BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3795—3799 (1973)

Studies of Nitrogen-Phosphorus Compounds. XXV.[1] The Synthesis of Guanidium Condensed Phosphates

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(Received April 13, 1973)

In order to develop fireproof materials, an attempt was made to prepare guanidium condensed phosphates ($(H_5CN_3)_n \cdot H_{n+2}P_nO_{3n+1}$, $n=1$—10) by means of a reaction between dicyandiamide ($H_4C_2N_4$) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$) in an autoclave; then the conditions of the synthesis were investigated, and the components of the product were also identified. In the synthesis of gaunidium salt by means of a reaction between dicyandiamide and ammonium salt, generally only ammonium salts of strong acid have been used; also, high yields of guanidium salt could not be obtained with the $(NH_4)_2HPO_4$ used previously. In the present study, a mixture of 1 mol of $H_4C_2N_4$ and 2 mol of $NH_4H_2PO_4$ was heated in an autoclave at 130—300 °C; 70—80% of the dicyandiamide was then converted into guanidium salt under the most suitable conditions. The majority of the product is soluble in water (the insoluble part is less than 3.5% at 150—220 °C), and the solution is almost neutral. The components of the soluble part were 25—26% N and 20—24% P, the mole ratio of N to P being 2.8—2.5; this ratio decreased with an increase in the reaction temperature. On the other hand, the phosphates in the product consist of ortho-, pyro-, tri-, and middlepoly phosphates ($n=4$—10). The guanidium condensed phosphates thus obtained can be utilized as useful flame retarders for paper and wood, as guanidium orthophosphate can be.

Among the derivatives of calcium cyanamide, dicyandiamide, guanylurea, guanidine, and melamine are useful industrial materials. Most of these compounds can readily be obtained from dicyandiamide, as is shown in Fig. 1. The guanidium salts have been formed by reaction fusing a mixture of dicyandiamide and the salt of a strong acid, such as ammonium nitrate or ammonium chloride. An attempt has already been made to prepare guanidium phosphate by means of a reaction between dicyandiamide and diammonium hydrogen phosphate in a sealed tube,[2] with water as the medium, however, a high yield of guanidium phosphate cannot be expected because of the slow reaction rate and the secondary reaction. Therefore, this method has not been employed as an economical process for manufacturing guanidium phosphate. Recently, however, monoguanidium and diguanidium phosphates, which are prepared by the neutralization of guanidium carbonate with phosphoric acid or by a double decomposition between guanidium chloride and sodium phosphate, have been recognized as fireproof materials. As guanidium orthophosphates, a certain derivative of calcium cyanamide and guanidium condensed phosphates may also be used as fireproof materials.

The present author has previously investigated the preparation of ammonium condensed phosphates by the thermal dehydration of $NH_4H_2PO_4$[3] and the

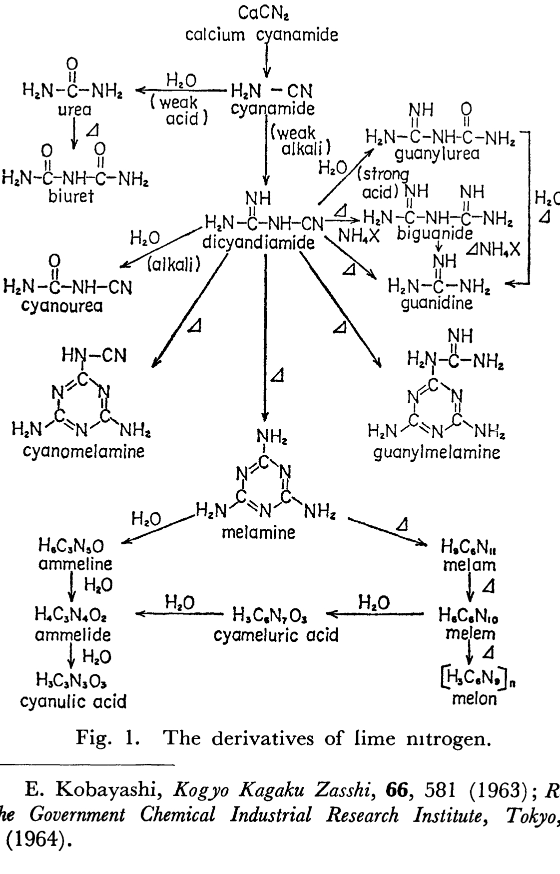

Fig. 1. The derivatives of lime nitrogen.

