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The Condensation and Decomposition of Phosphoramidates with Acids

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Several phosphoramidates were reacted with dried hydrogen chloride, acetic acid, and oxalic acid. The phosphoramidates reacted with the acids to produce ortho- and polyphosphates, but did not react with them to make polyphosphates containing imino groups, with the elimination of ammonia. The decomposition of the phosphoramidates to orthophosphate by the action of water was considered to be the first step in the production of polyphosphates:

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

The formation of polyphosphates can be explained, for example, by this equation:

$$MO\text{-}\overset{\overset{O}{\|}}{\underset{\underset{M}{O}}{P}}\text{-}ONH_4 + NH_2\text{-}\overset{\overset{O}{\|}}{\underset{\underset{M}{O}}{P}}\text{-}OM + 2HA \longrightarrow MO\text{-}\overset{\overset{O}{\|}}{\underset{\underset{M}{O}}{P}}\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{M}{O}}{P}}\text{-}OM + 2NH_4A,$$

where HA stands for acid.

Among phosphorus-nitrogen compounds, the most outstanding may be phosphazene polymers. Many studies have been made of these compounds, while other phosphorus-nitrogen compounds are not very well-known. We have reported on the syntheses and thermal properties of several phosphoramidates during the last few years.[1-6] The phosphoramidates are thought to be useful as new types of chemical fertilizers containing P-N covalent bonds and as flame-proof materials. These phosphoramidates produce ortho- and polyphosphates, but do not produce polyphosphates containing imino groups, when they are heated in air at a moderately high temperature (100—1000 °C). The chemical reactions of the phosphoramidates with inorganic and organic acids were performed in order to study the condensation and decomposition of the amino groups in the phosphoramidates. To prevent the hydrolysis of the phosphoramidates and the reaction products, hydrogen chloride, acetic acid, and oxalic acid were used.

Experimental

Preparation of Phosphoramidates. The phosphoramidic acid monohydrate, ammonium hydrogenphosphoramidate, sodium hydrogenphosphoramidate, potassium hydrogenphosphoramidate, and disodium phosphoramidate hexahydrate were made by the methods described in Reference 7.

Reaction of Phosphoramidates with Hydrogen Chloride. Hydrogen chloride was prepared by adding concentrated hydrochloric acid to concentrated sulfuric acid, and the HCl gas was dried with concentrated sulfuric acid. The dried HCl gas was introduced to a reaction glass-tube containing about 5 g of a phosphoramidate sample. The product was washed quickly with ethanol to remove the HCl gas adsorbed on the product.

Reaction of Phosphoramidates with Acetic Acid. A phosphoramidate sample (about 2 g) was placed in a mixture of 5 cm^3 of acetic acid and 20 cm^3 of chloroform, and the resulting mixture was reacted at 25 and 60 °C while being stirred. The solid product was filtered off and washed with ethanol. In the case of the reaction of disodium phosphoramidate hexahydrate, the reaction mixture was centrifuged and the solid product was washed with ethanol.

Reaction of Phosphoramidates with Oxalic Acid. Oxalic acid (3 g) was dissolved in 100 cm^3 of ethanol, and then a phosphoramidate sample (about 2 g) was added to the solution. The mixture was heated at 25 and 60 °C while being stirred. The solid product was filtered off and washed with ethanol.

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 was dissolved in water, and the pH of the solution was adjusted to about 7 with an aqueous sodium hydroxide solution if needed. The one-dimensional paper-chromatographic separation and the colorimetric determination of the phosphate species in the solution were done by the method described in our previous paper.[1]

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. A sample was dissolved in water and the ^{31}P NMR spectrum of the solution was taken by means of a JNM-GX270 spectrograph. The NMR chemical shifts are reported relative to external 85%-orthophosphoric acid, with the positive shifts being downfield.

