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The Condensation and Decomposition of Alkaline Earth and Phenyl Phosphoramidates with Acids

Shoji Sato, Takao Takayanagi, and Makoto Watanabe*
Department of Industrial Chemistry, Chubu University, Matsumoto-cho, Kasugai, Aichi 487
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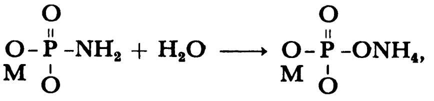
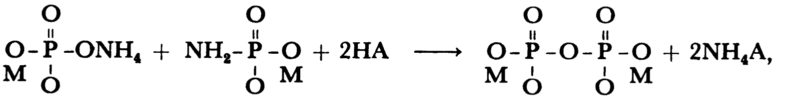
Alkaline earth and phenyl phosphoramidates were reacted with dried hydrogen chloride, acetic acid, and oxalic acid. The alkaline earth phosphoramidates other than the magnesium salt reacted with the acids to produce ortho- and polyphosphates, but did not react with them to make polyphosphates containing imino groups. The hydrolysis of the phosphoramidates to orthophosphate has been considered to be the initiation of the production of polyphosphates:



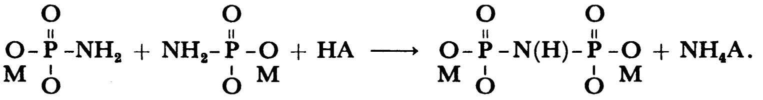
$$\underset{\mathrm{M}}{\mathrm{O}}-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}-\mathrm{NH_2}+\mathrm{H_2O}\longrightarrow\underset{\mathrm{M}}{\mathrm{O}}-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}-\mathrm{ONH_4},$$

where M stands for an alkaline earth metal ion. The formation of polyphosphates can be explained, for example, by this equation:



$$\underset{\mathrm{M}}{\mathrm{O}}-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}-\mathrm{ONH_4}+\mathrm{NH_2}-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}-\underset{\mathrm{M}}{\mathrm{O}}+2\mathrm{HA}\longrightarrow\underset{\mathrm{M}}{\mathrm{O}}-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}-\mathrm{O}-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}-\underset{\mathrm{M}}{\mathrm{O}}+2\mathrm{NH_4A},$$

where HA stands for acid. Magnesium phosphoramidate reacted with acetic acid and oxalic acid to produce orthophosphate, polyphosphates, and imidodiphosphate. The production of the imidodiphosphate can be indicated by the following equation:



$$\underset{\mathrm{M}}{\mathrm{O}}-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}-\mathrm{NH_2}+\mathrm{NH_2}-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}-\underset{\mathrm{M}}{\mathrm{O}}+\mathrm{HA}\longrightarrow\underset{\mathrm{M}}{\mathrm{O}}-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}-\mathrm{N(H)}-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{P}}}-\underset{\mathrm{M}}{\mathrm{O}}+\mathrm{NH_4A}.$$

There are many types of phosphorus-nitrogen compounds. Phosphazenes are the best-known and the most intensively investigated compounds because they can be used as inorganic rubber and have been thought to have widely varying applications in industry. Other phosphorus-nitrogen compounds have not yet been well-studied, however. Phosphoramidates can be used as a new type of chemical fertilizer, for they have a P–N covalent bond, and as flame-proof materials. They can also be used as starting materials for the preparation of many organic and inorganic phosphorus compounds. The present authors have previously reported the syntheses and thermal behavior of some phosphoramidates.[1–6] The phosphoramidates produced ortho- and polyphosphates and did not make polyphosphates containing imino groups when they were heated in air at a moderately high temperature (100—1000 °C). An amino group on phosphoramidates was, accordingly, thermally unstable in air, and it was impossible to make imidodiphosphate from phosphoramidates by thermal condensation. Therefore, in this work, the chemical reactions of alkaline earth and phenyl phosphoramidates with hydrogen chloride, acetic acid, and oxalic acid have been done in order to study the condensation and decomposition of the amino groups in the phosphoramidates.

Experimental

Preparation of Phosphoramidates. The phenyl phosphoramidate and potassium hydrogenphosphoramidate were prepared by the method described in Ref. 7. The alkaline earth phosphoramidates other than strontium phosphoramidate were prepared by wet processes.[3,4,6] The strontium phosphoramidate dihydrate, $SrPO_3NH_2\cdot 2H_2O$, was prepared by this method: Strontium dichloride hexahydrate (5.4 g) was dissolved in 120 cm^3 of water, and the pH of the solution was adjusted to 10.5 with aqueous ammonia. Potassium hydrogenphosphoramidate (5.4 g) was dissolved in 400 cm^3 of water. The solutions were mixed by stirring at 5 °C, and a precipitate was filtered off. Acetone was added to the filtrate, and a white precipitate was filtered off, washed with 50 vol% aqueous ethanol and acetone, and then dried in air at room temperature (15—25 °C).

