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The Synthesis and Chemical Reaction of Magnesium and Calcium Bis(phosphorodiamidates) with Acids

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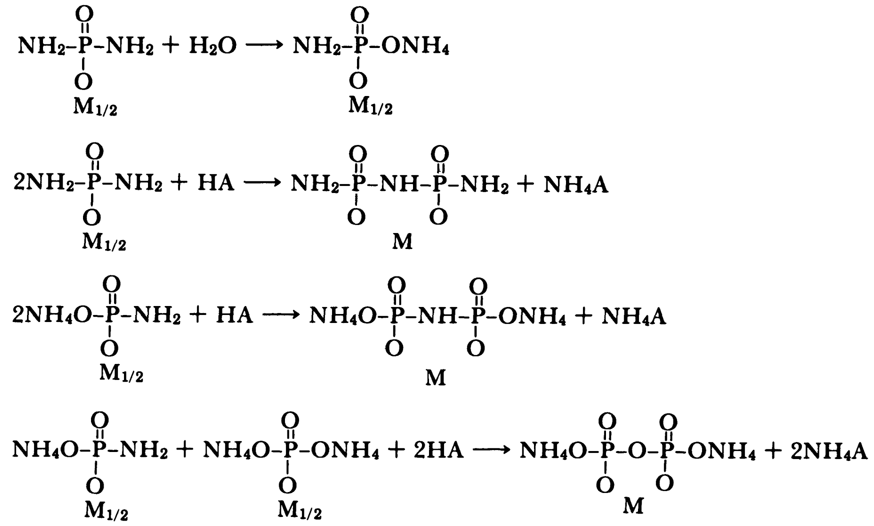
Magnesium bis(phosphorodiamidate) hexahydrate and calcium bis(phosphorodiamidate) dihydrate were made by adding an aqueous solution of magnesium chloride or calcium chloride to a sodium phosphorodiamidate solution. These phosphorodiamidates reacted with the water of crystallization and/or adsorbed water to produce phosphoramidate and orthophosphate. They also reacted with HCl gas, acetic acid, and oxalic acid to make polyphosphates and phosphates with amino and/or imino groups. Several typical reactions are as follows:



$$\mathrm{NH_2\text{-}\underset{\underset{M_{1/2}}{O}}{\overset{O}{P}}\text{-}NH_2 + H_2O \longrightarrow NH_2\text{-}\underset{\underset{M_{1/2}}{O}}{\overset{O}{P}}\text{-}ONH_4}$$

$$\mathrm{2NH_2\text{-}\underset{\underset{M_{1/2}}{O}}{\overset{O}{P}}\text{-}NH_2 + HA \longrightarrow \underset{M}{NH_2\text{-}\underset{O}{\overset{O}{P}}\text{-}NH\text{-}\underset{O}{\overset{O}{P}}\text{-}NH_2} + NH_4A}$$

$$\mathrm{2NH_4O\text{-}\underset{\underset{M_{1/2}}{O}}{\overset{O}{P}}\text{-}NH_2 + HA \longrightarrow \underset{M}{NH_4O\text{-}\underset{O}{\overset{O}{P}}\text{-}NH\text{-}\underset{O}{\overset{O}{P}}\text{-}ONH_4} + NH_4A}$$

$$\mathrm{NH_4O\text{-}\underset{\underset{M_{1/2}}{O}}{\overset{O}{P}}\text{-}NH_2 + NH_4O\text{-}\underset{\underset{M_{1/2}}{O}}{\overset{O}{P}}\text{-}ONH_4 + 2HA \longrightarrow \underset{M}{NH_4O\text{-}\underset{O}{\overset{O}{P}}\text{-}O\text{-}\underset{O}{\overset{O}{P}}\text{-}ONH_4} + 2NH_4A}$$

where M and HA stand for alkaline earth metal and acid respectively.

There are many kinds of phosphorus-nitrogen compounds. Among these compounds, the phosphazenes may be the best known and the most intesively studied ones. These compounds have attracted much attention from the theoretical, synthetic, mechanistic, and technological points of view.[1)] There are a series of phosphorus-nitrogen compounds which have amino groups on a phosphorus atom. These compounds can be used as fertilizers, flame retarders, and starting materials for the preparation of organic and inorganic phosphorus compounds.[2)] The present authors have previously reported the syntheses and thermal behavior of several phosphoramidates.[3—8)] When the phosphoramidates were heated in air at a moderately high temperature (100—1000 °C), they mainly produced ortho- and polyphosphates, although a small amount of polyphosphates containing imino groups was also formed. The present authors also studied the synthesis and thermal behavior of sodium phosphorodiamidate.[9)] The phosphorodiamidate was finally converted to sodium metaphosphate when it was heated in air above 300 °C. An amino group on these phosphoramidates was, accordingly, thermally unstable in air, and it was difficult to prepare phosphates containing imino groups from phosphoramidates by means of thermal condensation. The chemical reactions of alkaline earth bis(phosphorodiamidates) with hydrogen chloride, acetic acid, and oxalic acid have now been carried out in order to study the condensation and decomposition of the amino groups in the phosphorodiamidates.

Experimental

Preparation of Phosphorodiamidates. Sodium phosphorodiamidate pentahydrate was made by the method described in our previous paper.[9)] The phosphorodiamidate (20.8 g) was dissolved in 100 cm^3 of water, and then 100 cm^3 of a 0.5-mol dm^{-3} solution of magnesium chloride or calcium chloride was added. Acetone (500 cm^3) was put into the resulting mixed solution, and a white precipitate was filtered off. The product was dissolved in 150 cm^3 of water, and the residue was removed by filtration. The product was recrystallized by adding 300 cm^3 of acetone to the solution. The recrystallized product was filtered off, washed with 75 Vol%-aqueous acetone, and then dried in a silica-gel desiccator at room temperature for several days.