Results and Discussion

Reaction with Hydrogen Chloride. The data of the chemical compositions of the products are shown in Table 1, along with the X-ray diffraction data. The chromatographic separation between phosphoramidate and orthophosphate could not be performed with the developing solvents used in this experiment. According to the results listed in Table 1, the phos-

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

Phosphoramidates	Reaction time/min	Total N/%	N/% as NH_4^+	X-Ray dif.	Phosphates/P%			
					Amido and Ortho	Di	Tri	Higher
$H_2PO_3NH_2 \cdot H_2O$	60	14.4	1.5	SM	72.0	21.0	4.2	2.8
	180	14.4	2.2	SM	61.4	30.0	6.8	1.5
	300	14.2	2.3	SM	52.9	31.5	9.6	6.0
$NH_4HPO_3NH_2$	60	24.4	11.9	SM, NH_4Cl	70.9	17.3	3.1	8.7
	180	20.1	11.9	SM, UK, NH_4Cl	36.8	30.9	2.1	30.2
	300	16.2	13.7	UK, NH_4Cl	25.4	32.4	3.8	38.4
$NaHPO_3NH_2$	60	11.4	1.1	SM, UK, NH_4Cl	68.3	23.4	8.3	
	180	10.4	3.0	SM, UK, NH_4Cl	60.5	28.9	10.6	
	300	10.6	5.7	SM, UK, NH_4Cl	65.5	22.9	6.6	5.0
$KHPO_3NH_2$	60	10.4	0.2	SM	100	—	—	—
	180	10.3	0.7	SM	86.5	8.3	5.2	
	300	10.2	1.1	SM	83.7	12.1	4.2	
$Na_2PO_3NH_2 \cdot 6H_2O$	60	6.0	5.2	UK, NH_4Cl	92.8	7.2	—	—
	180	6.0	5.2	UK, NH_4Cl	96.3	3.7	—	—
	300	6.0	5.2	UK, NH_4Cl	100	—	—	—

SM and UK stand for the starting materials and an unknown substabce respectively.

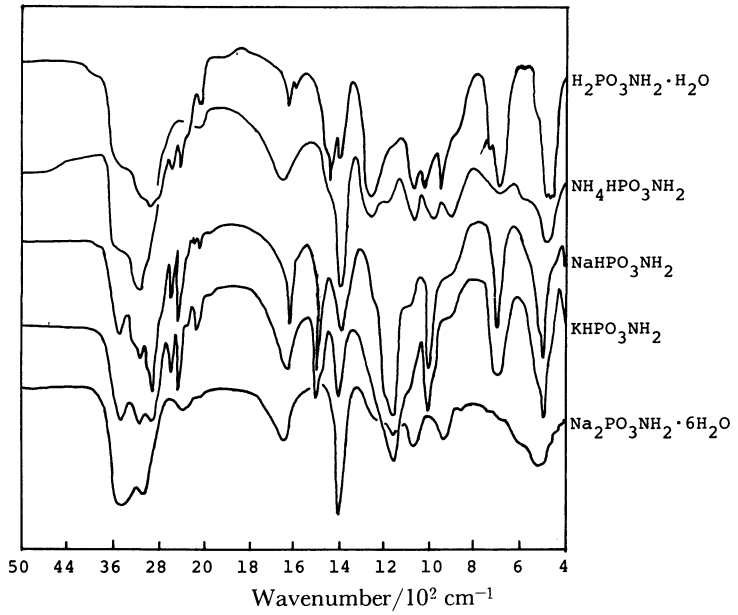


Fig. 1. IR spectra of the reaction products of phosphoramidates with HCl gas for 5 h.

phoramidic acid and phosphoramidates seemed to react with HCl gas to produce ortho- and polyphosphates. The amino group of the phosphoramidates decomposed to ammonia at the same time. The contents of NH_4^+ and polyphosphates increased with the passage of the reaction time in the reactions of $H_2PO_3NH_2 \cdot H_2O$, $NH_4HPO_3NH_2$, and $KHPO_3NH_2$. The IR spectra of the products in Fig. 1 agree well with the results in Table 1. The absorption at 1400 cm^{-1} is due to NH_4^+, while those at about 900 and 700 cm^{-1} are assigned to a P-O-P or a P-N(H)-P linkage respectively. The reaction rate of $KHPO_3NH_2$ was very low; this means that the phosphoramidate is very stable. In the reactions of $NaHPO_3NH_2$ and $Na_2PO_3NH_2 \cdot 6H_2O$, the degradation of polyphosphates to phosphates with shorter chain lengths was observed in addition to the formation of ortho- and polyphosphates. The results in Table 1 and Fig. 1 do