Reaction of Phosphoramidates with Hydrogen Chloride. About 3—5 g of a phosphoramidate sample was put in a reaction glass tube. Dried hydrogen chloride, which had been prepared by adding concentrated hydrochloric acid to concentrated sulfuric acid and by then passing the resulting gas through concentrated sulfuric acid, was introduced into the reaction tube. The reaction product was washed quickly with ethanol to remove the HCl gas adsorbed on the product.

Reaction of Phosphoramidates with Acetic Acid. About 2 g of a phosphoramidate sample was placed in a mixed solution of 5 cm^3 of acetic acid and 20 cm^3 of chloroform. The resulting mixture was heated at 25 and 60 °C while being stirred. The solid product was filtered off and washed with ethanol. The phenyl phosphoramidate dissolved in a solution of acetic acid. After the reaction, water was added to the reaction mixture; a white precipitate was filtered off and subjected to further analysis.

Reaction of Phosphoramidates with Oxalic Acid. Oxalic acid (3 g) was dissolved in 100 cm^3 of ethanol, after which about 2 g of phosphoramidate was added to the solution. The mixture was heated at 25 and 60 °C while being stirred. The product was treated in the same way as in the reaction with acetic acid.

Quantitative Analysis of Nitrogen. The amount of total nitrogen and that of ammonium ions in a sample were measured by the Kjeldahl technique.

Paper Chromatography and Colorimetry of Phosphates. A sample (0.1 g) was dissolved in a 6% EDTA (disodium dihydrogen ethylenediaminetetraacetate dihydrate) solution by adjusting the pH of the solution to 9—10. The paper-chromatographic separation and the colorimetric determination of the phosphate species in the solution were performed by the method described in our previous paper.[1)]

HPLC Technique. The HPLC system which was developed by Yoza was employed to achieve the separation and determination of phosphate species in a sample.[8)] A separation column (2.6 mm×500 mm) with TSK-GEL (SAX-F0011), a Shimadzu spectrophotometer (UV-110-02), and the KCl eluents of 0.20 and 0.40 mol dm^{-3} were used to separate and determine the phosphate species in the sample solution. About 10 mg of the reaction product was dissolved in water or a 6% EDTA solution, and 200 mm^3 of the solution was injected into the column.

X-Ray Diffractometry. An X-ray diffraction diagram of a sample was taken with nickel-filtered Cu $K\alpha$ 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. The reaction products of alkaline earth phosphoramidates and that of phenyl phosphoramidate were dissolved in a 6% EDTA solution and ethanol respectively. The ^{31}P NMR spectra of the sample solutions were taken by means of a JNM-GX270 spectrograph. The chemical shifts are reported relative to external 85%-orthophosphoric acid, with the positive shifts being downfield.

Results and Discussion

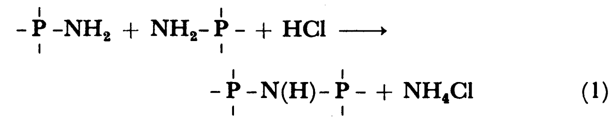
Reaction with Hydrogen Chloride. The contents of nitrogen and phosphate species in the reaction products are presented in Table 1, along with the X-ray-diffraction data. The paper-chromatographic separation between phosphoramidate and orthophosphate could not be achieved with the developing solvents employed in this experiment. According to the results shown in Table 1, alkaline earth phosphoramidate reacted with HCl gas to produce ortho- and polyphosphates. The amino groups of the phosphoramidates were converted to ammonia at the same time. The IR spectra of the products in Fig. 1 indicate the absorption of NH_4^+ at 1400 cm^{-1} and those of the P–O–P and/or P–N(H)–P linkages at about 900 and 700 cm^{-1} respectively. The IR data agree well with those in Table 1. The polyphosphates formed by the reaction of strontium phosphoramidate with HCl gas degraded to phosphates with shorter chain lengths with the passage of the reaction time. The data in Table 1 and Fig. 1 do not provide any information about the formation of a P–N(H)–P linkage in the products. The ^{31}P NMR spectra of the products of alkaline earth phosphoramidates gave peaks due to phosphoramidate, orthophosphate, and polyphosphates; they are shown

