm{P}}}}}-\mathrm{OM_{1/2}} + 2\mathrm{NH_4Cl} \qquad (3)$$



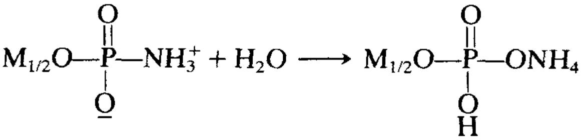
$$\mathrm{M_{1/2}O{-}P(=O)(OH){-}O{-}P(=O)(OH){-}OM_{1/2} + NH_2{-}P(=O)(OH){-}OM_{1/2} + 2HCl \longrightarrow M_{1/2}O{-}P(=O)(OH){-}O{-}P(=O)(OH){-}O{-}P(=O)(OH){-}OM_{1/2} + M_{1/2}Cl + NH_4Cl} \quad (4)$$

where M stands for an alkaline earth metal. Phosphoramidate with an OH group is associated with the formation of a zwitterion:[7]

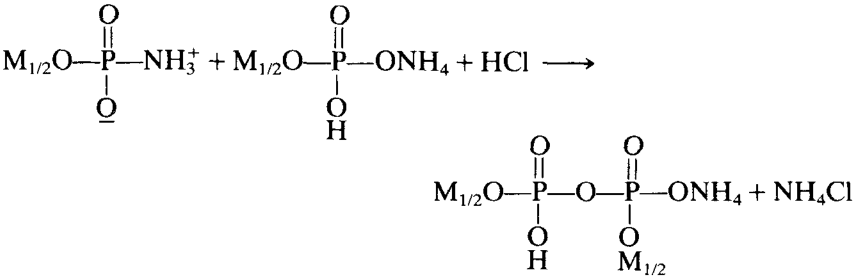


$$\mathrm{M_{1/2}O{-}P(=O)(OH){-}NH_2 \longrightarrow M_{1/2}O{-}P(=O)(O^-){-}NH_3^+} \quad (5)$$

The zwitterion may be very active and can react with water and phosphates to form ortho- and polyphosphates respectively:



$$\mathrm{M_{1/2}O{-}P(=O)(O^-){-}NH_3^+ + H_2O \longrightarrow M_{1/2}O{-}P(=O)(OH){-}ONH_4} \quad (6)$$



$$\mathrm{M_{1/2}O{-}P(=O)(O^-){-}NH_3^+ + M_{1/2}O{-}P(=O)(OH){-}ONH_4 + HCl \longrightarrow M_{1/2}O{-}P(=O)(OH){-}O{-}P(=O)(OM_{1/2}){-}ONH_4 + NH_4Cl} \quad (7)$$

We were unable to obtain any information concerning the formation of this zwitterion. It was difficult to decide which process is reasonable for the reaction systems. The water taking part in the reactions can come from the crystal water of the phosphoramidates and/or a slight amount of water contained in the gas in the reaction systems. As Table I shows, the degradation of polyphosphates to phosphates with shorter chain lengths seemed to occur in the reaction systems. Usually, the degradation of polyphosphates does not take place in a solid state at room temperature. The bound water in the products may be strongly acidic due to dissolution of HCl gas. The hydrolysis of polyphosphates to phosphates with shorter chain lengths is greatly accelerated by protons.[8,9]

Reaction with Acetic Acid

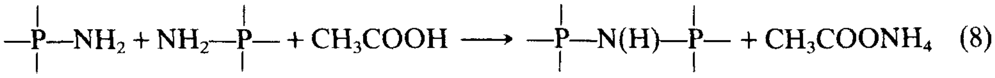
The observed compositions of the reaction products of 60°C are listed in Table II. The reactions of the phosphoramidates showed much slower rates with the similar processes at 25°C. All the phosphoramidates reacted with acetic acid to produce ortho- and polyphosphates. The ^{31}P NMR spectra in Figure 3 indicated the same result. The NMR spectra of the products were taken by dissolving them in the basic 6%-EDTA solution. Phosphoramidate, orthophosphate, and an end-PO$_4$

TABLE II

Compositions of the reaction products of phosphoramidates with acetic acid at 60°C for 25 hr