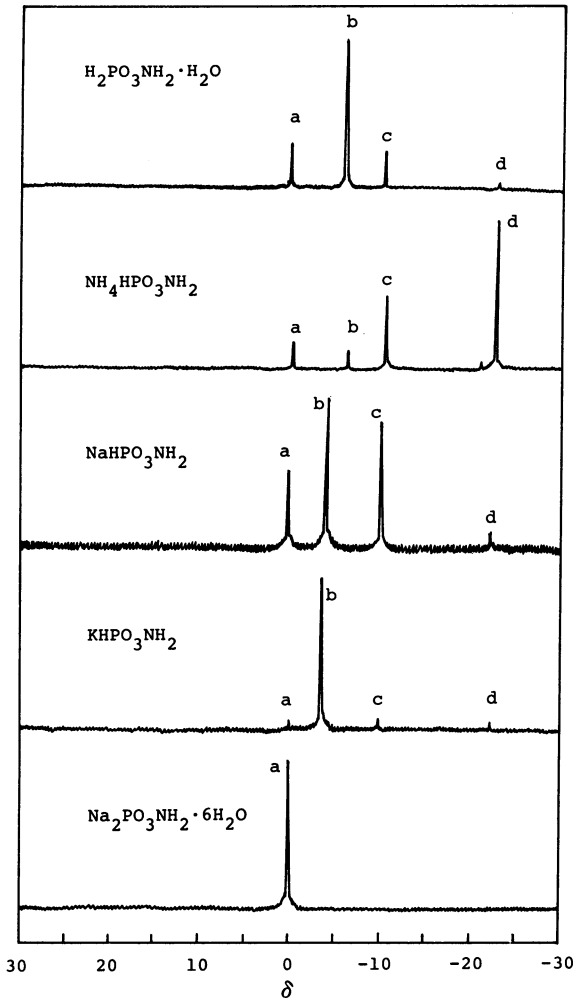


Fig. 2. ^{31}P NMR spectra of the reaction products of phosphoramidates with HCl gas at room temperature for 5 h.
a: Orthophosphate, b: phosphoramidate, c: end-PO_4 group, d: middle-PO_4 group.

not, however, give any information about the formation of a P-N(H)-P linkage. The ^{31}P NMR peaks of the products in Fig. 2 were assigned to phosphoramidate, orthophosphate, and polyphosphates. The NMR data did not give any peak of a compound with a P-N-(H)-P linkage. Accordingly, the formation of a P-N-(H)-P linkage, with the elimination of ammonia, by the following reaction did not occur in these reaction systems:

$$\text{-P(O)(O)-NH}_2 + \text{NH}_2\text{-P(O)(O)-} + \text{HCl} \longrightarrow \text{-P(O)(O)-N(H)-P(O)(O)-} + \text{NH}_4\text{Cl}. \quad (1)$$

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

$$\text{MO-P(=O)(O)-NH}_2 + \text{H}_2\text{O} \longrightarrow \text{MO-P(=O)(O)-ONH}_4, \quad (2)$$

$$\text{MO-P(=O)(O)-ONH}_4 + \text{NH}_2\text{-P(=O)(O)-OM} + 2\text{HCl} \longrightarrow$$

$$\text{MO-P(=O)(O)-O-P(=O)(O)-OM} + 2\text{NH}_4\text{Cl}, \quad (3)$$

$$\text{MO-P(=O)(O)-O-P(=O)(O)-OM} + \text{NH}_2\text{-P(=O)(O)-OM} + 2\text{HCl} \longrightarrow$$

$$\text{MO-P(=O)(O)-O-P(=O)(O)-O-P(=O)(O)-OM} + \text{MCl} + \text{NH}_4\text{Cl}. \quad (4)$$