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[1] a) The article was presented at the 29th Annual Meeting of the Chemical Society of Japan, Hiroshima, October, 1973.
b) Part XXIV of this series: E. Kobayashi, *Nippon Kagaku Kaishi*, **1973**, 1437.

[2] K. Sugino, *Nippon Kagaku Zasshi*, **60**, 267 (1937).

[3] E. Kobayashi, *Kogyo Kagaku Zasshi*, **66**, 581 (1963); *Reports of the Government Chemical Industrial Research Institute, Tokyo*, **59**, **516** (1964).

reaction between $NH_4H_2PO_4$, $(NH_2)_2CO$, and H_2O.[4] In the present work, a mixture of 1 mol of dicyandiamide and 2 mols of ammonium dihydrogen phosphate is heated in an autoclave. From the analysis of the resulting products, it is found that most of the orthophosphate is converted into condensed phosphates, and also that 70—80% of the dicyandiamide used is converted into guanidine under the most suitable conditions. In order to ascertain the mechanism of this reaction, the thermal decomposition of monoguanidium phosphate itself is also examined. In this paper, an experimental study of the preparation of guanidium condensed phosphates will also be described.

Experimental

Synthesis. Heat Treatment of Monoguanidium Phosphate: Monoguanidium phosphate was prepared by the neutralization of guanidium carbonate with phosphoric acid. Found: N, 26.7; P, 19.5%. Calcd for $CN_3H_5 \cdot H_3PO_4$: N, 26.7; P, 19.74%. A 20-g portion of this phosphate is placed in a 100-ml test tube; the vessel is then immersed in an oil bath regulated at a proper temperature. The resulting melted products are sampled at proper intervals, and their weight loss on heating and the components are estimated.

Reaction between Dicyandiamide and Ammonium Dihydrogen Phosphate: A mixture of 1 mol of dicyandiamide ($H_4C_2N_4$) and 2 mol of ammonium dihydrogen phosphate ($NH_4H_2PO_4$) was employed as the starting material. A 5-g portion of the mixture was placed in a 100-ml test tube; the vessel was then immersed in an oil bath regulated at a proper temperature for 60 min. After the reaction product had swollen and solidified, it was collected as a powder by raking.

Analysis. A sample solution for analysis was prepared in the following way. A 1.25-g portion of the heating product of $H_5CN_3 \cdot H_3PO_4$ was weighed exactly and dissolved in water, and the volume of the solution was adjusted to 250 ml. A 2.00-g portion of the reaction product between $H_4C_2N_4$ and $NH_4H_2PO_4$ was also weighed exactly, a 50-ml portion of water was added, and the mixture was stirred for 2 hr. The resulting insoluble part was separated from the filtrate, dried for 60 min at 110 °C, and then weighed, while the volume of the filtrate was adjusted to 100 ml.

The phosphorus content was determined gravimetrically as magnesium pyrophosphate. The total nitrogen content was determined by Kjeldahl's method.

In the separation and determination of the condensed phosphates, we used ion-exchange chromatography,[5] the procedures being those of the previously-reported successive elution (see Fig. 5 I, II) and gradient elution (see Fig. 5 III), and paper chromatography using an acid solvent.[6]

In the separation of non-cyclic cyanamide derivatives, we used Takimoto and Koeda's[7] paper chromatography. The non-cyclic cyanamide derivatives were also analysed by Takimoto and Yao's[8] ion-exchange chromatography. The results of the determination of guanidine as the main product accorded with those of Kurabayashi and Yanagiya's[9] method.

