Mechanism of the Formation of Guanidine and its Derivatives by the Fusion of Dicyandiamide with Amine Salt

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This contribution is the abstract of my papers already published in Japanese in the Journal of the Chemical Society of Japan in 1939 and 1944.[1] Some new facts found by the further experiments are added.

I. Mechanism of the Reaction between Dicyandiamide and Ammonium Salt

Dicyandiamide is converted by its reaction with ammonium salt into guanidine salt.

$$C_2H_4N_4+2NH_3\cdot HX=2CH_5N_3\cdot HX$$

This reaction was studied using several ammonium salts in fused state and also in aqueous solution.[2] The difference of the reaction velocity and the yield of guanidine salt due to the difference of ammonium salt was discussed systematically. For each salt, especially the nitrate, the conditions were determined under which the good yield of guanidine salt should be expected. The result was later applied to the commercial preparation of guanidine nitrate by Dr. K. Odo.[3]

The mechanism of this reaction has not yet been clearly explained except that biguanide salt is probably the intermediate product.[4] In order to clarify this mechanism, the following items were studied successively.

a) The condition of the formation of biguanide salt by the fusion of dicyandiamide with ammonium salt.

b) The fusion of biguanide monosalt* with ammonium salt.

c) The thermal decomposition of biguanide monosalt in fused state.

Quantitative determination of the reaction products, the measurement of the heating curve and also the heat of reaction were carried out for each reaction. The main results obtained are summarized as follows.

a) By the fusion of 1 mol. of dicyanidiamide with 2 mol. of ammonium salt, biguanide salt was first formed preceding the guanidine formation. But the former was converted to guanidine salt even at the temperature as low as 120°C according to the reaction (2, 2′) described later. The results are shown in Table I.

TABLE I

Dicyandiamide 4.2 g.
NH_4NO_3 8.0 g.
M. p. of the mixture, 116°C.

Temp.	Time	Biguanide-HNO_3*		Guanidine-HNO_3**		Insoluble residue of water extraction	Dicyandiamide (unconverted)
(°C)	(hr.)	(g.)	(%)	(g.)	(%)	(g)	
120	2	1.79	21.8	—	—	0.01	remains quantitatively
120	3	1.85	22.6	2.25	18.4	0.01	〃 〃
120	4	1.85	22.6	3.26	26.7	0.01	〃 〃

* Determined as nickel-biguanide and reduced to nitrate.

** Determined as picrate and reduced to nitrate.

TABLE II

Biguanide mononitrate 8.2 g.
NH_4NO_3 4.0 g.
M. p. of the mixture, 131°C.

Temp.	Time	Guanidine-HNO_3*		Insoluble residue of water extraction	Biguanide
(°C)	(min.)	(g.)	(%)	(g.)	
above 180	10	11.7	96	0.02	trace
〃 180	17	10.7	88	0.02	〃

* Determined as picrate and reduced to nitrate.

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[1] K. Sugino, *J. Chem. Soc. Japan*, **60**, 351, 411 (1939); K. Sugino, M. Yamashita and S. Izumi, **65**, 265, 271 (1944); C.A., **35**, 5097 (1941); 3763 c (1947).

[2] K. Sugino, *J. Chem. Soc. Japan*. **60**, 267 (1939).

[3] K. Odo, *J. Chem. Soc. Japan* (Industrial Chemistry Section), **52**, 210 (1949).

[4] Blair, Braham *J. Am. Chem. Soc.*, **44**, 2342 (1922); Smith, Sabetta, Steibach, *Ind, Eng. Chem.* **23**, 1124 (1931).

* Biguanide dinitrate did not give any guanidine salt by its reaction with ammonium salt. The description of Smith, Sabetta and Steinbach (4) is erroneous.

b) By the fusion of 1 mol. of biguanide monosalt with 1 mol. of ammonium salt, corresponding guanidine salt was obtained in yield as same as that obtained by the reaction between 1 mol. of dicyandiamide and 2 mol. of ammonium salt. The results obtained using nitrate are shown in Table II.*

The phenomenon of the heat evolution due to the guanidine formation was observed in the heating curve of their reactions (Fig. 1).