The phosphoramidate with an OH group is considered to form a zwitterion:[8]

$$\text{MO-P(=O)(O)-NH}_2 + \text{H}_2\text{O(HCl)} \longrightarrow$$

$$\text{HO-P(=O)(O)-NH}_2 + \text{MOH(MCl)}, \quad (5)$$

$$\text{HO-P(=O)(O)-NH}_2 \longrightarrow {}^{-}\text{O-P(=O)(O)-NH}_3^{+}. \quad (6)$$

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

$$^{-}\text{O-P(=O)(O)-NH}_3^{+} + \text{H}_2\text{O} \longrightarrow \text{HO-P(=O)(O)-ONH}_4, \quad (7)$$

$$^{-}\text{O-P(=O)(O)-NH}_3^{+} + \text{HO-P(=O)(O)-ONH}_4 + \text{HCl} \longrightarrow$$

$$\text{HO-P(=O)(O)-O-P(=O)(O)-ONH}_4 + \text{NH}_4\text{Cl}. \quad (8)$$

It is difficult at present to obtain information about the formation of the zwitterion, so it cannot be determined which process is more reasonable for the reaction system. The water in the reactions can come from the crystal water and/or the adsorbed water of the phosphoramidates and a 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 $NaHPO_3NH_2$ and $Na_2PO_3NH_2 \cdot 6H_2O$, a degradation of polyphosphates to phosphates with shorter chain lengths was observed. Usually this degradation can not take place in a solid state at room temperature. The water contained in the products may be strongly acidic as a result of the dissolution of HCl gas. The hydrolysis

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

Phosphoramidates	Total N/%	N/% as NH_4^+	X-Ray dif.	Phosphates/P%			
				Amido and Ortho	Di	Tri	Higher
$H_2PO_3NH_2 \cdot H_2O$	12.3	10.9	UK	16.9	13.9	7.4	61.8
$NH_4HPO_3NH_2$	22.3	11.9	SM	91.2	5.9	0.2	2.7
$NaHPO_3NH_2$	11.1	0.3	SM	100	—	—	—
$KHPO_3NH_2$	9.9	0.4	SM	96.4	3.6	—	—
$Na_2PO_3NH_2 \cdot 6H_2O$	9.0	0.2	UK	100	—	—	—