Reaction of Phosphorodiamidates with Hydrogen Chloride. About 3—4 g of a phosphorodiamidate sample was placed in a reaction glass tube. The air in the tube was replaced with dried nitrogen gas. 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 Phosphorodiamidates with Acetic Acid. Magnesium phosphorodiamidate (5 g) or calcium phosphorodiamidate (4 g) was placed in a mixed solution of 2 cm^3 of acetic acid and 20 cm^3 of chloroform. The mixture was then heated at 25 or 60 °C in a water bath while being stirred. The solid product was filtered off and washed with ethanol.

Reaction of Phosphorodiamidates with Oxalic Acid. Phosphorodiamidate (2 g) and oxalic acid (3 g) were added to 100 cm^3 of ethanol. The mixture was then heated at 25 or 60 °C in a water bath, after which the solid product was filtered off and then washed with ethanol.

Chemical Analysis. Alkaline earth cations, phosphorus, and nitrogen in a sample solution were determined by, respectively, the EDTA (disodium dihydrogen ethylenediaminetetraacetate dihydrate) titration method with a BT indicator, Molybdenum Blue colorimetric analysis, and the Kjeldahl technique.

The Paper Chromatography and Colorimetry of Phosphates. A sample (0.1 g) was dissolved in 10 cm^3 of a 6% EDTA solution by adjusting the pH of the solution to 9—10. The paper-chromatographic separation and colorimetric determination of the phosphate species in the solution were carried by the methods described in our previous paper.3) A modified stock solution of a molybdenum(V)–molybdenum(VI) reagent was used.10)

HPLC Technique. The HPLC analysis which was developed by Yoza was employed to separate and determine the phosphate species in a sample.11) A separation column (2.6 mm×500 mm) with TSK-GEL (SAX-F0011), a Shimadzu spectrophotometer (UV-110-02), and KCl eluents (0.20 and 0.40 mol dm^{-3}) were used for the analysis. About 10 mg of a sample was dissolved in 10 cm^3 of 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 powder 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. A sample was dissolved in water or a 6% EDTA solution. The ^{31}P NMR spectrum of the sample solution was taken by means of a JNM-GX 270 spectrograph. The chemical shifts are reported relative to external 85%-orthophosphoric acid, with the positive shifts being downfield.

Results and Discussion

Composition of Phosphorodiamidates. The phosphorodiamidates gave a single ^{31}P NMR peak at +14.4 ppm at pH 9. (The peak shifted to +8.5 ppm at pH 5—4.) Found for magnesium salt: Mg, 7.5; P, 19.7; N, 17.5%. Found for calcium salt: Ca, 15.1; P, 23.5; N, 21.1%. Calcd for $Mg[PO_2(NH_2)_2]_2\cdot 6H_2O$: Mg, 7.5; P, 19.2; N, 17.4%. Calcd for $Ca[PO_2(NH_2)_2]_2\cdot 2H_2O$: Ca, 15.1; P, 23.3; N, 21.1%. Accordingly, the products are magnesium bis(phosphorodiamidate) hexahydrate and calcium bis(phosphorodiamidate) dihydrate. The yields of the products were about 80%. The magnesium phosphorodiamidate was stable below 5 °C, but it gradually decomposed above room temperature (15—25 °C). On the other hand, the calcium phosphorodiamidate was stable at room temperature.

Reaction with Hydrogen Chloride. When hydrogen chloride gas was introduced into the reaction tube, an elevation of the temperature in the tube was observed. The highest temperature was about 50—60 °C. The analytical data of the nitrogen content and the X-ray diffraction analysis of the reaction products are given in Table 1. (Since the paper-chromatographic separation between phosphate species in the products could not be achieved with the developing solvents employed in this experiment, the analytical data of the composition of the products as obtained by paper chromatography are not given in the table.) According to the results shown in the table, the magnesium phosphorodiamidate reacted with HCl gas to produce an ammonium ion. In the case of the reaction of the calcium phosphorodiamidate, the reaction rate seemed much slower than that of the magnesium salt. The IR spectral data in Fig. 1 show the absorption of NH_4^+ at 1400 cm^{-1} in good agreement with the results in Table 1. The IR spectra of the products also give peaks due to P–O–P and/or P–NH–P linkages at 920 and 730 cm^{-1}. This means that the phosphorodiamidates produce polymers associated with P–O–P and/or P–NH–P linkages by the reaction with HCl gas. The

Table 1. Nitrogen Content and X-Ray Diffraction Data of the Reaction Products of Phosphorodiamidates with HCl Gas

Phosphorodiamidate	Reaction time/min	Total N/%	N as NH_4^+/%	X-Ray dif.
$Mg[PO_2(NH_2)_2]_2\cdot 6H_2O$	60	17.4	8.4	NH_4Cl, UK
	180	15.8	9.5	NH_4Cl, UK
	300	15.5	9.3	NH_4Cl, UK
$Ca[PO_2(NH_2)_2]_2\cdot 2H_2O$	60	20.7	—	SM
	180	20.7	—	SM
	300	19.7	—	SM