Table 1. Compositions of the Reaction Products of Phosphoramidates with HCl Gas

Phosphoramidate	Reaction time/min	Total N/%	N/% as NH_4^+	X-Ray dif.	Phosphate (P%)			
					Amido and Ortho	Di	Tri	Higher
$MgPO_3NH_2\cdot7H_2O$	60	5.5	4.0	NH_4Cl, UK	41.5	31.1	20.1	7.3
	180	5.1	4.5	NH_4Cl, UK	44.3	49.4	6.2	
	300	4.9	4.8	NH_4Cl, UK	41.3	47.5	5.5	5.7
$CaPO_3NH_2\cdot H_2O$	60	6.6	3.3	NH_4Cl, UK	59.3	19.5	8.8	12.4
	180	5.9	4.3	NH_4Cl, UK	57.3	18.0	12.6	12.1
	300	5.7	5.4	NH_4Cl, UK	57.1	18.3	13.5	11.1
$SrPO_3NH_2\cdot2H_2O$	60	3.9	3.1	NH_4Cl, UK	45.3	23.5	18.2	13.0
	180	3.4	3.3	NH_4Cl, UK	68.4	15.5	9.8	6.3
	300	4.0	4.0	NH_4Cl, UK	93.9	6.1	—	—
$BaPO_3NH_2\cdot H_2O$	60	4.6	1.8	SM, UK	50.9	38.6	10.5	
	180	4.5	3.8	UK	63.8	26.6	9.6	
	300	4.0	3.0	UK	47.6	34.3	18.1	
$PONH_2(OC_6H_5)_2$	60	5.6	—	SM	100	—	—	—
	180	5.6	—	SM	100	—	—	—
	300	5.6	—	SM	100	—	—	—

SM and UK stand for the starting material and an unknown substance respectively.

in Fig. 2. The peaks of phosphoramidate (−3—−6 ppm) and an end-PO_4 group (−9—−11 ppm) in an acidic solution shifted to +7—+9 ppm and −4—−6 ppm respectively in a basic solution. The NMR data did not give any peak of a compound with a P–N(H)–P linkage. The reaction of alkaline earth phosphoramidates with HCl did not exhibit the following process:



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

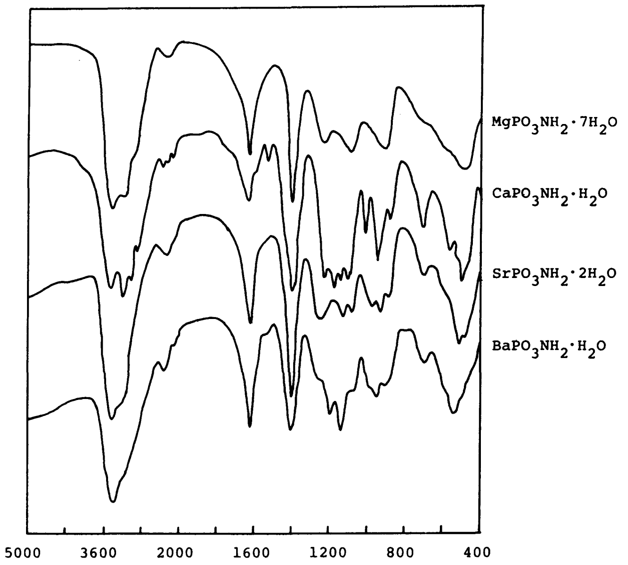


Fig. 1. IR spectra of the reaction products of phosphoramidates with HCl gas for 1 h.

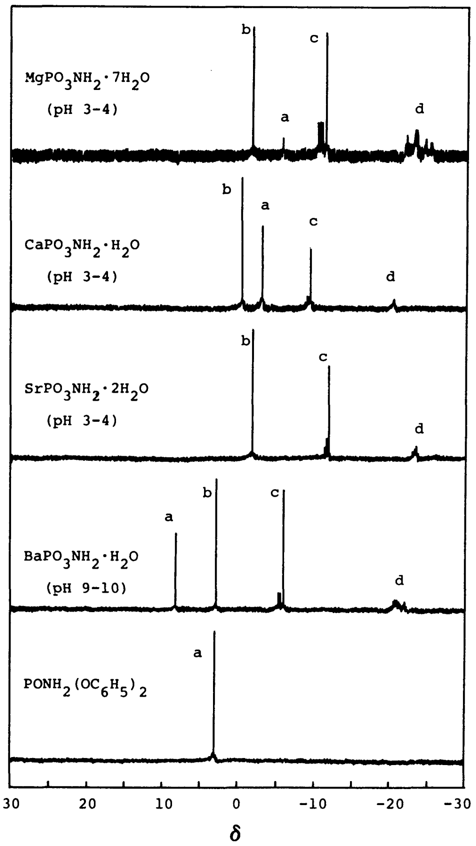
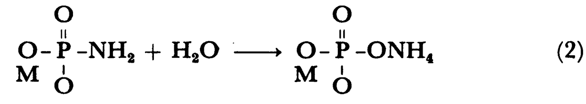
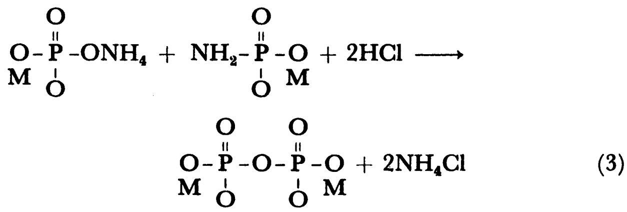


Fig. 2. ^{31}P NMR spectra of the reaction products of phosphoramidates with HCl.
a: Phosphoramidate, b: orthophosphate, c: end-PO_4 group, d: middle-PO_4 group.