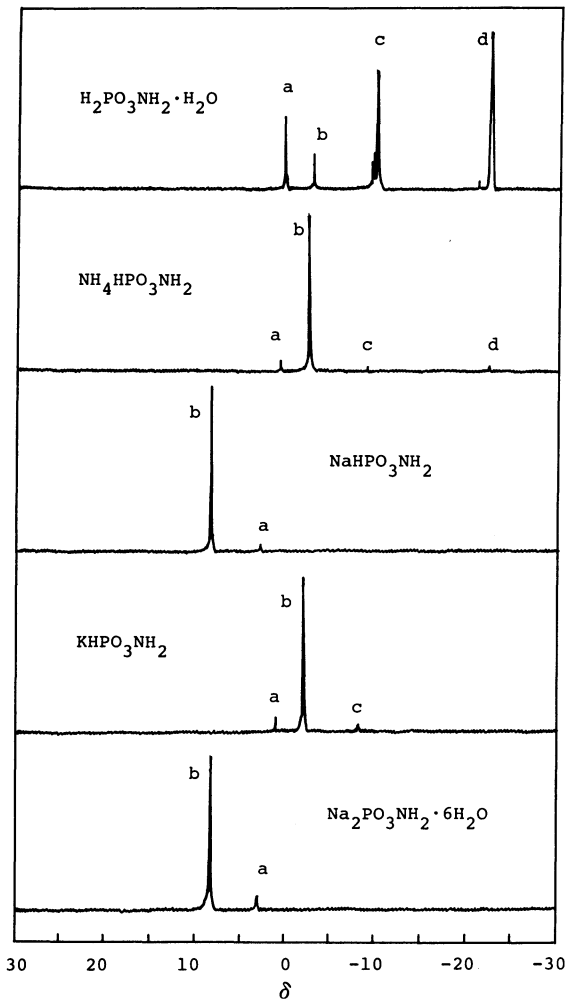


Fig. 3. ^{31}P NMR spectra of the reaction products of phosphoramidates with acetic acid at 60 °C for 25 h. a: Orthophosphate, b: phosphoramidate, c: end-PO_4 group, d: middle-PO_4 group.

of polyphosphates is very much accelerated by an H^+ ion.[9]

Reaction with Acetic Acid. The chemical compositions and X-ray diffraction data of the reaction products at 60 °C are shown in Table 2. The data at 25 °C are not listed because the reaction processes of the phosphoramidates with acetic acid at 25 °C were almost the same as those at 60 °C except for the reaction rates. As Table 2 shows, the reaction rate of the phosphoramidic acid was much faster than those of other phosphoramidates. The ^{31}P NMR spectral data in Fig. 3 support the results in Table 2. The NMR spectra of $NaHPO_3NH_2$ and $Na_2PO_3NH_2 \cdot 6H_2O$ gave a large peak of the amidate and a very small peak of orthophosphate. The NMR spectra of $NH_4HPO_3NH_2$ and $KHPO_3NH_2$ included small peaks of orthophosphate, an end-PO_4 group, and/or a middle-PO_4 group other than the large peak of the phosphoramidate. The NMR spectra of the products of $NaHPO_3NH_2$ and $Na_2PO_3NH_2 \cdot 6H_2O$ were taken by dissolving them in a basic solution (pH 9—10). The peak of phosphoramidate at about −3 — −5 in an acidic solution shifted to about +8.5 in a basic solution. The spectrum of $H_2PO_3NH_2 \cdot H_2O$ exhibited large peaks of orthophosphate, an end-PO_4 group, and a middle-PO_4 group, and a small peak of the phosphoramidic acid. No proof of the presence of imidopolyphosphates was obtained by either the chromatography or the NMR. Therefore, the formation of a P-N(H)-P linkage according to the following reaction did not occur in these systems:

$$\text{-P-NH}_2 + \text{NH}_2\text{-P-} + \text{CH}_3\text{COOH} \longrightarrow \text{-P-N(H)-P-} + \text{CH}_3\text{COONH}_4. \quad (9)$$

Considering the above results, several reaction processes can be written for these systems:

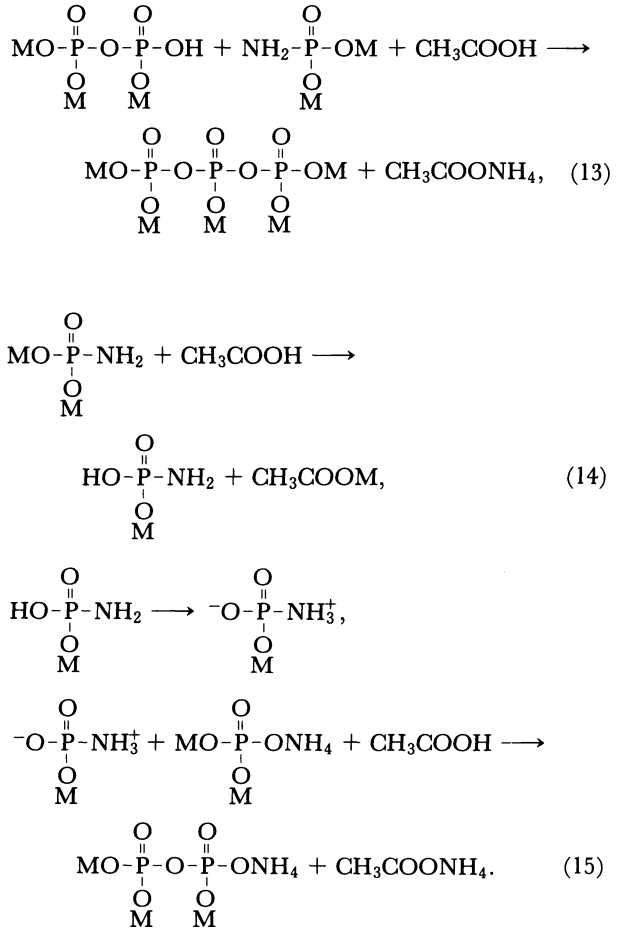
$$\text{MO-P(=O)(O M)-NH}_2 + \text{H}_2\text{O} \longrightarrow \text{MO-P(=O)(O M)-ONH}_4, \quad (10)$$

