The Synthesis and Thermal Decomposition of Magnesium Phosphoramidate

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Magnesium phosphoramidate-water (1/7) was made by adding an aqueous magnesium chloride solution to an aqueous potassium hydrogenphosphoramidate solution at pH 9.0—9.5. The product was stable at room temperature, while it decomposed on heating. The product decomposed to produce polyphosphates when it was heated in air. The decomposition product heated above 600 °C was magnesium diphosphate. A small amount of imidodiphosphate was made when the phosphoramidate was heated in dried N_2.

Phosphoramidates with P–N covalent bonds have potential as new chemical fertilizers and as flameproof materials because they produce polyphosphates containing imino and amino groups when they are heated. There have been many papers on phosphoric triamide and several papers concerning synthesis, thermal decomposition, or hydrolysis of ammonium and alkali-metal salts of phosphoramidic or phosphorodiamidic acid have been published.[1] Other salts of these phosphoramidic and phosphorodiamidic acids have not been studied. The present authors investigated the syntheses and thermal decompositions of magnesium and calcium bis(hydrogenphosphoramidate).[2,3] This paper describes the synthesis and thermal decomposition of magnesium phosphoramidate.

Experimental

Materials and Procedure. Potassium hydrogenphosphoramidate was prepared by the method described in a textbook.[4] About 0.1 mol of the phosphoramidate was dissolved in 100 cm^3 of water. Magnesium chloride hexahydrate was dissolved in 100 cm^3 of water by 0.1 mol. The magnesium chloride solution was added slowly to the phosphoramidate solution below 5 °C to prevent the hydrolysis of the latter. The resulting mixture was stirred for about 15 min. The pH of the solution was kept at 9.0—9.5 with aqueous ammonia during the treatment. A white precipitate was produced and was filtered off, washed with cooled water, ethanol, and then acetone. The product was dried under 5330 Pa at 20—25 °C for 2 d.

Chemical Analysis. About 0.2 g of the product was dissolved in 20 cm^3 of 6-mol dm^{-3} nitric acid and the solution was heated on a water bath for 1 h. The orthophosphate in the solution was determined to be $Mg_2P_2O_7$ by the gravimetric method.[5] Nitrogen and magnesium in the product were determined by the Kjeldahl method and by the EDTA (disodium dihydrogen ethylenediaminetetraacetate dihydrate) titration technique respectively.

Paper Chromatography and Colorimetry of Phosphates. One-dimensional paper chromatographic separation was run for the separation of the phosphate species in a sample with acidic (for the separation of chain phosphates) and basic (for the separation of ring phosphates) solvents.[6] A sample was dissolved in a 2% EDTA aqueous solution and the pH of the solution was adjusted to about 7 with an aqueous sodium hydroxide solution. The resulting solution was spotted on Toyo No. 51A filter paper (2 by 50 cm). The development was run at 5 °C for 2 d. Phosphates on the chromatogram were extracted with a 0.1-mol dm^{-3} aqueous ammonia and determined colorimetrically by means of the molybdenum-blue method with Lucena-Conde and Prat's reagent.[7]

X-Ray Diffractometry. An X-ray diffraction pattern of a powder sample was taken with nickel-filtered Cu $K\alpha$ radiation by using a Toshiba X-ray diffractometer, ADG-102.

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

DTA and TG. A sample was heated at the heating rate of 5 °C min^{-1} in air and in dried N_2 by using a Cho Balance TRDA$_1$-H-type apparatus.

^{31}P NMR. A sample was dissolved in a 6% EDTA deuterated-water solution. The ^{31}P NMR spectrum of the solution was taken by a JEOL-FX-60-FT-NMR instrument.

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

Results and Discussion

Composition of the Product. The yield of the product was about 18 g. Found: P, 12.5; N, 5.7; Mg, 9.8%. Calcd for $MgPO_3NH_2 \cdot 7H_2O$: P, 12.6; N, 5.7; Mg, 9.9%. Accordingly, the product is magnesium phosphoramidate heptahydrate. The product was stable in air at room temperature.