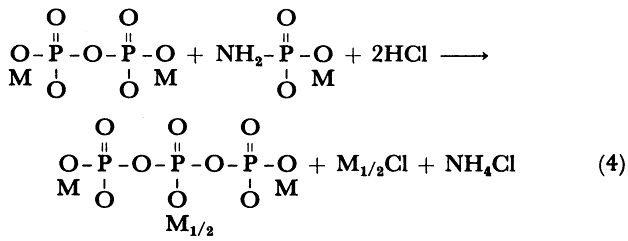
Instead, the processes can be written thus for these reaction systems:



$$\underset{M}{O}-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-NH_2 + H_2O \longrightarrow \underset{M}{O}-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-ONH_4 \qquad (2)$$

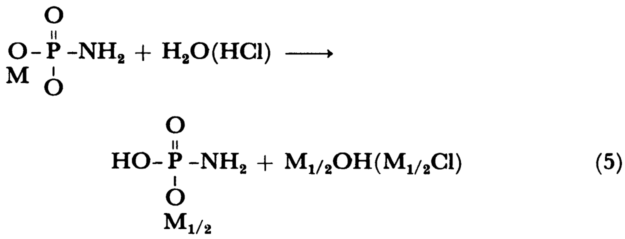


$$\underset{M}{O}-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-ONH_4 + NH_2-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-\underset{M}{O} + 2HCl \longrightarrow \underset{M}{O}-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-\underset{M}{O} + 2NH_4Cl \qquad (3)$$

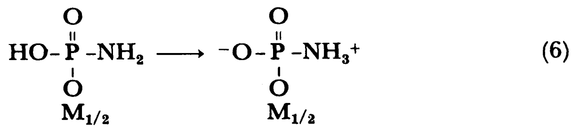


$$\underset{M}{O}-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-\underset{M}{O} + NH_2-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-\underset{M}{O} + 2HCl \longrightarrow \underset{M}{O}-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{\underset{M_{1/2}}{O}}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-\underset{M}{O} + M_{1/2}Cl + NH_4Cl \qquad (4)$$

The phosphoramidate with an OH group was considered to form a zwitterion:[9]

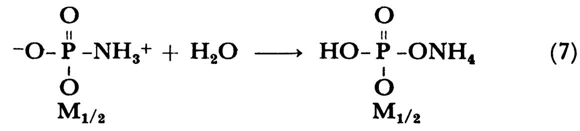


$$\underset{M}{O}-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-NH_2 + H_2O(HCl) \longrightarrow HO-\overset{\overset{O}{\|}}{\underset{\underset{\underset{M_{1/2}}{O}}{|}}{P}}-NH_2 + M_{1/2}OH(M_{1/2}Cl) \qquad (5)$$

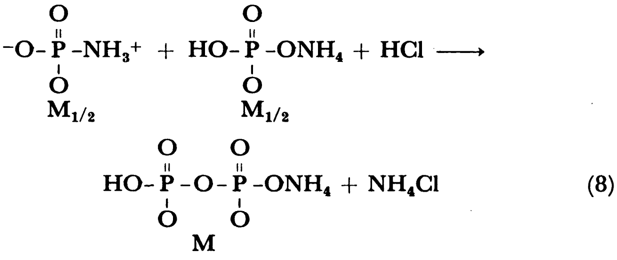


$$HO-\overset{\overset{O}{\|}}{\underset{\underset{\underset{M_{1/2}}{O}}{|}}{P}}-NH_2 \longrightarrow {}^{-}O-\overset{\overset{O}{\|}}{\underset{\underset{\underset{M_{1/2}}{O}}{|}}{P}}-NH_3^{+} \qquad (6)$$

This zwitterion is active and can react with water and phosphates to form ortho- and polyphosphates respectively:



$$^{-}O-\overset{\overset{O}{\|}}{\underset{\underset{\underset{M_{1/2}}{O}}{|}}{P}}-NH_3^{+} + H_2O \longrightarrow HO-\overset{\overset{O}{\|}}{\underset{\underset{\underset{M_{1/2}}{O}}{|}}{P}}-ONH_4 \qquad (7)$$



$$^{-}O-\overset{\overset{O}{\|}}{\underset{\underset{\underset{M_{1/2}}{O}}{|}}{P}}-NH_3^{+} + HO-\overset{\overset{O}{\|}}{\underset{\underset{\underset{M_{1/2}}{O}}{|}}{P}}-ONH_4 + HCl \longrightarrow HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-\underset{M}{O}-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-ONH_4 + NH_4Cl \qquad (8)$$

It is difficult to get information about the presence of the zwitterion, so it is impossible to determine which process is most reasonable for the reaction system. The water in the reaction is, however, thought to come from the crystal water and/or the adsorbed water of the phosphoramidates and from the slight amount of water in the gas in the reaction systems. It was difficult to remove the adsorbed water and the water in the gas completely. In the reactions of magnesium and strontium phosphoramidates, a degradation of polyphosphates to phosphates with shorter chain lengths was observed. Usually this reaction does not occur in a solid state at room temperature. The water contained in the products may be strongly acidic as a result of the dissolution of the HCl gas. The degradation can be caused by the acidic water. Phenyl phosphoramidate did not react with HCl gas at all.