				Phosphates (P%)				
Phosphoramidates	Total N(%)	N(%) as NH_4^+	X-Ray dif.	Amido & Ortho	Di	Tri		Higher
$Mg(HPO_3NH_2)_2 \cdot 4H_2O$	8.8	1.9	SM	69.1	23.9	5.2		1.8
$Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$	9.3	1.7	SM	78.3	18.4		3.3	
$Sr(HPO_3NH_2)_2$	8.9	1.1	SM	98.7	2.0		1.3	
$Ba(HPO_3NH_2)_2 \cdot H_2O$	7.0	0.7	SM	78.0	16.5	4.7		0.8

group exhibited peaks, respectively, at +7.5 to +8.5, +3.1 to +3.2, and −4.8 to −6.1 ppm in the basic solution (pH 9–10). The reactions of the phosphoramidates with acetic acid were not active and the rate increased with an increase in the content of crystal water. No proof to indicate the presence of imidopolyphosphates in the products was obtained, and the formation of a P–N(H)–P linkage according to the following reaction did not occur in the systems:



$$-P-NH_2 + NH_2-P- + CH_3COOH \longrightarrow -P-N(H)-P- + CH_3COONH_4 \quad (8)$$

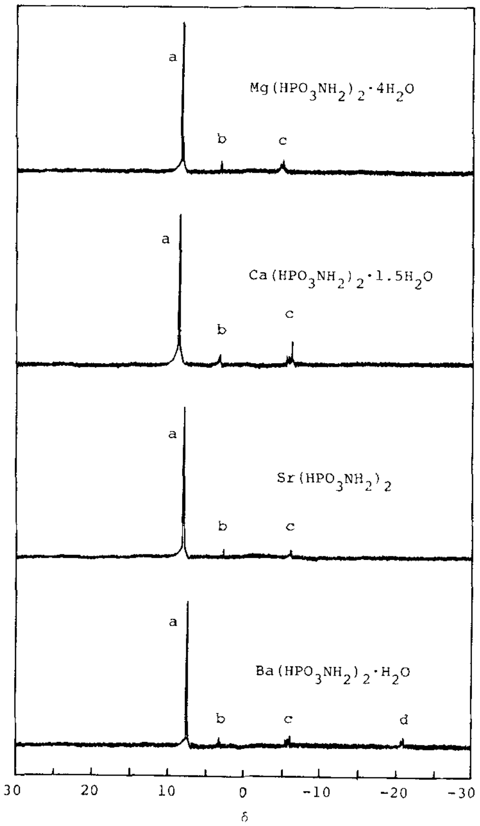
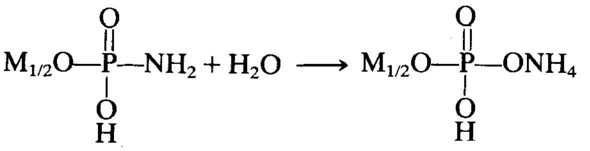
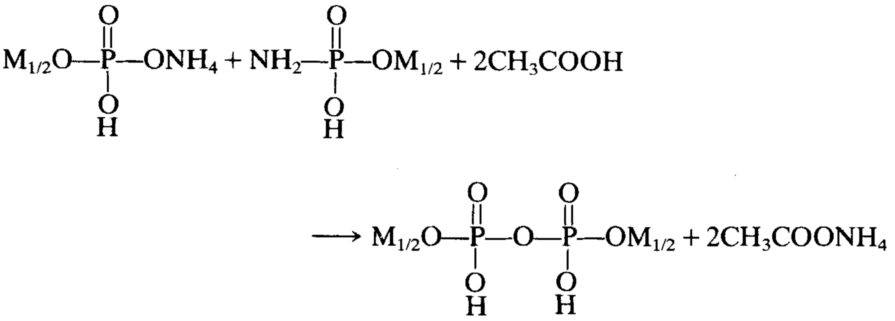


FIGURE 3 ^{31}P NMR spectra of the reaction products of phosphoramidates with acetic acid at 60°C for 25 hr. a: Phosphoramidate, b: orthophosphate, c: end-PO_4 group, d: middle-PO_4 group.

The reaction processes can be written for the systems:

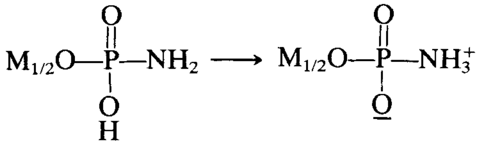


$$M_{1/2}O{-}P(=O)(OH){-}NH_2 + H_2O \longrightarrow M_{1/2}O{-}P(=O)(OH){-}ONH_4 \qquad (9)$$