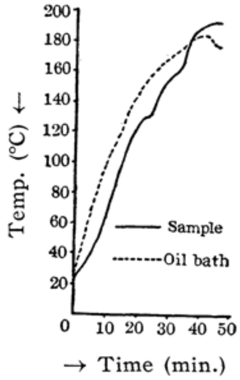

Fig. 1. Biguanide HNO_3 8.2 g. NH_4NO_3. 4.0 g.

But it was not very great compared with the same phenomena found in the heating curve of the reaction between 1 mol. of dicyandiamide and 2 mol. of ammonium salt (Fig. 2). In order to clarify these observations, the heat of reaction of each reaction must be be determined. For this purpose, the heats of combustion and formation of dicyandiamide and biguanide mononitrate were measured by the usual method (calorimetrical), which were found to be as follows.

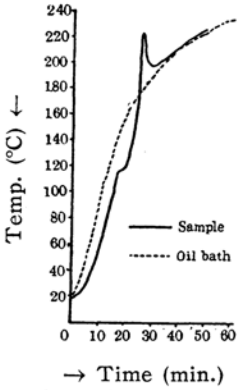

Fig. 2. Dicyandiamide 4.2 g. NH_4NO_3 8.0 g.

Substance	Heat of combustion per g.	Heat of combustion per mol. at constant pressure	Heat of formation per mol. from its elements at constant pressure** (ΔH_f)
Biguanide mononitrate	2274 cal	371.49 Kcal	−90.9 Kcal
Dicyandiamide	3926 cal	329.40 Kcal*	3.76 Kcal

* Later, the heat of combustion of dicyandiamide was measured by Salley and Gray (*J. Am. Chem. Soc.*, **70**, 2650 (1948)), his figure being 331.88 Kcal/mol.

** The heats of formation from the elements, ΔH_f, were calculated using 94.45 and 68.37 Kcal/mol. (18°C) for the heat of formation of gaseous carbon dioxide and of liquid water, respectively.[5] But recently, for these values, 94.05 and 68.32 Kcal/mol. (25°C, 1 atm.) seem to be used commonly.

For the heats of formation of ammonium nitrate and guanidine nitrate, the following data were taken from the literature.

Ammonium nitrate[5] ΔH_f/mol. −87.1 Kcal.,

Guanidine nitrate[6] ΔH_f/mol. −91.8 Kcal.

Then the heats of reaction of following reactions could be calculated which were given as follows.

$$NH_2\cdot C(NH)\cdot NH\cdot CN + NH_4NO_3 = (NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HNO_3 + 7.6\ \text{Kcal}$$

$$\underline{(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HNO_3 + NH_4NO_3 = 2(NH_2\cdot C(NH)\cdot NH_2)HNO_3 + 5.6\ \text{Kcal}}$$

$$NH_2\cdot C(NH)\cdot NH\cdot CN + 2NH_4NO_3 = 2(NH_2\cdot C(NH)\cdot NH_2)HNO_3 + 13.2\ \text{Kcal.}$$

These data seemed to correspond to the heat evolution in two heating curves.

c) The thermal decomposition of biguanide monosalt under fused state was found to give guanidine salt quantitatively as shown in Table III. Melamine was also found in a fair yield in the reaction product.

The most important observation was the existence of regenerated dicyandiamide in the reaction product when biguanide monosalt was cautiously decomposed under fused state at 190–195°C for 2–3 minutes so as to

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[5] Bichowsky und Rossini, "Thermochemistry of Chemical Substances," (Reinhold Publ. Corp.) 34 (1936).

* The same results were obtained using chloride or sulfate.

[6] Calculated by the author from the data of Matignon, *Chem. Centr.*, (1892) II, 199.

Table III

Biguanide-mononitrate: 10.00 g. (m.p. 202–3°C).
Conditions: According to Fig. 3.

Guanidine nitrate*		Melamine**		
(g.)	(%)	From solution	From insoluble residue of water extraction (1.67 g.)	(%)
7.31	98.3	0.54	1.05	62
		1.59 g.		
7.20	96.8	—		—

* Determined as picrate and reduced to nitrate.
** The amount of melamine is not quantitative.