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

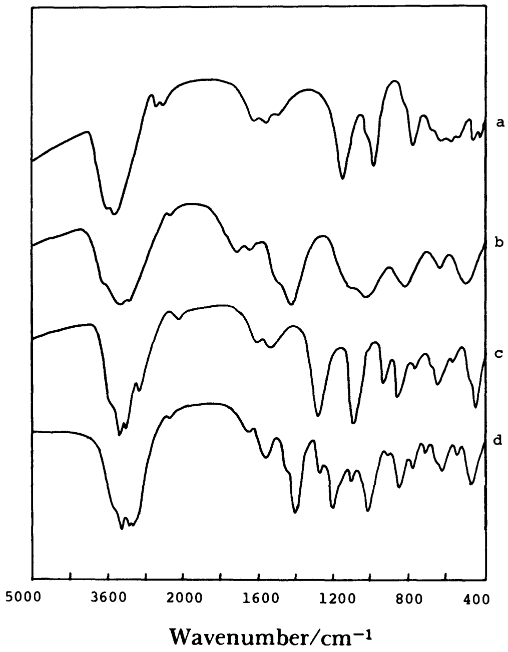


Fig. 1. IR spectra of the phosphorodiamidates and the reaction products of the phosphorodiamidates with HCl gas for 300 min.
a: $Mg[PO_2(NH_2)_2]_2\cdot 6H_2O$, b: reaction product of $Mg[PO_2(NH_2)_2]_2\cdot 6H_2O$, c: $Ca[PO_2(NH_2)_2]_2\cdot 2H_2O$, d: reaction product of $Ca[PO_2(NH_2)_2]_2\cdot 2H_2O$.

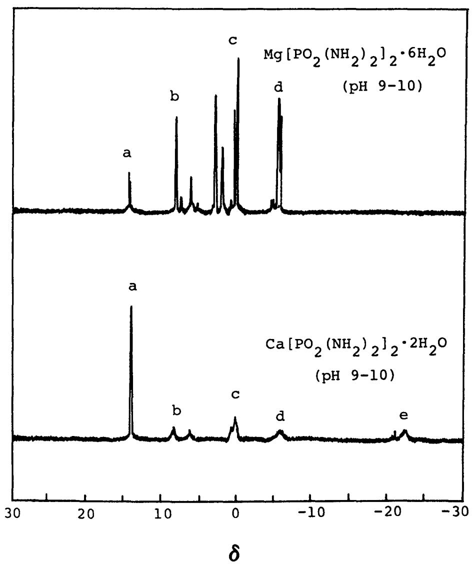


Fig. 2. ^{31}P NMR spectra of the reaction products of the phosphorodiamidates with HCl gas for 300 min.
a: Phosphorodiamidate, b: phosphoramidate, c: orthophosphate, d: end-PO_4 group, e: middle-PO_4 group.

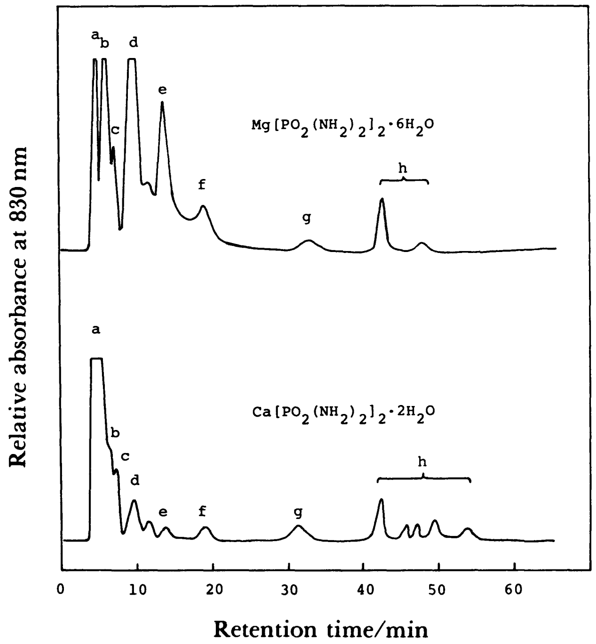
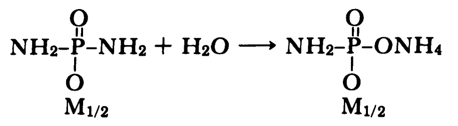


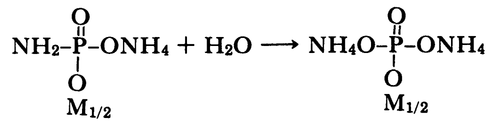
Fig. 3. HPLC profiles of the reaction products of the phosphorodiamidates with HCl gas for 300 min.
a: Phosphorodiamidate, b: phosphoramidate, c: orthophosphate, d: imidodiphosphate, e: diphosphate, f: triphosphate, g: chain polyphosphates, h: ring and higher chain polyphosphates.