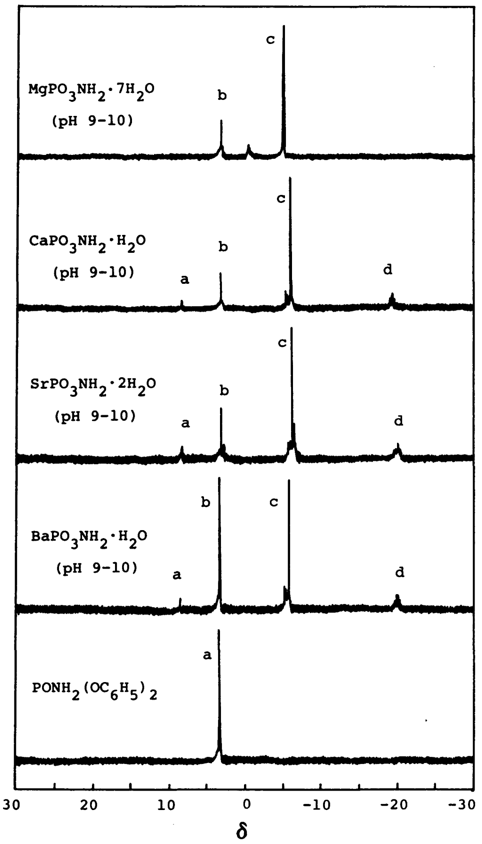
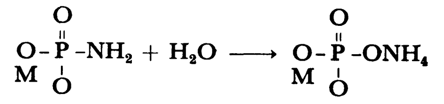
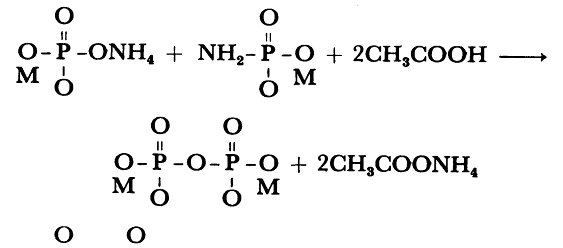


Fig. 3. ^{31}P NMR spectra of the reaction products of phosphoramidates with acetic acid.
a: Phosphoramidate, b: orthophosphate, c: end-PO_4 group, d: middle-PO_4 group.

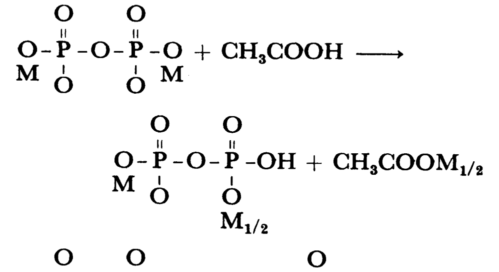
Reaction with Acetic Acid. The chemical compositions and X-ray diffraction data of the products at 60 °C are shown in Table 2. (The data of the reaction products at 25 °C are not listed because the processes at 25 °C are almost the same as those at 60 °C except for the reaction rates.) Alkaline earth phosphoramidates reacted with acetic acid to produce ortho- and polyphosphates. The amino groups in the phosphoramidates seemed to be converted to ammonia at the same time. The total content of nitrogen in the products was small. Phenyl phosphoramidate did not react with acetic acid at all. The ^{31}P NMR spectral data in Fig. 3 indicate that the products of the alkaline earth phosphoramidates give peaks due to phosphoramidate, orthophosphate, and polyphosphates. Accordingly, the following several reaction processes can be written for the reaction systems:



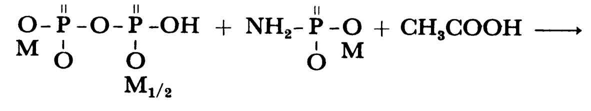
$$\mathrm{O{-}\overset{\overset{O}{\|}}{\underset{\mathrm{M}\ \underset{O}{|}}{P}}{-}NH_2 + H_2O \longrightarrow O{-}\overset{\overset{O}{\|}}{\underset{\mathrm{M}\ \underset{O}{|}}{P}}{-}ONH_4} \qquad (9)$$



$$\mathrm{O{-}\overset{\overset{O}{\|}}{\underset{\mathrm{M}\ \underset{O}{|}}{P}}{-}ONH_4 + NH_2{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}\ \mathrm{M}}{P}}{-}O + 2CH_3COOH \longrightarrow O{-}\overset{\overset{O}{\|}}{\underset{\mathrm{M}\ \underset{O}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}\ \mathrm{M}}{P}}{-}O + 2CH_3COONH_4} \qquad (10)$$



$$\mathrm{O{-}\overset{\overset{O}{\|}}{\underset{\mathrm{M}\ \underset{O}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}\ \mathrm{M}}{P}}{-}O + CH_3COOH \longrightarrow O{-}\overset{\overset{O}{\|}}{\underset{\mathrm{M}\ \underset{O}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{M_{1/2}}{\underset{O}{|}}}{P}}{-}OH + CH_3COOM_{1/2}} \qquad (11)$$