The differential thermal analysis (DTA) and thermogravimetric measurements (TGA) were performed simultaneously under a nitrogen atmosphere and at a heating rate of 5 °C/min, using a Rigaku-Denki model DC-Cl-S thermal analyser.

Results and Discussion

Change in Monoguanidium Phosphate upon Heating. It is supposed that guanidium phosphate, which may be formed by the reaction of dicyandiamide and ammonium phosphate, is converted into the condensed phosphates at a high temperature, and that it finally decomposes into condensed phosphoric acids and ammonia. Therefore, the thermal decomposition of guanidium phosphate was examined.

Thermal Analysis. The DTA and TGA curves for diguanidium phosphate and monoguanidium phosphate are shown in Fig. 2. Diguanidium phosphate begins to decompose at about 235 °C, and a remarkable weight loss is observed. From the diagrams, it is supposed that guanidine radicals are decomposed above 300 °C. Monoguanidium phosphate begins to melt at 110 °C; consequently, an endothermic peak appears. A weight loss of 2—5% is observed at 110—250 °C. It is considered that, in this temperature range, the condensation occurs as a result of the thermal dehydration of monoguanidium phosphate,

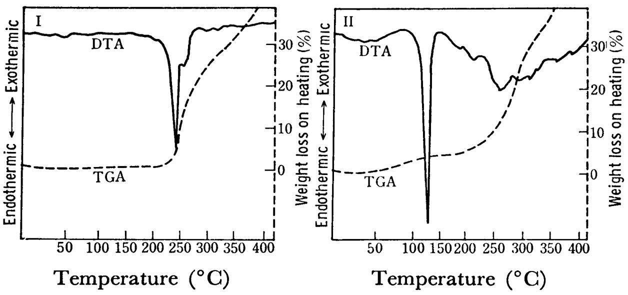

Fig. 2. DTA and TGA curves for guanidium phosphates.
I: diguanidium phosphate
II: monoguanidium phosphate
Sample: 100 mg, Heating rate: 5°C/min, Current gas: Nitrogen 0.3 l/min.

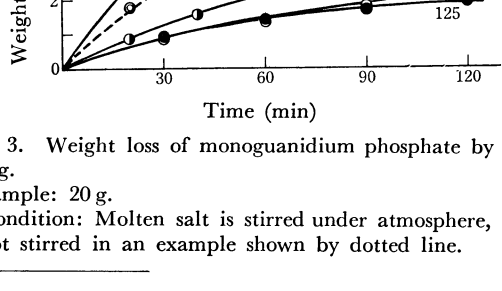

Fig. 3. Weight loss of monoguanidium phosphate by Heating.
Sample: 20 g.
Condition: Molten salt is stirred under atmosphere, but is not stirred in an example shown by dotted line.

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[4] E. Kobayashi, *Kogyo Kagaku Zasshi*, **69**, 2065 (1966); *Reports of the Government Chemical Industrial Research Institute, Tokyo*, **63**, 263 (1968).

[5] E. Kobayashi, *Nippon Kagaku Zasshi*, **85**, 317 (1964).

[6] E. Karl -Kroupa, *Anal. Chem*, **28**, 1091 (1956).

[7] M. Takimoto and I. Koeda, *Kogyo Kagaku Zasshi*, **63**, 797 (1960).

[8] M. Takimoto and T. Yao, *ibid.*, **63**, 1936 (1960); *ibid.*, **63**, 1941 (1960).

[9] M. Kurabayashi and K. Yanagiya, *Reports of the Government Chemical Industrial Research Institute, Tokyo*, **51**, 39 (1956).