^{31}P NMR spectral data in Fig. 2 give the peaks of phosphoramidate, orthophosphate, an end-PO_4 group, a middle-PO_4 group, and unknown materials other than phosphorodiamidate. The unknown peaks which appeared in lower fields than that of orthophosphate might be caused by compounds with amino and/or imino groups.[12] The HPLC profile of the products in Fig. 3 indicates that the products contain phosphorodiamidate, phosphoramidate, orthophosphate, diphosphate, imidodiphosphate, triphosphate, and higher-chain and ring polyphosphates with P–O–P and P–NH–P linkages. According to the results, the following reaction processes can be written for the reaction systems:

(1) Decomposition



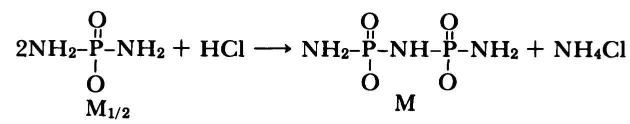
$$NH_2\text{-}\underset{\underset{M_{1/2}}{O}}{\overset{\overset{O}{\|}}{\underset{|}{P}}}\text{-}NH_2 + H_2O \longrightarrow NH_2\text{-}\underset{\underset{M_{1/2}}{O}}{\overset{\overset{O}{\|}}{\underset{|}{P}}}\text{-}ONH_4 \qquad (1)$$



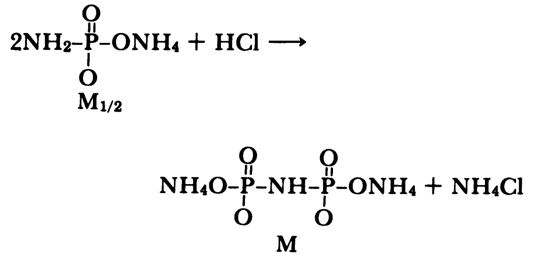
$$NH_2\text{-}\underset{\underset{M_{1/2}}{O}}{\overset{\overset{O}{\|}}{\underset{|}{P}}}\text{-}ONH_4 + H_2O \longrightarrow NH_4O\text{-}\underset{\underset{M_{1/2}}{O}}{\overset{\overset{O}{\|}}{\underset{|}{P}}}\text{-}ONH_4 \qquad (2)$$

The water in the above reaction can come from the water of crystallization and/or the adsorbed water of the phosphorodiamidates and from the slight amount of water in the gas in the reaction systems.

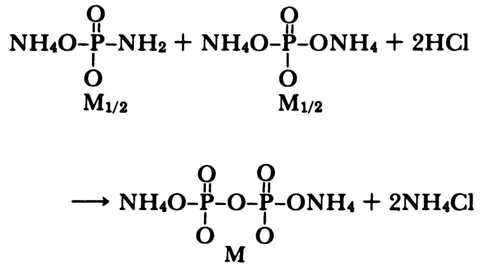
(2) Condensation



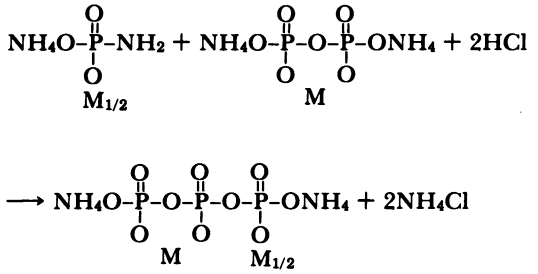
$$2NH_2\text{-}\underset{\underset{M_{1/2}}{O}}{\overset{\overset{O}{\|}}{\underset{|}{P}}}\text{-}NH_2 + HCl \longrightarrow \underset{M}{NH_2\text{-}\underset{O}{\overset{\overset{O}{\|}}{\underset{|}{P}}}\text{-}NH\text{-}\underset{O}{\overset{\overset{O}{\|}}{\underset{|}{P}}}\text{-}NH_2} + NH_4Cl \qquad (3)$$



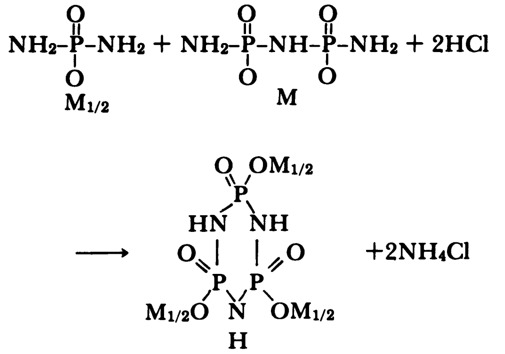
$$\mathrm{2NH_2-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-ONH_4 + HCl \longrightarrow \underset{M}{NH_4O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O}}{P}}-NH-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O}}{P}}-ONH_4} + NH_4Cl} \tag{4}$$



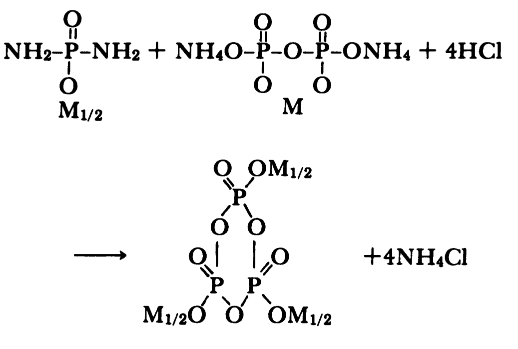
$$\mathrm{NH_4O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-NH_2 + NH_4O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-ONH_4 + 2HCl \longrightarrow \underset{M}{NH_4O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O}}{P}}-O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O}}{P}}-ONH_4} + 2NH_4Cl} \tag{5}$$



$$\mathrm{NH_4O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-NH_2 + \underset{M}{NH_4O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O}}{P}}-O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O}}{P}}-ONH_4} + 2HCl \longrightarrow \underset{M}{NH_4O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O}}{P}}-O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O}}{P}}}-O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-ONH_4 + 2NH_4Cl} \tag{6}$$



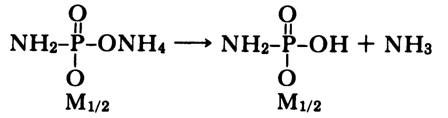
(7)



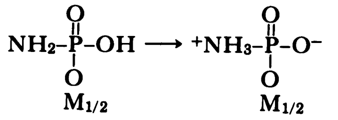
(8)

where M stands for alkaline earth metal. (Only typical reactions are shown above.)