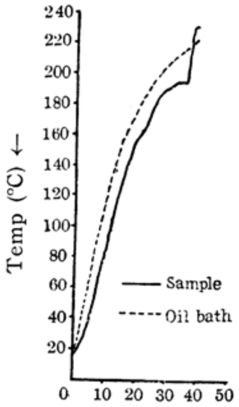

Fig. 3.

prevent spontaneous superheating due to the melamine formation*. For this purpose, about 2.0 g. or less amount of the sample must be used at a time. By extracting the pulverized reaction product by acetone and evaporating the extract to dryness, the crystal of dicyandiamide could be obtained. (From 15,00 g. of the reaction product, about 0.80 g. of dicyandiamide melting at 200°C was isolated. The melting point of the mixture of the sample with pure dicyandiamide was 203–205°C).

Then, the thermal decomposition of biguanide mononitrate may be represented as follows:

$$(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HNO_3=(NH_2\cdot C(NH)\cdot NH_2)HNO_3+NH_2\cdot CN$$
$$NH_2\cdot CN=1/3\ C_3H_6N_6$$
$$(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HNO_3=(NH_2\cdot C(NH)\cdot NH_2)HNO_3+\tfrac{1}{2}NH_2C(NH)\cdot NH\cdot CN$$

As the result of these ovservations, the author proposed a mechanism which is summarised as follows.

1) Dicyandiamide is first converted into biguanide monosalt by the addition of 1 mol. of ammonium salt.

$$NH_2\cdot C(NH)\cdot NH\cdot CN+NH_3\cdot HX$$
$$=(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX \quad (1)$$

2) Biguanide monosalt is next converted into 1 mol. of guanidine salt and 1 mol. of cyanamide or ½ mol. of dicyandiamide by the thermal decomposition.

$$(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX$$
$$=(NH_2\cdot C(NH)\cdot NH_2)HX+NH_2\cdot CN \quad (2)$$
$$(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX$$
$$=(NH_2\cdot C(NH)\cdot NH_2)HX+\tfrac{1}{2}NH_2\cdot C(NH)\cdot NH\cdot CN \quad (2')$$

3) The cyanamide or dicyandiamide formed in nascent state, reacts immediately with ammonium salt to give 1 mol. of guanidine salt or 0.5 mol. of biguanide monosalt successively.

$$NH_2\cdot CN+NH_3\cdot HX$$
$$=(NH_2\cdot C(NH)\cdot NH_2)HX \quad (3)$$
$$\tfrac{1}{2}NH_2\cdot C(NH)\cdot NH\cdot CN+\tfrac{1}{2}NH_3\cdot HX$$
$$=\tfrac{1}{2}(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX \quad (3')$$

The biguanide monosalt formed according to the reaction (3′) is again decomposed to guanidine salt and dicyandiamide (2′). The reaction (2) and (3) may take place at higher temperatures (at least above 160°C), whereas the reaction (2') and (3') at lower temperatures.

II. Mechanism of the Reaction between Dicyandiamide and Aniline Hydrochloride

The mechanism of the reactian between dicyandiamide and aniline hydrochloride was studied in order to generalise the mechanism of guanidine formation by the reaction between dicyandiamide and ammonium salt.

In this case, it was well known that the phenylbiguanide-HCl (the primary reaction product) was formed quantitatively.[7] Then,

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* The heats of reaction of (2), (2′) are endothermic.

[7] Lumière and Perrin, *Bull. soc. chim.*, [3] **33**, 205 (1905). Sugino et al, *Japanese Patent* 125272.

TABLE IV

Phenylbiguanide-HCl 15.00 g. (molar ratio 1)

Conditions* (A) 230°C. 2 min.
(B) 230°C. 2 min. after the heat evolution.
(C) 220–230°C. 2 min.