$$\text{MO-P(=O)(O M)-ONH}_4 + \text{NH}_2\text{-P(=O)(O M)-OM} + 2\text{CH}_3\text{COOH} \longrightarrow \text{MO-P(=O)(O M)-O-P(=O)(O M)-OM} + 2\text{CH}_3\text{COONH}_4, \quad (11)$$

$$\text{MO-P(=O)(O M)-O-P(=O)(O M)-OM} + \text{CH}_3\text{COOH} \longrightarrow \text{MO-P(=O)(O M)-O-P(=O)(O M)-OH} + \text{CH}_3\text{COOM}, \quad (12)$$

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

Phosphoramidates	Total N/%	N/% as NH_4^+	X-Ray dif.	Phosphates/P%			
				Amido and Ortho	Di	Tri	Higher
$H_2PO_3NH_2 \cdot H_2O$	12.3	7.6	SM, UK	22.3	39.0	4.2	34.5
$NH_4HPO_3NH_2$	12.2	12.2	UK	8.8	14.1	4.2	72.9
$NaHPO_3NH_2$	11.6	0.5	SM	100	—	—	—
$KHPO_3NH_2$	5.4	5.2	UK	11.6	8.6	6.2	73.6
$Na_2PO_3NH_2 \cdot 6H_2O$	6.1	0.5	UK	87.0	9.2	3.8	



$$MO\text{-}P(O)(O)\text{-}O\text{-}P(O)(O)\text{-}OH + NH_2\text{-}P(O)(O)\text{-}OM + CH_3COOH \longrightarrow MO\text{-}P(O)(O)\text{-}O\text{-}P(O)(O)\text{-}O\text{-}P(O)(O)\text{-}OM + CH_3COONH_4, \quad (13)$$

or

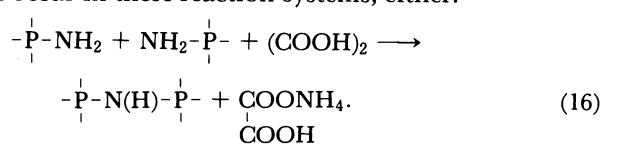
$$MO\text{-}P(O)(O)\text{-}NH_2 + CH_3COOH \longrightarrow HO\text{-}P(O)(O)\text{-}NH_2 + CH_3COOM, \quad (14)$$

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

$$^-O\text{-}P(O)(O)\text{-}NH_3^+ + MO\text{-}P(O)(O)\text{-}ONH_4 + CH_3COOH \longrightarrow MO\text{-}P(O)(O)\text{-}O\text{-}P(O)(O)\text{-}ONH_4 + CH_3COONH_4. \quad (15)$$

The water in Eq. 10 can come from crystal water and the adsorbed water of the phosphoramidates. As has been mentioned above, because of the lack of suitable data it is difficult to chose the most reasonable processes for the reaction systems.