DTA and TG in Air. DTA and TG curves of $MgPO_3NH_2 \cdot 7H_2O$ are shown in Fig. 1. The samples as numbered on Fig. 1 were removed from a furnace, cooled in a silica-gel desiccator, and then subjected to further analysis. The results are presented in Table 1 and Fig. 2. As Table 1 shows, the first large endo-

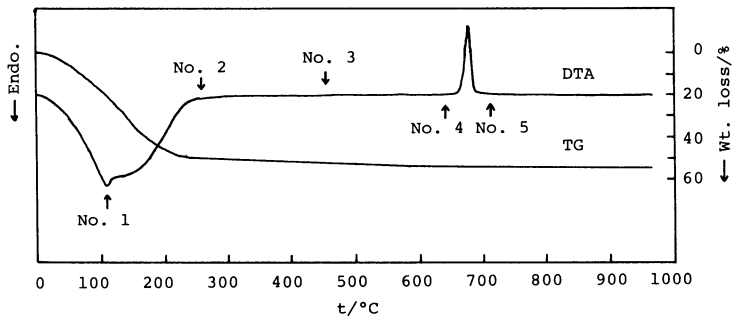


Fig. 1. DTA and TG curves of $MgPO_3NH_2 \cdot 7H_2O$ in air.

Table 1. Weight loss of the product and composition of the thermal decomposition products

Sample	Total N/%	Water/%	Wt. loss/%	Phosphates/P%			
				Ortho & Amido	Di & Imidodi	Tri	Higher
Product	5.7	51.4	—	100	0.0	0.0	0.0
No. 1	6.1	32.2	20.8	85.6	8.0	6.3	0.0
No. 2	3.5	6.1	49.9	61.0	35.0	4.0	0.0
No. 3	0.6	1.9	53.3	28.6	46.3	15.1	10.0
No. 4	0.0	0.0	54.7	—	—	—	—

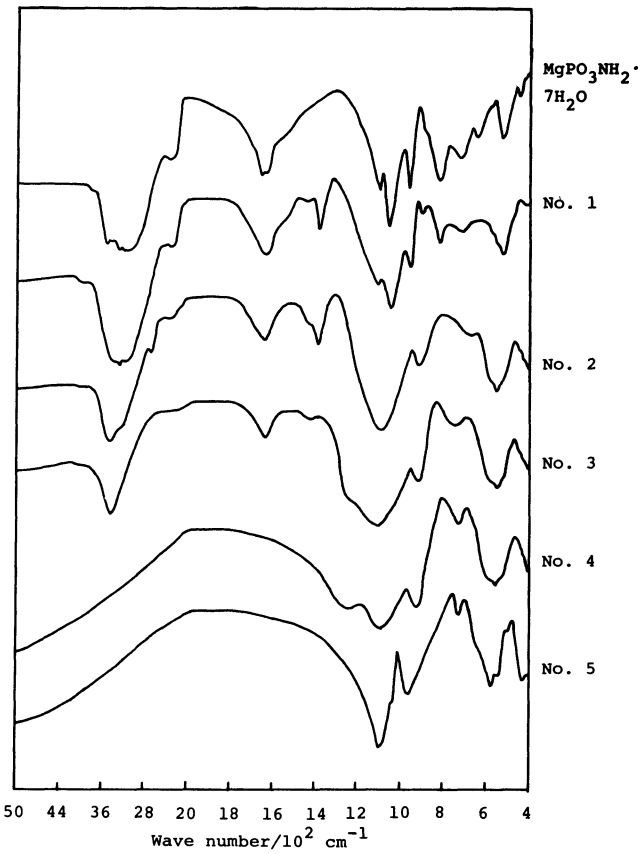
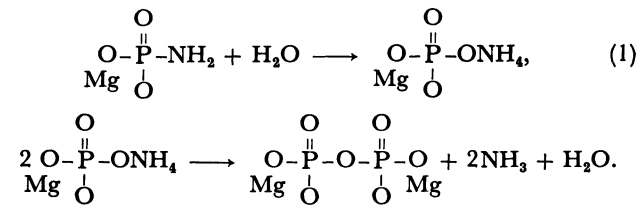


Fig. 2. IR spectra of the thermal decomposition products of $MgPO_3NH_2 \cdot 7H_2O$ in air.