The phosphoramidate with an OH group was considered to from a zwitterion:[2)]

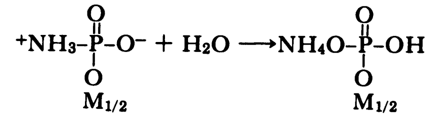


$$\mathrm{NH_2-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-ONH_4 \longrightarrow NH_2-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-OH + NH_3} \tag{9}$$

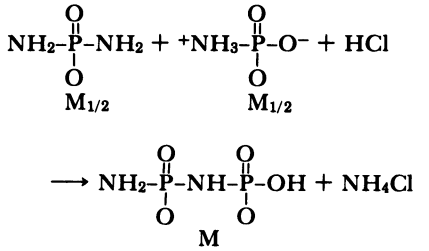


$$\mathrm{NH_2-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-OH \longrightarrow {}^{+}NH_3-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-O^{-}} \tag{10}$$

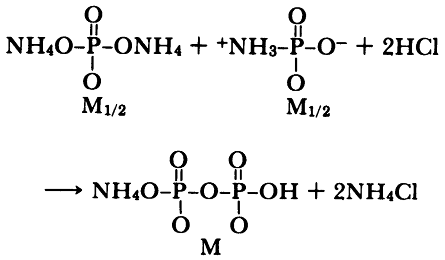
The zwitterion is very active and can react with water, phosphoramidates, and phosphates to produce orthophosphate, polyphosphates, and phosphates with amino and/or imino groups:



$$\mathrm{{}^{+}NH_3-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-O^{-} + H_2O \longrightarrow NH_4O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-OH} \tag{11}$$



$$\mathrm{NH_2-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-NH_2 + {}^{+}NH_3-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-O^{-} + HCl \longrightarrow \underset{M}{NH_2-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O}}{P}}-NH-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O}}{P}}-OH} + NH_4Cl} \tag{12}$$



$$\mathrm{NH_4O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-ONH_4 + {}^{+}NH_3-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O\\ M_{1/2}}}{P}}-O^{-} + 2HCl \longrightarrow \underset{M}{NH_4O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O}}{P}}-O-\overset{\substack{O\\ \|}}{\underset{\substack{|\\ O}}{P}}-OH} + 2NH_4Cl} \tag{13}$$

It was difficult, however, to obtain exact information about the zwitterion, so it is impossible to decide which process is most reasonable for the reaction systems.

Reaction with Acetic Acid. The nitrogen content and the results of the X-ray diffraction analysis of the reaction products of the phosphorodiamidates with acetic acid are listed in Table 2. The results show that the amino group in the phosphorodiamidates was converted to an ammonium ion by the reaction with acetic acid. The IR spectra of the products in Fig. 4 exhibit an absorption of an NH_4^+ ion at 1400 cm^{-1}. The results agree well with those in Table 2. The IR spectra also show that the products have P–O–P and/or P–NH–P linkages by means of the absorption at 920 cm^{-1}. The ^{31}P NMR spectra of the reaction products in Fig. 5 give peaks due to orthophosphate, phosphoramidate, and an end-PO_4 group, a middle-PO_4 group, and unknown materials. As has been men-

Table 2. Nitrogen Content and X-Ray Diffraction Data of the Reaction Products of Phosphorodiamidates with Acetic Acid

Phosphorodiamidate	Reaction temp/°C	Reaction time/h	Total N/%	N as NH_4^+/%	X-Ray dif.
$Mg[PO_2(NH_2)_2]_2\cdot6H_2O$	25	15	14.3	4.1	SM
		25	14.0	4.1	UK
	60	15	11.1	7.6	AM
		25	8.1	6.5	AM
$Ca[PO_2(NH_2)_2]_2\cdot2H_2O$	25	15	15.1	2.8	SM
		25	12.8	3.8	UK
	60	15	11.6	5.9	AM
		25	9.5	5.4	AM

SM, UK, and AM stand for the starting material, the unknown crystalline substance, and the amorphous product respectively.

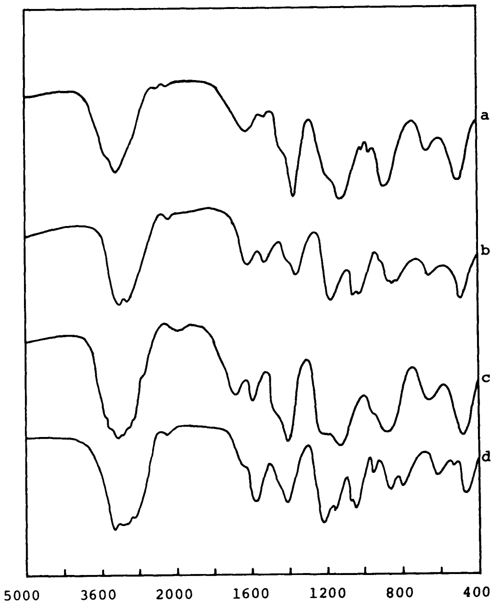


Fig. 4. IR spectra of the reaction products of the phosphorodiamidates with acetic acid for 25 h.
a: $Mg[PO_2(NH_2)_2]_2\cdot6H_2O$ at 60 °C, b: $Mg[PO_2(NH_2)_2]_2\cdot6H_2O$ at 25 °C, c: $Ca[PO_2(NH_2)_2]_2\cdot2H_2O$ at 60 °C, d: $Ca[PO_2(NH_2)_2]_2\cdot2H_2O$ at 25 °C.