Table 1. Dehydration products of guanidium dihydrogen orthophosphate

No.	Reaction conditions			Analysis							
	$H_5CN_3 \cdot H_3PO_4$ (g)	Temp. (°C)	Time (min)	N (%)	P (%)	N/P Atomic ratio	pH	Ortho- (%)	Pyro- (%)	Tri- (%)	Middle poly (%)
1	20	125	120	26.4	19.8	2.93	—	69	31	0	0
2	20	150	120	26.5	19.7	2.97	5.03	50	50	0	0
3	20	175	120	26.7	19.7	3.00	5.55	44	51	5	0
4	20	200	90	26.8	19.9	2.97	6.12	34	52	13	1
5—1	20	225	20	27.9	20.5	3.02	5.83	51	33	16	0
5—2	20	225	40	27.6	21.1	2.89	5.99	48	19	20	13
5—3	20	225	60	27.2	21.5	2.80	5.90	25	29	19	27
5—4	20	225	90	27.1	22.1	2.72	5.90	21	23	18	38
5—5	20	225	120	26.9	22.7	2.62	5.80	18	18	19	45

and that the guanidine radical does not decompose very much.

Then, the weight changes in monoguanidium phosphate at various temperatures were measured. The results are shown in Fig. 3. Monoguanidium phosphate melts when heated; the rate of dehydration increases with the rise in the temperature, but it does not change very much at 125, 150, and 175 °C. The weight loss is 5.5% for 1 hr and 7.5% for 2 hr at 200 °C. In this case, the rate of thermal dehydration is affected by the considerable viscosity of the salt, so the melting salt was stirred while being heated.

Components of Products. The heating conditions of monoguanidium phosphate and the results of the analysis of the products are summarized in Table 1.

The contents of phosphorus and nitrogen in the product are not very different at 125—250 °C. In this temperature range, the atomic ratio of N to P in the products is roughly analogous to that (3 : 1) in the monoguanidium phosphate used as the starting material. The odor of ammonia is remarkable upon the thermal decomposition of the guanidium radical above 200 °C. It can be supposed that other cyanamide compounds are also formed upon the decomposition of guanidium phosphate. Therefore, a paper chromatogram of the product was compared with those of various cyanamide derivatives used as standard materials; they are shown in Fig. 4.

In these results, the R_f values of the cyanamide derivatives are as follows: biguanidium sulfate (A), 0.10—0.14; monoguanidium dihydrogen phosphate (B), 0.16—0.27; guanylurea (C), 0.34; urea (D), 0.41; biuret (E), 0.44; and dicyandiamide (F); 0.54. From the values of the spots of the heating product, the existence of a little biguanide and guanylurea in addittion to the guanidium salt, which is the main constituent, is recognized. Therefore, the guanidium salt is converted into biguanide by the separation of 1 mol of ammonium from its 2 mol; a part of the biguanide thus formed is also converted into guanylurea by hydration and deammonation. It can be considered that the formation of biguanide described above corresponds to a reverse reaction of the formation of guanidium salt from dicyandiamide and ammonium salt; an equilibrium exists between these reactions. The species of phosphate in the heating product are estimated by paper chromatography and ion-exchange chromatography (see Fig. 5 II); the results are summarized in Table 1,

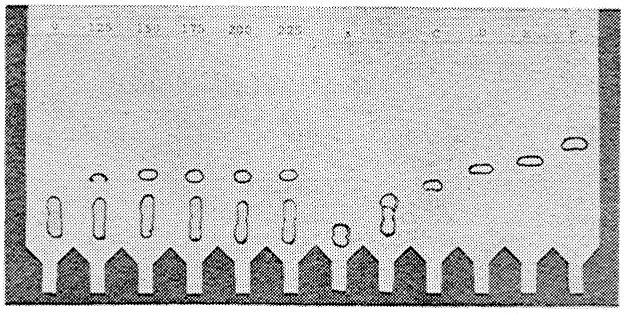

Fig. 4. Paper chromatogram for various cyanamide derivatives and heating products of monoguanidium dihydrogen phosphate.

Numerals in the photograph indicate heating temperatures (°C).