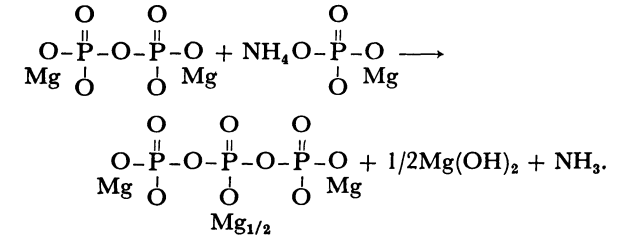
thermic peak, with an accompanying rapid weight loss, seemed to be due to the elimination of bound water, and the endothermic reaction between 120 and 250 °C also included the elimination of ammonia. IR spectra of Nos. 1 and 2 showed the absorption of NH_4^+ at 1400 cm^{-1} and those of a P-O-P or a P-NH-P linkage at 940 and 740 cm^{-1}. Sample No. 1 gave X-ray diffraction peaks of $MgPO_3NH_2 \cdot 7H_2O$. Samples Nos. 2—4 were X-ray diffractometrically amorphous. After the large endothermic peaks, the weights of the samples gradually decreased until about 600 °C. The IR spectra of Nos. 3 and 4 had a large absorption due to a $(PO_3)^{2-}$ group at 1100 cm^{-1}. The absorptions of the two samples at 940 and 720 cm^{-1} seemed to be associated with a P-O-P linkage because, as Table 1 shows, the samples contained only a slight amount of nitrogen or did not contain any nitrogen at all. The two samples also exhibited an absorption at around 1250 cm^{-1}. Table 1 shows that sample No. 3 involves tri- and higher polyphosphates. So the absorption at 1250 cm^{-1} may be caused by the middle-PO_4 group of these polyphosphates. Samples Nos. 4 and 5 were insoluble in water or an aqueous EDTA solution and it was impossible to check the composition of the phosphates in the samples by the paper chromatography. The absorption of No. 4 at 1250 cm^{-1} may be due to a middle-PO_4 group of polyphosphates with chain lengths longer than that of diphosphate. The sample No. 5 did not show the absorption of a middle-PO_4 group and exhibited an X-ray diffraction diagram of $Mg_2P_2O_7$ (ASTM card, No. 8—38). So the exothermic peak at about 670 °C seemed to be due to crystallization of the amorphous phosphates to the diphosphate. According to stoichiometric considerations and the results obtained above, one can write the following thermal decomposition and condensation equations for the product:



(1)

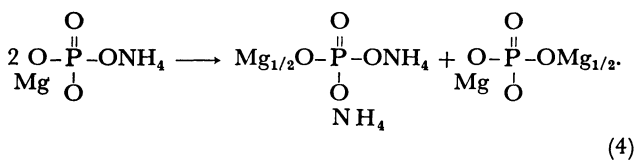
(2)

The above equations show it is unreasonable for tri- and higher polyphosphates to be produced as intermediates of the thermal decomposition products. The following condensation reaction is considered to be difficult to occur at the relatively low temperature range of 100—600 °C; it has not been known to take place in this temperature range:



(3)

The conflict can be resolved by the consideration that the following disproportionation reaction is taking place in the amorphous thermal decomposition products:

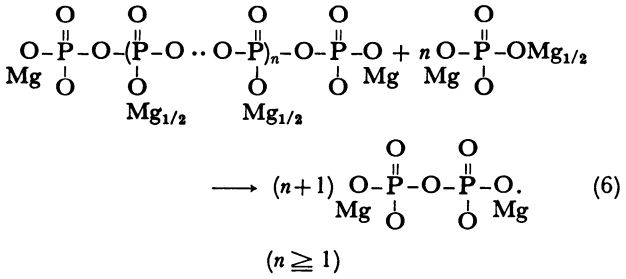


(4)

The species, $Mg_{1/2}(NH_4)_2PO_4$, is bifunctional for thermal condensation and can produce tri- and higher polyphosphates. As the final thermal decomposition product of $MgPO_3NH_2 \cdot 7H_2O$ showed an X-ray diffraction diagram of magnesium diphosphate and did not show an IR absorption of a $(PO_2)^-$ group, the following overall-thermal decomposition reaction can be written for the phosphoramidate:

$$2MgPO_3NH_2 \cdot 7H_2O \longrightarrow Mg_2P_2O_7 + 2NH_3 + 13H_2O. \quad (5)$$

The experimental final weight loss of the product showed a value very close to the calculated one for this decomposition reaction. The disappearance of polyphosphates with chain lengths longer than that of diphosphate in the thermal product can be explained by the following reorganization or degradation of the amorphous phosphates to diphosphate:



$$\longrightarrow (n+1)\ \mathrm{Mg}\text{-}\mathrm{O}\text{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}\text{-}\mathrm{O}\text{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}\text{-}\mathrm{O}\text{-}\mathrm{Mg}. \quad (6)$$

$(n \geqq 1)$

According to these results, it is not definitive yet that P-NH_2 linkages thermally decompose to form P-NH-P linkages by the elimination of ammonia. To obtain the data about this point, ^{31}P NMR spectrum of No. 2 was taken, because the thermal reaction seemed active at the temerature range and the sample still contained 3.5% of nitrogen. The sample indicated the ^{31}P NMR peaks of orthophosphate, phosphoramidate, and diphosphate, and did not show any peak of phosphates with an imino group. Therefore, magnesium phosphoramidate-water (1/7) did not decompose to make P-NH-P linkages thermally in air.

Isothermal Reaction at 150 °C. To obtain more detailed data about the thermal decomposition of the phosphoramidate, the isothermal decomposition of the phosphoramidate was carried out in air at 150 °C. This temperature is suitable for the analysis because the thermal reaction of the product was active and the elimination of ammonia from the decomposition product was not so rapid at this temperature. IR spectra of the isothermal decomposition products are presented in Fig. 3. With the passage of heating time, the

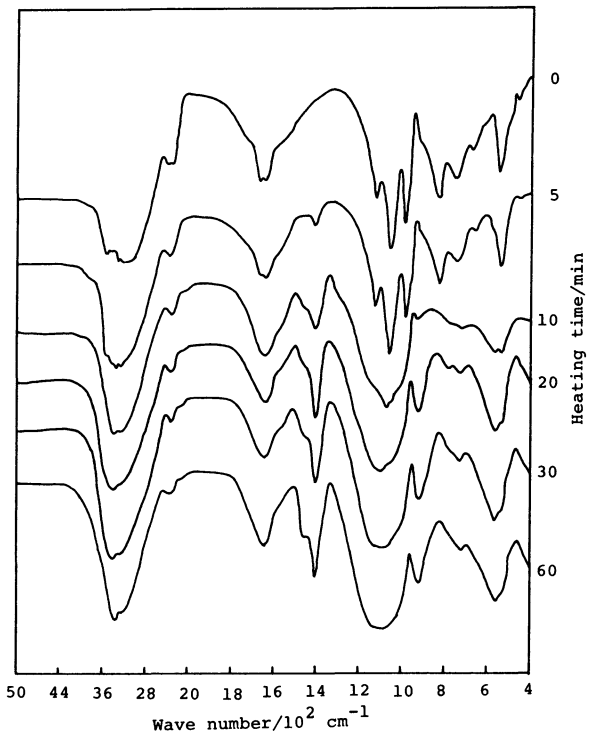


Fig. 3. IR spectra of the thermal decomposition products in air at 150 °C.