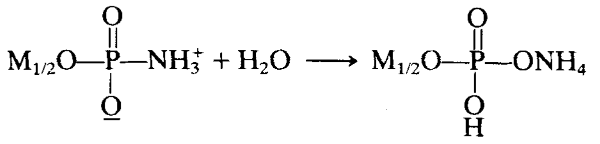


$$M_{1/2}O{-}P(=O)(OH){-}ONH_4 + NH_2{-}P(=O)(OH){-}OM_{1/2} + 2CH_3COOH \longrightarrow M_{1/2}O{-}P(=O)(OH){-}O{-}P(=O)(OH){-}OM_{1/2} + 2CH_3COONH_4 \qquad (10)$$

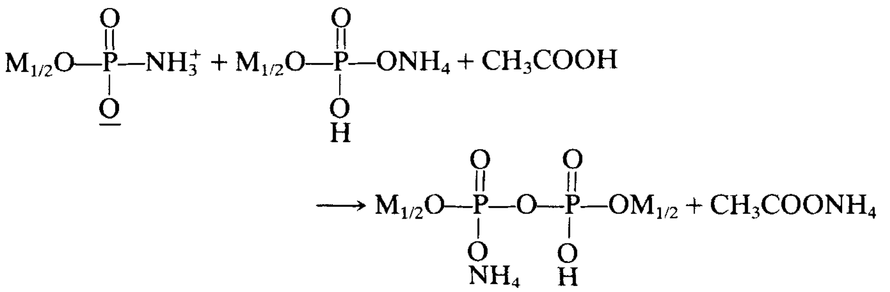
or



$$M_{1/2}O{-}P(=O)(OH){-}NH_2 \longrightarrow M_{1/2}O{-}P(=O)(O^-){-}NH_3^+ \qquad (11)$$



$$M_{1/2}O{-}P(=O)(O^-){-}NH_3^+ + H_2O \longrightarrow M_{1/2}O{-}P(=O)(OH){-}ONH_4 \qquad (12)$$



$$M_{1/2}O{-}P(=O)(O^-){-}NH_3^+ + M_{1/2}O{-}P(=O)(OH){-}ONH_4 + CH_3COOH \longrightarrow M_{1/2}O{-}P(=O)(ONH_4){-}O{-}P(=O)(OH){-}OM_{1/2} + CH_3COONH_4 \qquad (13)$$

Since no analytical data supporting formation of the zwitterion were obtained, it was impossible to decide suitable reaction processes for the reaction systems.

Reaction with Oxalic Acid

The observed chemical compositions and X-ray diffraction data of the reaction products are listed in Table III. ^{31}P NMR spectral data of the products are given in Figure 4. The phosphoramidates produced only ortho- and polyphosphates except for the reaction of $Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$, and the same reaction processes as those of the reaction with acetic acid can be concluded to the reaction systems. In the case of the reaction of the calcium salt, the reaction product gave unknown NMR peaks at +4.5 and −9.8 ppm. The peaks may be attributed to the following reaction products

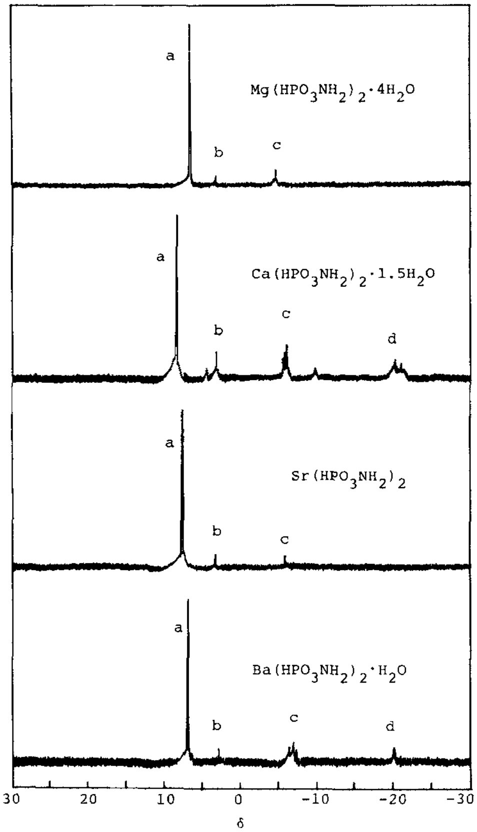


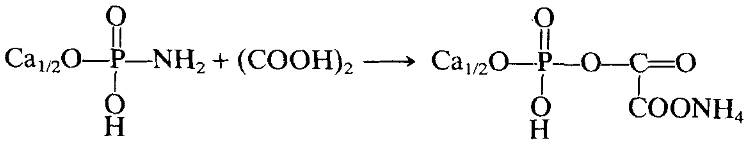
FIGURE 4 ^{31}P NMR spectra of the reaction products of phosphoramidates with oxalic acid at 60°C for 25 hr. a: Phosphoramidate, b: orthophosphate, c: end-PO_4 group, d: middle-PO_4 group.