Symbols (A-F) indicate species of cyanamide compound, A: biguanidium sulfate, B: monoguanidium dihydrogen phosphate, C: guanylurea, D: urea, E: biuret, F: dicyandiamide.

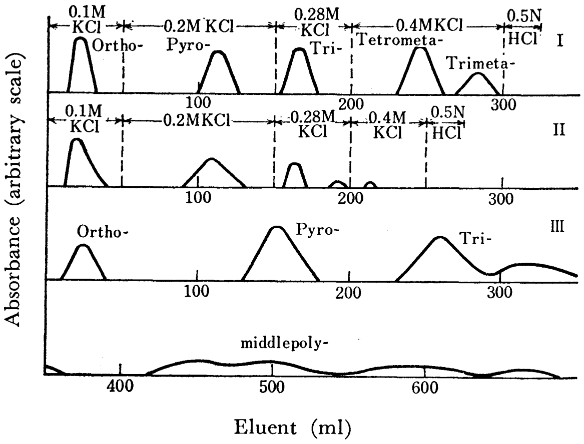

Fig. 5. Chromatographic analysis of condensed phosphates and reaction products.

I: Mixture of condensed phosphates.

II: Heating product of $H_5CN_3 \cdot H_3PO_4$ (Table 1, No. 4)

III: Reaction product between $H_4C_2N_4$ and $NH_4H_2PO_4$ (Table 2, No. 7)

Eluent for gradient elution method: 400 ml 0.2 mol/l KCl in mixing bottle, 500 ml 0.35 mol/l KCl in stock bottle.

while an ion-exchange chromatogram is shown in Fig. 5 (II). The orthophosphate used as the starting material is converted partially into pyrophosphate and triphosphate at 125—200 °C; besides, middlepoly phosphates (n=4—8) are formed above 225 °C.

Reaction between $H_4C_2N_4$ and $NH_4H_2PO_4$. Generally, guanidium salts are formed by a reaction between dicyandiamide and ammonium salt such as:

$$H_4C_2N_4 + 2NH_3 \cdot HX \rightleftharpoons 2H_5CN_3 \cdot HX$$

Sugino2) has already reported the formation of guanidium phosphate by the heating of a mixture consisting of 1 mol of dicyandiamide, 1 mol of diammonium hydrogen phosphate, and about 4.5 mol of water in a sealed tube. The yields of guanidine were 25, 48, and 61% at 140, 160, and 180 °C respectively. His report concluded that the deficiency of NH_4^+ required for the reaction rises from the separation of ammonia from $(NH_4)_2HPO_4$ at high temperatures; simultaneously, the reactant is converted into an alkaline solution, and the dicyandiamide used is immediately decomposed by the alkaline solution. It was also described that the pyrolysis of phosphate occurs in this reaction system. However, the formation of condensed phosphates was not investigated at all. As has already been described, the use of the ammonium salt of a strong acid is suitable for the synthesis of guanidium salt; therefore, $NH_4H_2PO_4$ instead of $(NH_4)_2HPO_4$ was employed initially in this work.

Reaction under Atmospheric Pressure. The reaction between 1 mol of dicyandiamide and 2 mol of ammonium dihydrogen phosphate was examined under atmospheric pressure. Consequently, remarkable weight losses were observed upon heating for 60 min; 6.5% at 150 °C, 22.2% at 185 °C, 23.5% at 200 °C, and 27.0% at 220 °C. Thus, the product decomposes, and its volume expands up to fifty times. Therefore, it has been concluded that the synthesis of guanidium phosphate is difficult under atmospheric pressure. However, the reactant in an autoclave is expanded slightly under the effect of the gas produced by its thermal decomposition.