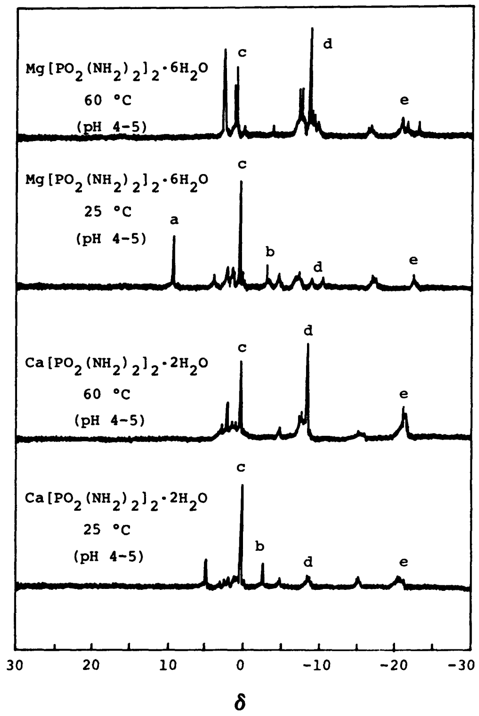
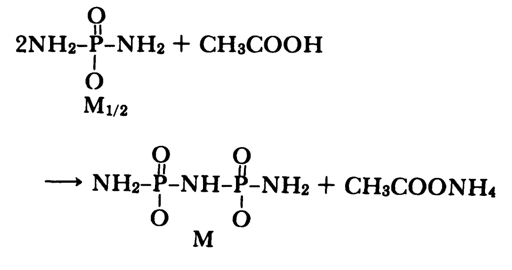


Fig. 5. ^{31}P NMR spectra of the reaction products of the phosphorodiamidates with acetic acid for 25 h.
a: Phosphorodiamidate, b: phosphoramidate, c: orthophosphate, d: end-PO_4 group, e: middle-PO_4 group.

tioned above, the peaks in the magnetic fields lower than that of orthophosphate seemed to be attributable to the peaks of phosphates associated with amino and/or imino groups. The HPLC profiles of the products in Fig. 6 give peaks of orthophosphate, phosphoramidate, diphosphate, imidodiphosphate, triphosphate, and higher-chain and ring polyphosphates containing P–O–P and/or P–NH–P linkages. Accordingly, the same decomposition reactions as in Eqs. 1 and 2 can be given for the reaction systems. The following condensations of phosphate species with acetic acid can be described for the systems:



$$2NH_2\text{-}\underset{\substack{|\\O\\M_{1/2}}}{\overset{O}{\overset{\|}{P}}}\text{-}NH_2 + CH_3COOH \longrightarrow NH_2\text{-}\underset{|\\O}{\overset{O}{\overset{\|}{P}}}\text{-}NH\text{-}\underset{|\\O}{\overset{O}{\overset{\|}{P}}}\text{-}NH_2 + CH_3COONH_4 \quad (14)$$

M

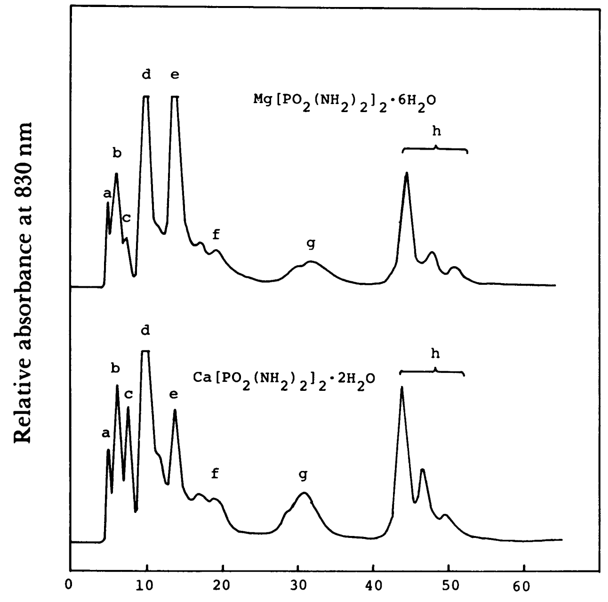


Fig. 6. HPLC profiles of the reaction products of the phosphorodiamidates with acetic acid at 60 °C for 15 h.
a: Phosphorodiamidate, b: phosphoramidate, c: orthophosphate, d: imidodiphosphate, e: diphosphate, f: triphosphate, g: chain polyphosphates, h: ring and higher chain polyphosphates.