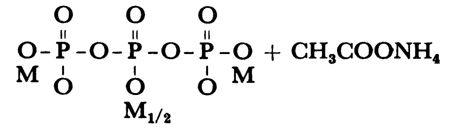


$$\mathrm{O{-}\overset{\overset{O}{\|}}{\underset{\mathrm{M}\ \underset{O}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{M_{1/2}}{\underset{O}{|}}}{P}}{-}OH + NH_2{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}\ \mathrm{M}}{P}}{-}O + CH_3COOH \longrightarrow}$$

Table 2. Compositions of the Reaction Products of Phosphoramidates with Acetic Acid at 60 °C for 25 h

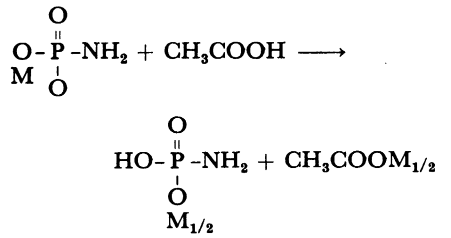
Phosphoramidate	Total N/%	N/% as NH_4^+	X-Ray dif.	Phosphate (P%)			
				Amido and Ortho	Di	Tri	Higher
$MgPO_3NH_2 \cdot 7H_2O$	2.9	2.5	AM	10.2	81.8	5.5	2.5
$CaPO_3NH_2 \cdot H_2O$	2.2	2.1	AM	18.0	64.6	17.4	
$SrPO_3NH_2 \cdot 2H_2O$	1.6	1.4	AM	23.0	60.3	15.9	0.8
$BaPO_3NH_2 \cdot H_2O$	1.9	0.5	UK	34.6	44.5	13.3	7.6
$PONH_2(OC_6H_5)_2$	5.6	—	SM	100	—	—	—

AM stands for an amorphous substance.

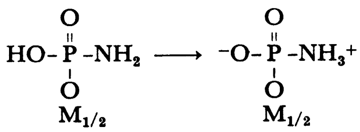


$$\mathrm{\underset{M}{O}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O\,M_{1/2}}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}\underset{M}{O} + CH_3COONH_4} \qquad (12)$$

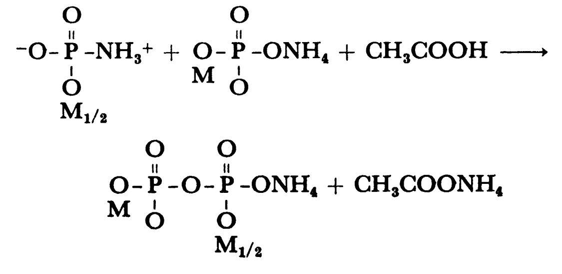
or



$$\mathrm{\underset{M}{O}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}NH_2 + CH_3COOH \longrightarrow HO{-}\overset{\overset{O}{\|}}{\underset{\underset{O\,M_{1/2}}{|}}{P}}{-}NH_2 + CH_3COOM_{1/2}} \qquad (13)$$

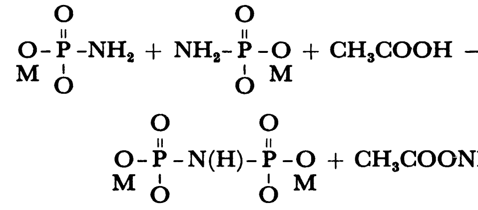


$$\mathrm{HO{-}\overset{\overset{O}{\|}}{\underset{\underset{O\,M_{1/2}}{|}}{P}}{-}NH_2 \longrightarrow {}^{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O\,M_{1/2}}{|}}{P}}{-}NH_3^+}$$



$$\mathrm{{}^{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O\,M_{1/2}}{|}}{P}}{-}NH_3^+ + \underset{M}{O}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}ONH_4 + CH_3COOH \longrightarrow \underset{M}{O}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O\,M_{1/2}}{|}}{P}}{-}ONH_4 + CH_3COONH_4} \qquad (14)$$