TABLE III

Compositions of the reaction products of phosphoramidates with oxalic acid at 60°C for 25 hr

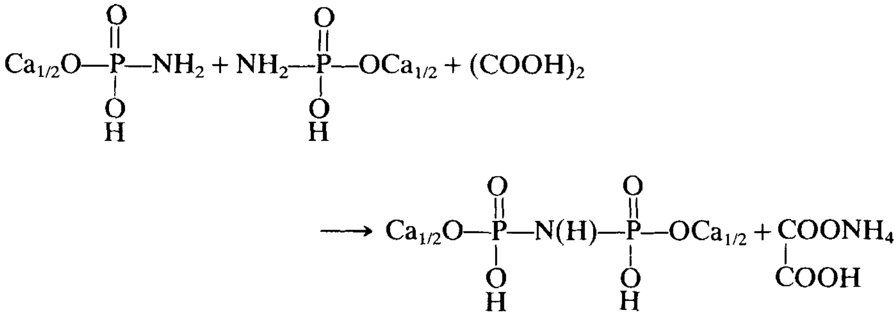
				Phosphates (P%)				
Phosphoramidates	Total N(%)	N(%) as NH_4^+	X-Ray dif.	Amido & Ortho	Di	Tri		Higher
$Mg(HPO_3NH_2)_2 \cdot 4H_2O$	9.8	1.4	SM	78.8	16.2	4.3		0.7
$Ca(HPO_3NH_2)_2 \cdot 1.5H_2O$	8.3	2.2	SM	61.0	19.0	13.3		6.7
$Sr(HPO_3NH_2)_2$	8.6	1.3	SM	82.1	9.8		8.1	
$Ba(HPO_3NH_2)_2 \cdot H_2O$	7.3	0.9	SM	78.4	15.3	3.3		3.0

respectively:



$$\mathrm{Ca_{1/2}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\overset{|}{O}}}{P}}{-}NH_2 + (COOH)_2 \longrightarrow Ca_{1/2}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\overset{|}{O}}}{P}}{-}O{-}\underset{\underset{\displaystyle COONH_4}{|}}{C}{=}O} \qquad (14)$$

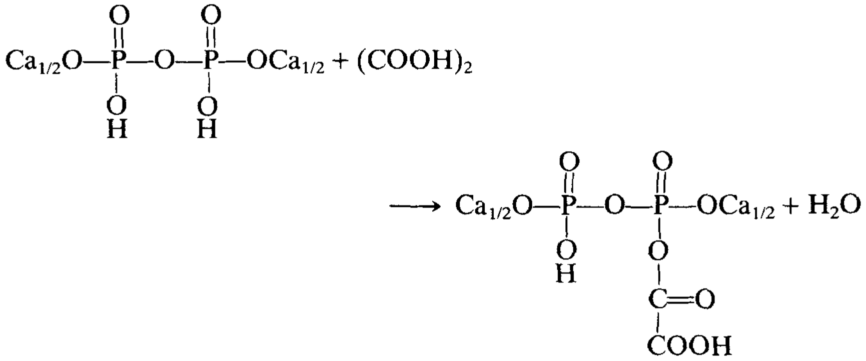
or



$$\mathrm{Ca_{1/2}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\overset{|}{O}}}{P}}{-}NH_2 + NH_2{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\overset{|}{O}}}{P}}{-}OCa_{1/2} + (COOH)_2}$$

$$\mathrm{\longrightarrow Ca_{1/2}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\overset{|}{O}}}{P}}{-}N(H){-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\overset{|}{O}}}{P}}{-}OCa_{1/2} + \underset{\underset{\displaystyle COOH}{|}}{COONH_4}} \qquad (15)$$

and



$$\mathrm{Ca_{1/2}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\overset{|}{O}}}{P}}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\overset{|}{O}}}{P}}{-}OCa_{1/2} + (COOH)_2}$$

$$\mathrm{\longrightarrow Ca_{1/2}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\overset{|}{O}}}{P}}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\underset{\underset{\displaystyle COOH}{|}}{C=O}}{|}}{\underset{|}{\underset{\displaystyle O}{P}}}}{-}OCa_{1/2} + H_2O} \qquad (16)$$

The reaction rates of the processes were very slow.

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