Components of the Reaction Products. The reaction conditions between dicyandiamide and ammonium dihydrogen phosphate under pressure, and the results of the analysis of the products, are summarized in Table 2. The majority of the products were soluble in water; the insoluble part increases slightly with the rise in the reaction temperature, being within 3.5% at 150—220 °C. The pH of a 1% aqueous solution is 6.3—7.6. The content of nitrogen is about 25% at 150—220 °C; it decreases slightly above 250 °C. The content of phosphorus in the soluble part of a product increases as a result of the large dehydration

Table 2. Synthesis and analysis of guanidium condensed phosphates

No.	Reaction conditions				Reaction products			
	$H_4C_2N_4$ (g)	$NH_4H_2PO_4$ (g)	Temp. (°C)	Time (min)	1% Soln. pH	N (%)	P (%)	N/P Atomic ratio
1	1.34	3.66	120	60	4.60	25.8	19.7	2.90
2	1.34	3.66	130	60	5.71	25.4	20.1	2.80
3	1.34	3.66	140	60	6.30	25.5	20.3	2.79
4	1.34	3.66	150	60	6.99	26.0	20.7	2.77
5	1.34	3.66	170	60	7.29	25.2	20.9	2.66
6	1.34	3.66	185	60	7.32	25.5	22.4	2.51
7	1.34	3.66	200	60	7.40	26.2	23.2	2.50
8	1.34	3.66	220	60	7.61	26.4	23.9	2.44
9	1.34	3.66	250	60	7.40	25.0	23.3	2.37
10	1.34	3.66	300	60	7.26	24.8	20.9	2.36

No.	Reaction products								
	Cyanamide derivatives					Condensed phosphates			
	$H_4C_2N_4$ (%)	H_5CN_3 (%)a)	$H_7C_2N_5$ (%)	$H_6C_3N_6$ (%)	I·Sc) (%)	Ortho- (%)	Pyro- (%)	Tri- (%)	Middlepoly (%)
1	100				0	100			
2	98.5			trace	0.11	98	2		
3	36.8	17.4	0.6	trace	1.92	35	24	20	21
4	3.5	62.0			3.05	19	30	23	28
5	0.6	69.3			2.66	15	28	24	33
6	0.3	72.8			3.22	13	26	22	39
7		75.0			3.51	12	25	22	41
8		78.9			3.49	12	19	23	46
9	0.7b)	62.6			6.46	14	17	21	48
14	1.4b)	47.7			6.70	18	15	22	45

a) Yield of guanidine to dicyandiamide as low material. b) Content of biuret. c) I·S; Insoluble product.

with a rise in the reaction temperature, but it decreases with an increase in the insoluble part above 250 °C. The mole ratio of N to P in the mixture of dicyandiamide and ammonium dihydrogen phosphate is theoretically 3 : 1; however, the mole ratios of the products are less than 3 : 1, and the separation of ammonia from the reactant is observed.

Condensed Phosphate in Product. The results of the analysis of the condensed phosphates by means of paper chromatography are summarized in Table 2, while an example of an ion-exchange chromatogram is shown in Fig. 5 (III). The phosphate species from ortho- to decapolyphosphate can be separated by employing gradient elution chromatography,[5] but the ion-exchange chromatogram of the phosphates in a product is separated into eight fractions with tailing because of the effect of the cations connected to the cyanamide derivatives. That is, the reaction products consist of ortho-, pyro-, tri-, and middlepoly phosphates, which have polymerization degrees of about 4—10.

Formation of Cyanamide Derivatives. The paper chromatogram for a mixture of standard materials (S) and the products is shown in Fig. 6. The products do not change at 120 °C and give only the spot of dicyandiamide as the starting material. The proportion of dicyandiamide decreases at 140 °C, and the spots of guanidium salt, a little guanylurea, and biguanide appear. The spot of a little dicyandiamide remains at 150 and 170 °C, but most of the products are converted into guanidium salt; here, the spot of guanidium salt is long and elliptical, and it also possesses the position of the spot for biguanidium salt. As has been described previously, the biguanide is formed upon the heating of monoguanidium phosphate; therefore, although we do not say specifically that biguanidium salt is not formed in this reaction, the existence of its salt is not observed by the chemical analysis. In this case, the long ellipse of the spot seems to be characteristic of guanidium condensed phosphates. The only spot of guanidium condensed phosphates appeared at 185—220 °C. Another spot appeared in the position under the spot of dicyandiamide above 250 °C. Perhaps, this spot indicates the biuret formed by the thermal decomposition of the products. The paper chromatography can distinguish various cyanamide derivatives in the product, but the color of the spot is not clear and its decolorization is remarkable. Therefore, the ion-exchange chromatography of cyanamide derivatives was also examined; an example of a chromatogram is shown in Fig. 7.