absorption of NH_4^+ at 1400 cm^{-1} and of a P-O-P or a P-NH-P linkage at 940 and 740 cm^{-1} appeared and their intensity increased, while the intensity of the absorption of a P-N linkage at 820 cm^{-1} decreased and disappeared after 10 min. These data show that Reactions 1 and 2 are taking place in the isothermal reaction of the phosphoramidate. The result listed in Table 2 well explains the change in the IR spectra of the decomposition products. The separation between orthophosphate and phosphoramidate and between di- and imidodiphosphate was not clear, but the result well agrees with the appearance of a P-O-P or a P-NH-P linkage in the IR spectra of the decomposition products. The above results do not indicate clearly that P-NH_2 linkages thermally decompose to form P-NH-P linkages with the elimination of ammonia at 150 °C. The ^{31}P NMR spectrum of the isothermal decomposition product at the reaction time of 30 min was taken. The sample did not show any peaks other than those of ortho-, monoamido-, and diphosphates. Therefore, magnesium phosphoramidate-water (1/7) may isothermally decompose at 150 °C according to

Table 2. Weight loss of the product and composition of the thermal decomposition products in air at 150 °C

Reaction time/min	Total N/%	N/% as NH_4^+	Water/%	Wt. loss/%	Phosphates/P%		
					Ortho & Amido	Di & Imidodi	Tri
0	5.7	—	51.4	—	100	0.0	0.0
5	5.6	1.2	40.4	8.3	84.1	12.4	3.5
10	5.5	2.2	31.2	19.9	70.8	22.9	6.3
20	5.4	2.3	15.5	37.7	68.7	26.4	4.9
30	5.2	2.5	8.9	44.8	68.2	27.4	4.4
60	4.4	2.8	5.9	48.4	68.1	28.2	3.7
120	3.8	2.7	4.6	49.3	66.1	30.2	3.7

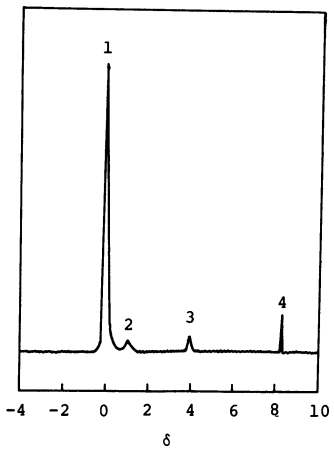


Fig. 4. ^{31}P NMR spectrum of the thermal decomposition product in dried N_2.
1: Orthophosphate, 2: imidodiphosphate, 3: phosphoramidate, 4: diphosphate.[10]

Reactions 1 and 2, and does not decompose to form a P-NH-P linkage. The result in Table 2 also seems to show that Reaction 4 and a condensation reaction of the product made by the disproportionation are taking place at the same time.

DTA and TG in Dried N_2. In dried N_2, $MgPO_3NH_2 \cdot 7H_2O$ gave quite similar DTA and TG curves to those in air and the decomposition products showed the same IR and X-ray diffraction data as those in air. It could be concluded that the product decomposes in dried N_2 according to a process analogous to that in air. A ^{31}P NMR spectrum of the decomposition product which was produced by heating the phosphoramidate by 250 °C by the DTA-TG instrument in dried N_2 is shown in Fig. 4. The small peak at 1.1 ppm was considered to be caused by imidodiphosphate. A small amount of the phosphoramidate may decompose in dried N_2 to make a P-NH-P linkage by the elimination of ammonia according to the following reaction:

$$2\ \mathrm{O{-}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{|}}{P}}{-}NH_2} \longrightarrow \mathrm{O{-}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{|}}{P}}{-}NH{-}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{|}}{P}}{-}O} + NH_3. \qquad (7)$$

Mg Mg Mg

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