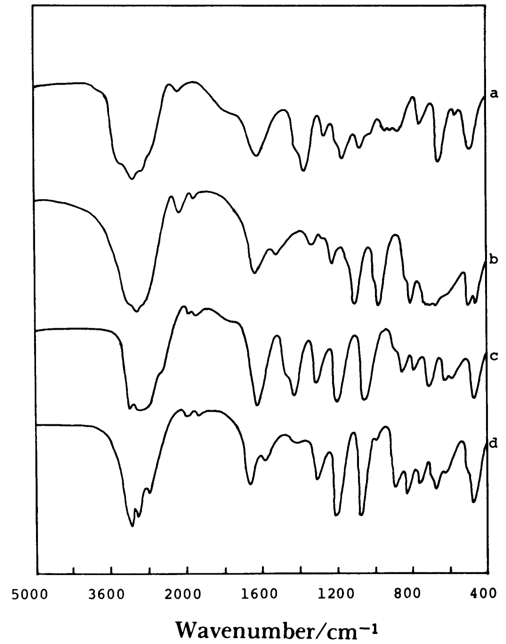
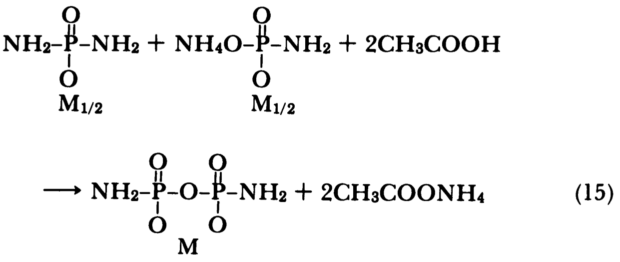
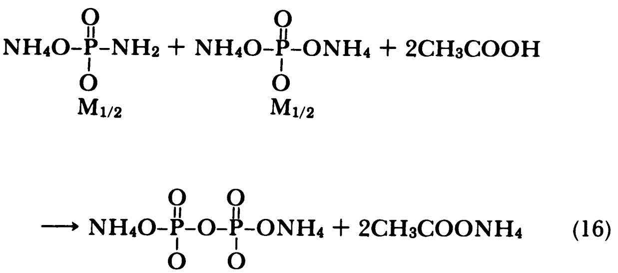


Fig. 7. IR spectra of the reaction products of the phosphorodiamidates with oxalic acid for 25 h.
a: $Mg[PO_2(NH_2)_2]_2\cdot 6H_2O$ at 60 °C, b: $Mg[PO_2(NH_2)_2]_2\cdot 6H_2O$ at 25 °C, c: $Ca[PO_2(NH_2)_2]_2\cdot 2H_2$ at 60 °C, d: $Ca[PO_2(NH_2)_2]_2\cdot 2H_2O$ at 25 °C.

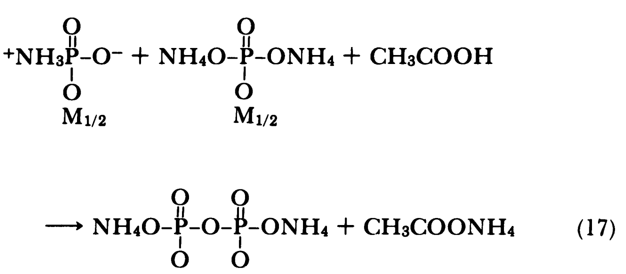


$$NH_2-\underset{\underset{M_{1/2}}{O}}{\overset{O}{\overset{\|}{P}}}-NH_2 + NH_4O-\underset{\underset{M_{1/2}}{O}}{\overset{O}{\overset{\|}{P}}}-NH_2 + 2CH_3COOH \longrightarrow \underset{M}{NH_2-\underset{O}{\overset{O}{\overset{\|}{P}}}-O-\underset{O}{\overset{O}{\overset{\|}{P}}}-NH_2} + 2CH_3COONH_4 \qquad (15)$$



$$NH_4O-\underset{\underset{M_{1/2}}{O}}{\overset{O}{\overset{\|}{P}}}-NH_2 + NH_4O-\underset{\underset{M_{1/2}}{O}}{\overset{O}{\overset{\|}{P}}}-ONH_4 + 2CH_3COOH \longrightarrow \underset{M}{NH_4O-\underset{O}{\overset{O}{\overset{\|}{P}}}-O-\underset{O}{\overset{O}{\overset{\|}{P}}}-ONH_4} + 2CH_3COONH_4 \qquad (16)$$

or



$$^{+}NH_3\underset{\underset{M_{1/2}}{O}}{\overset{O}{\overset{\|}{P}}}-O^{-} + NH_4O-\underset{\underset{M_{1/2}}{O}}{\overset{O}{\overset{\|}{P}}}-ONH_4 + CH_3COOH \longrightarrow \underset{M}{NH_4O-\underset{O}{\overset{O}{\overset{\|}{P}}}-O-\underset{O}{\overset{O}{\overset{\|}{P}}}-ONH_4} + CH_3COONH_4 \qquad (17)$$

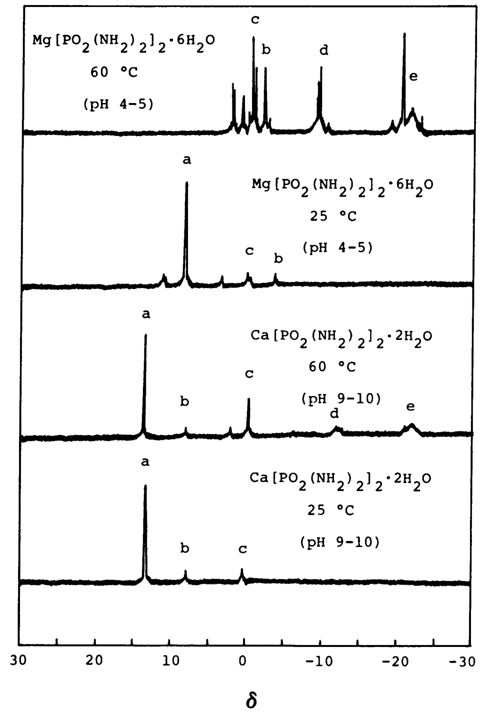


Fig. 8. ^{31}P NMR spectra of the reaction products of the phosphorodiamidates with oxalic acid for 25 h.
a: Phosphorodiamidate, b: phosphoramidate, c: orthophosphate, d: end-PO_4 group, e: middle-PO_4 group.