The water in the above equation can come from the crystal water and the adsorbed water of the phosphoramidates. The reaction product of magnesium phosphoramidate showed a small unknown ^{31}P NMR peak at about −0.3 ppm. An HPLC analysis of the product was performed in order to get information about the unknown substance. As Fig. 4 shows, the peak at 10.1 min was identified as that of imidodiphosphate. It was, therefore, concluded that magnesium phosphoramidate reacted with HCl to form orthophosphate, polyphosphates, and also imidodiphosphate according to this reaction:



$$\mathrm{\underset{M}{O}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}NH_2 + NH_2{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}\underset{M}{O} + CH_3COOH \longrightarrow \underset{M}{O}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}N(H){-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}\underset{M}{O} + CH_3COONH_4} \qquad (15)$$

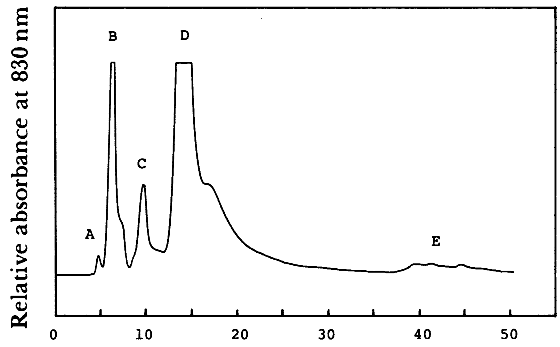
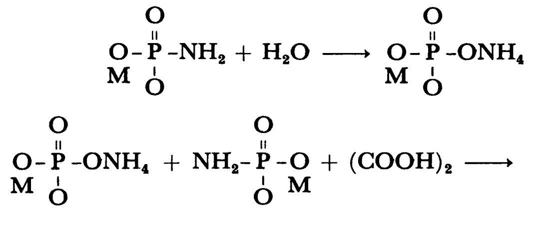


Fig. 4. HPLC profile of the reaction product of magnesium phosphoramidate with acetic acid at 60 °C for 25 h.
A: Phosphoramidate, B: orthophosphate, C: imidodiphosphate, D: diphosphate, E: higher polyphosphates.

Reaction with Oxalic Acid. The chemical compositions and X-ray diffraction data of the products are shown in Table 3, while the ^{31}P NMR spectra of the products are presented in Fig. 5. All the products except for that of the reaction of magnesium phosphoramidate were ortho- and polyphosphates. The ^{31}P NMR spectrum of the reaction product of magnesium phosphoramidate showed unknown peaks at about −0.3 and 2—4 ppm. The HPLC profile in Fig. 6 indicates that the product contains imidodiphosphate (10.3 min). Therefore, the unknown NMR peak at −0.3 ppm was concluded to be due to imidodiphosphate. The other NMR peaks at 2—4 ppm were thought to be caused by the polyphosphates containing a P–N(H)–P linkage, for the phosphates having a structure associated with a PO$_4$ group exhibit ^{31}P NMR peaks in a magnetic field higher than that of orthophosphate. Accordingly, one can write the following equation, for example, for the reaction of the phosphoramidates with oxalic acid:



$$\mathrm{\underset{M}{O}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}NH_2 + H_2O \longrightarrow \underset{M}{O}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}ONH_4}$$

$$\mathrm{\underset{M}{O}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}ONH_4 + NH_2{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}{-}\underset{M}{O} + (COOH)_2 \longrightarrow}$$

Table 3. Compositions of the Reaction Products of Phosphoramidates with Oxalic Acid at 60 °C for 25 h

Phosphoramidate	Total N/%	N/% as NH$_4^+$	X-Ray dif.	Phosphate (P%)			
				Amido and Ortho	Di	Tri	Higher
$MgPO_3NH_2 \cdot 7H_2O$	4.1	2.5	UK	42.8	36.8	11.8	8.6
$CaPO_3NH_2 \cdot H_2O$	4.4	3.3	SM, UK	45.2	30.3	24.5	
$SrPO_3NH_2 \cdot 2H_2O$	3.0	2.7	UK	28.2	30.8	41.0	
$BaPO_3NH_2 \cdot H_2O$	4.9	0.3	SM	85.7	10.4	3.9	
$PONH_2(OC_6H_5)_2$	5.6	—	SM	100	—	—	—