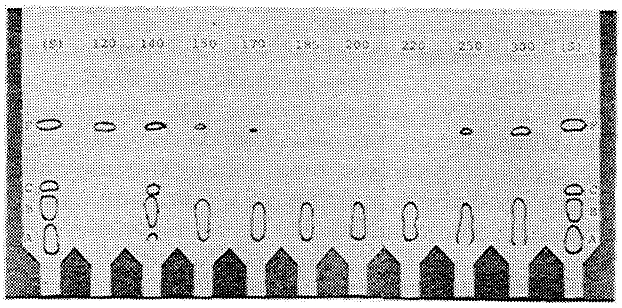

Fig. 6. Paper chromatogram for cyanamide derivatives in reaction product.
Numerals in the photograph indicate the reaction temperatures (°C).
(S): standard material, A: biguanide, B: guanidine, C: guanylurea, F: dicyandiamide.

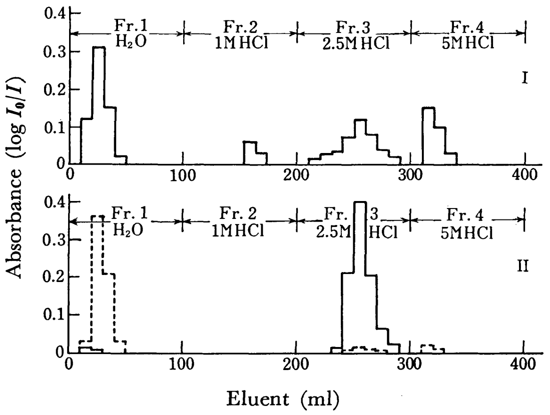

Fig. 7. Chromatographic analysis of cyanamide derivative and reaction product.
I: Mixture of cyanamide compounds (Fr. 1; dicyandiamide or biuret, Fr. 2; guanylurea, Fr. 3; guanidine, Fr. 4; biguanide).
II: Reaction products (----; Table 2 No. 3, ——; Table 2 No. 8).

Dicyandiamide and biuret on a cation-exchange resin are easily carried away by water and are received almost quantitatively. On the other hand, guanylurea, guanidine, and biguanide can be separated by using hydrochloric acid in different concentration as eluates, though the yields expected from the description in a previous paper[8] are not obtained because of the decomposition of these compounds by the acid used. Therefore, the ion-exchange chromatography also confirms the existence of cyanamide derivatives in a product; it is employed for the estimation of dicyandiamide and biuret. The results are shown in Table 2.

The main product, guanidine, was estimated by means of the chemical analysis already described for cyanamide derivatives; the results are shown in Table 2. Dicyandiamide is converted into guanidium salt beginning at 140 °C, and the yield of guanidine increases with the increase in the reaction temperature. more than 70% of the dicyandiamide used is converted at 185—220 °C; the maximum is 78.9%. This value is improved remarkably as compared with the yields when diammonium hydrogen phosphate is used as the starting material. Upon a further increase in the reaction temperature, the decomposition of the product occurs, the yield of guanidine decreases, and a little biuret is formed. Guanylmelamine and melamine can be also estimated by chemical analysis; the former can not be detected in any products, while the latter exists in small amounts in the products at 130—140 °C.

The author wishes to thank Dr. Masahiro Kurabayashi for his helpful advice.