Table 3. Nitrogen Content and X-Ray Diffraction Data of the Reaction Products of Phosphorodiamidates with Oxalic Acid

Phosphorodiamidate	Reaction temp/°C	Reaction time/h	Total N/%	N as NH_4^+/%	X-Ray dif.
$Mg[PO_2(NH_2)_2]_2\cdot 6H_2O$	25	15	17.0	0.3	SM
		25	16.5	0.5	SM
	60	15	13.0	6.0	UK
		25	10.9	7.2	UK
$Ca[PO_2(NH_2)_2]_2\cdot 2H_2O$	25	15	20.2	0.4	SM
		25	19.4	0.9	SM
	60	15	18.2	2.1	SM
		25	14.0	4.8	SM

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

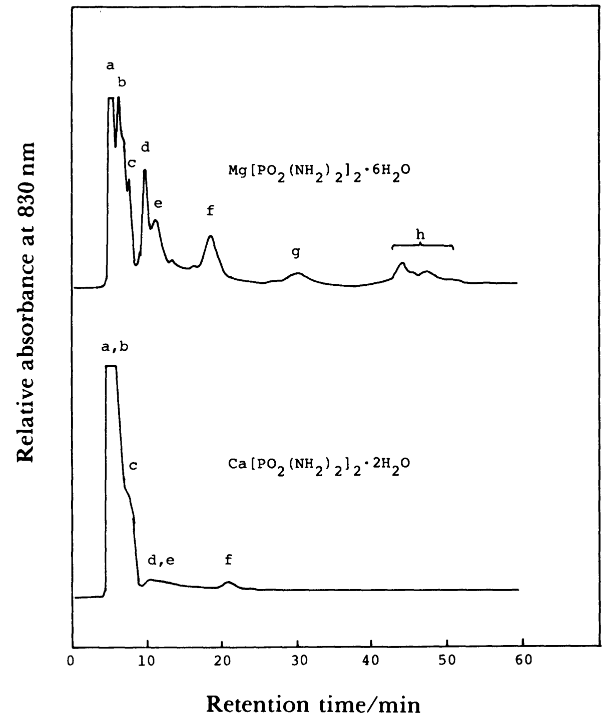
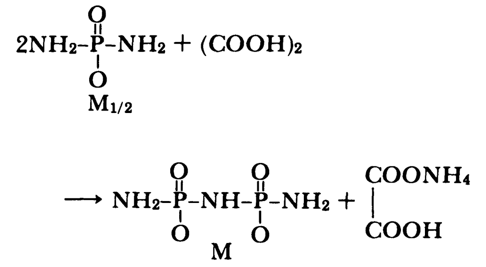


Fig. 9. HPLC profiles of the reaction products of the phosphorodiamidates with oxalic acid at 60 °C for 15 h.

a: Phosphorodiamidate, b: phosphoramidate, c: orthophosphate, d: imidodiphosphate, e: diphosphate, f: triphosphate, g: chain polyphosphates, h: ring and higher chain polyphosphates.

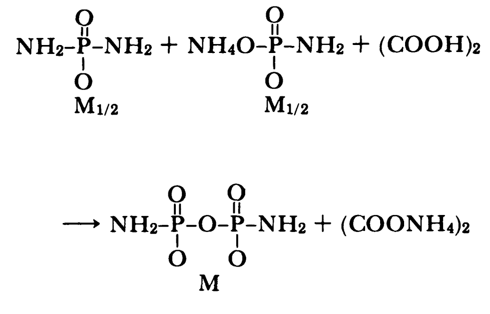
(Only a few typical reaction models are described here.)

Reaction with Oxalic Acid. The chemical analysis of the nitrogen content and X-ray diffraction data of the products in Table 3 show that the phosphorodiamidates react little with oxalic acid at 25 °C. The amino group in the phosphorodiamidates is converted to an ammonium ion at 60 °C. The IR spectra of the reaction products in Fig. 7 show an absorption of NH_4^+ at 1400 cm^{-1} and support the results in Table 3. The ^{31}P NMR spectra of the products of the magnesium phosphorodiamidate in Fig. 8 indicate large peaks of orthophosphate, phosphoramidate, an end-PO_4 group, a middle-PO_4, group, and unknown species. The ^{31}P NMR spectra of the other reaction products gave a large peak of phosphorodiamidate and very small peaks of the other species. This means that the rates of the reactions other than that of the magnesium salt at 60 °C are very small. These results are well supported by the HPLC data in Fig. 9. According to the above results, one can write the same decomposition reactions as Eqs. 1 and 2, and the condensation reaction processes similar to those of acetic acid for the reactions with oxalic acid, thus:



$$2NH_2\text{-}\overset{\overset{O}{\|}}{\underset{\underset{\underset{M_{1/2}}{O}}{|}}{P}}\text{-}NH_2 + (COOH)_2$$

$$\longrightarrow \underset{M}{NH_2\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}\text{-}NH\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}\text{-}NH_2} + \begin{matrix}COONH_4\\|\\COOH\end{matrix} \qquad (18)$$



$$NH_2\text{-}\overset{\overset{O}{\|}}{\underset{\underset{\underset{M_{1/2}}{O}}{|}}{P}}\text{-}NH_2 + NH_4O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{\underset{M_{1/2}}{O}}{|}}{P}}\text{-}NH_2 + (COOH)_2$$

$$\longrightarrow \underset{M}{NH_2\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}\text{-}NH_2} + (COONH_4)_2 \qquad (19)$$

(Only typical reactions are shown.)

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