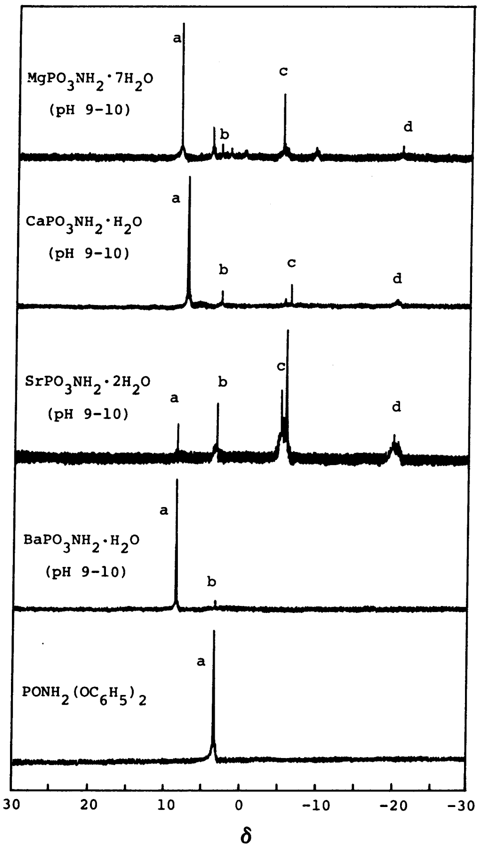
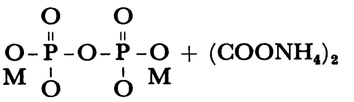
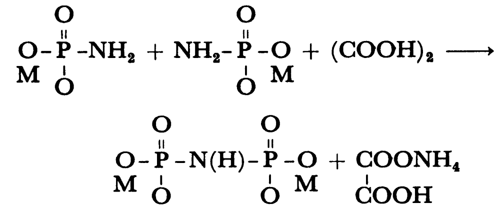


Fig. 5. ^{31}P NMR spectra of the reaction products of phosphoramidates with oxalic acid.
a: Phosphoramidate, b: orthophosphate, c: end-PO$_4$ group, d: middle-PO$_4$ group.



$$\mathrm{\underset{M}{O}-\overset{O}{\underset{O}{P}}-O-\overset{O}{\underset{O}{P}}-\underset{M}{O} + (COONH_4)_2} \qquad (16)$$

This condensation can also be written for magnesium phosphoramidate as:



$$\mathrm{\underset{M}{O}-\overset{O}{\underset{O}{P}}-NH_2 + NH_2-\overset{O}{\underset{O}{P}}-\underset{M}{O} + (COOH)_2 \longrightarrow}$$

$$\mathrm{\underset{M}{O}-\overset{O}{\underset{O}{P}}-N(H)-\overset{O}{\underset{O}{P}}-\underset{M}{O} + \underset{COOH}{COONH_4}} \qquad (17)$$

The reaction rate of the phosphoramidates with oxalic acid seemed to be slower than that with acetic acid, because the amounts of unreacted phosphoramidates in the reaction products with oxalic acid were larger than those with acetic acid.

Conclusion

Alkaline earth phosphoramidates other than magnesium salt reacted with hydrogen chloride, acetic acid, and oxalic acid to produce ortho- and polyphosphates. Magnesium phosphoramidate also produced ortho- and polyphosphates when it was reacted with hydrogen chloride, while the magnesium phosphoramidate reacted with acetic acid and oxalic acid to make orthophosphate, polyphosphates, and imidodiphosphate. The amount of the imidophosphate was small. Therefore, an amino group on alkaline earth phosphoramidates was unstable in these reaction systems and was decomposed to an ammonium ion. It seemed to be difficult to make imidodiphosphate by the chemical condensation of the phosphoramidates with the acids. Phenyl phosphoramidate was very stable and did not react with these acids at all.

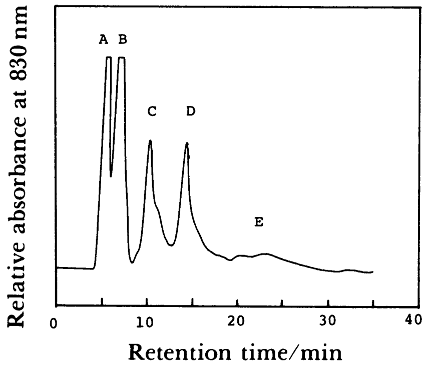


Fig. 6. HPLC profile of the reaction product of magnesium phosphoramidate with oxalic acid at 60 °C for 25 h.
A: Phosphoramidate, B: orthophosphate, C: imidodiphosphate D: diphosphate, E: higher polyphosphates.

References

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

2) M. Watanabe, T. Inagaki, Y. Morii, and T. Yamada, *Setsuko To Setsukai*, **184**, 111 (1983).

3) M. Watanabe, Y. Morii, and S. Sato, *Bull. Chem. Soc. Jpn.*, **57**, 2087 (1984).

4) M. Watanabe, Y. Morii, and S. Sato, *Bull. Chem. Soc. Jpn.*, **57**, 2914 (1984).

5) S. Sato, M. Watanabe, and T. Yamada, *Setsuko To Setsukai*, **199**, 357 (1985).

6) S. Sato and M. Watanabe, *Bull. Chem. Soc. Jpn.*, **58**, 3513 (1985).

7) A. H. Herzog and M. L. Nielsen, *Anal. Chem.*, **30**, 1490 (1958), and the references cited therein.

8) Presented at the 4th symposium of Inorganic Phosphorus Chemistry, Nagoya, November 1983.

9) D. E. C. Corbridge, "Phosphorus," Elsevier, Amsterdam (1980), p. 222.