Reaction with Oxalic Acid. The data on the chemical composition and the results of the X-ray diffractometry of the products are shown in Table 3, while ^{31}P NMR spectra of the products are presented in Fig. 4. Since the products were ortho- and polyphosphates, while imidopolyphosphates were not produced, the condensation with the elimination of ammonia did not occur in these reaction systems, either:



$$-P(-)\text{-}NH_2 + NH_2\text{-}P(-)- + (COOH)_2 \longrightarrow -P(-)\text{-}N(H)\text{-}P(-)- + \underset{\displaystyle COOH}{\overset{\displaystyle COOH}{|}}\!\!COONH_4. \quad (16)$$

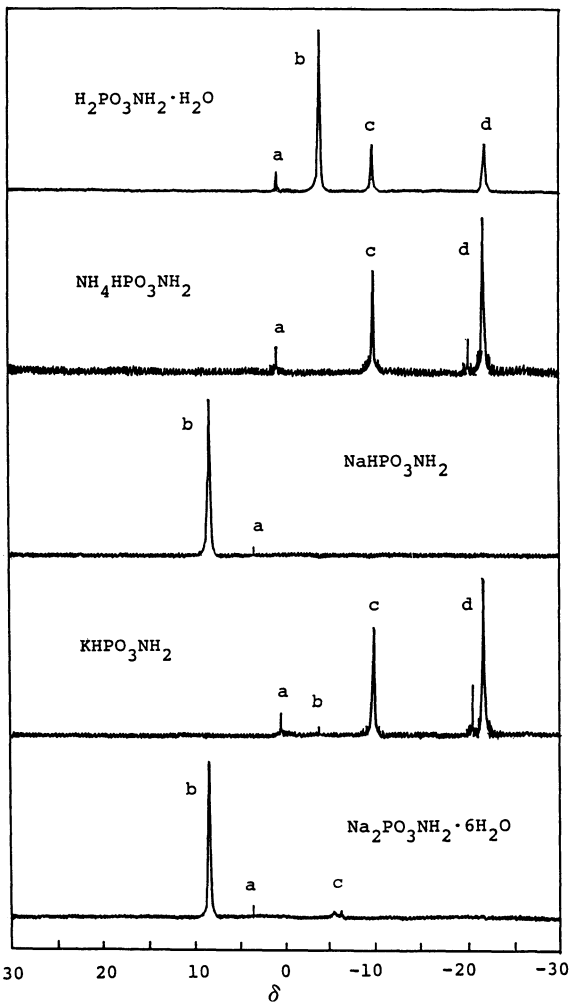
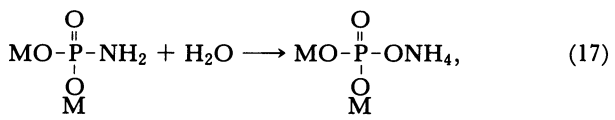


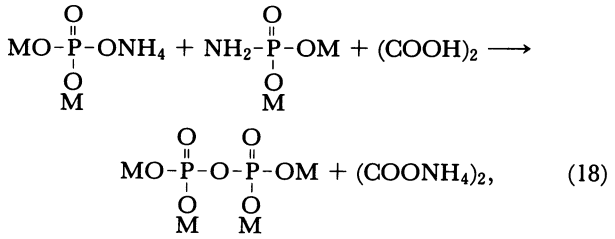
Fig. 4. ^{31}P NMR spectra of the reaction products of phosphoramidates with oxalic acid at 60 °C for 25 h. a: Orthophosphate, b: phosphoramidate, c: end-PO_4 group, d: middle-PO_4 group.

In the reaction with oxalic acid, phosphoramidic acid monohydrate, ammonium hydrogenphosphoramidate, and potassium hydrogenphosphoramidate showed a high reactivity. The reactions of sodium hydrogenphosphoramidate and disodium phosphoramidate hexahydrate were very slow. Accordingly, the reactivity of oxalic acid with the phosphoramidates seemed to be higher than that of acetic acid. As has been described above, since all the products are ortho- and polyphosphates, reaction processes similar to those of acetic

acid must take place in the reaction with oxalic acid, for example, as follows:



(17)



(18)

The water in Eq. 17 can come from the crystal water and/or the adsorbed water of the phosphoramidates. Oxalic acid has a higher reactivity to the phosphoramidates than does acetic acid. This may be explained by, for example, the faster reaction rate of Eq. 18 than that of Eq. 11.

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