Product / Reaction	Monophenyl-guanidine*** Yield** (g.)	Monophenyl-guanidine*** Molar ratio	Guanidine*** Yield** (g.)	Guanidine*** Moler ratio	Diphenyl-guanidine Yield** (g.)	Diphenyl-guanidine Molar ratio	Inosoluble residue of Boiling water extraction (melamine derivatives) Yield** (g.)	Others Yield** (g.)
(A) Thermal decomposition of phenylbiguanide-HCl	2.70 2.81	0.29 0.30	1.26 0.96	0.30 0.23	—	—	3.38 3.40	— 2.87
(B) Reaction with ammonium chloride (3.78 g.)	4.68	0.49	1.88	0.45	—	—	1.66	1.57
(C) Reaction with aniline-HCl (9.12 g.)	4.72	0.50	0.67	0.16	5.55	0.37	3.22	2.40

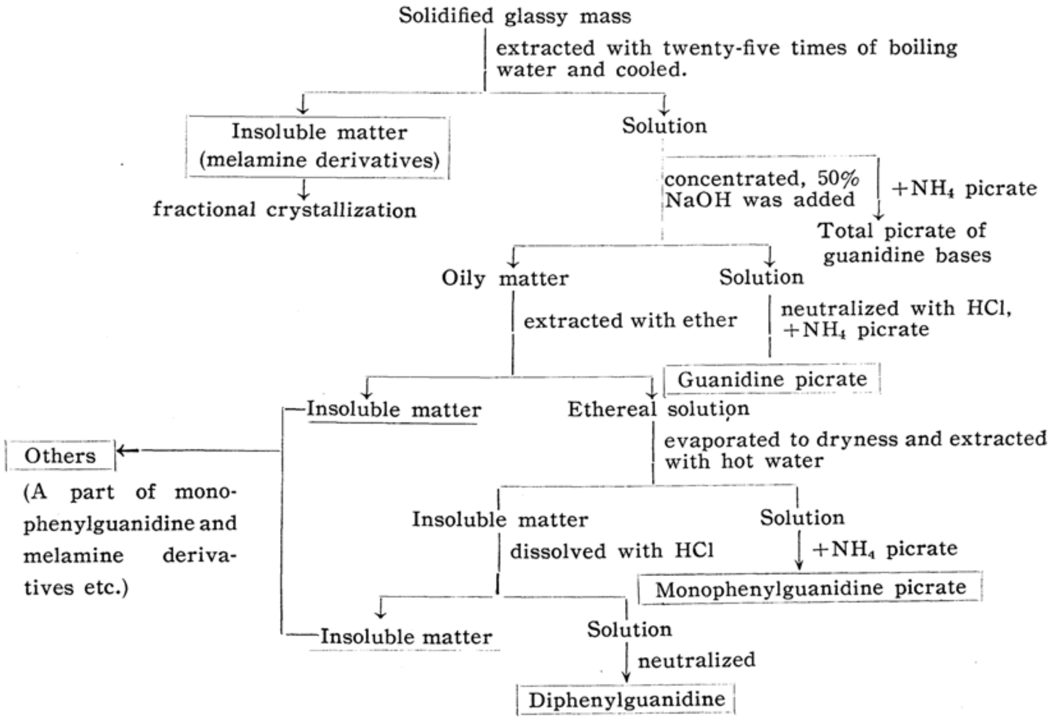
* The mixture melted at (A) 237°C., (B) 230°C. and (C) 185°C. respectively and a small heat evolution occurred spontaneously at about 230°C. By maintaining the mixture at that temperature for 2–3 minutes after the heat evolution, no phenylbiguanide was already present in the fused mass.

** Due to the difficulty of the perfect separation of each product, the yield did not mean the total amount of each product and a part of them may be included in "others". But these data may seem to be useful to compare the amount of each reaction product between three reactions.

*** Determined as picrate and reduced to free base.

TABLE V

SCHEMES OF THE METHOD OF THE SEPARATION OF EACH REACTION PRODUCT



in fused state, the thermal decomposition of phenylbiguanide-HCl and the reaction between phenylbiguanide-HCl and aniline-HCl or ammonium chloride were studied successively.

An example of the quantitative separation of the products of three reactions is shown in Table IV and the method of the separation of each reaction product is also schematically shown in Table V.

It was first observed that the thermal decomposition of phenylbiguanide-HCl in fused state gave not only phenylguanidine-HCl, but also guanidine-HCl. This reaction may be represented as follows by referring the mechanism of the thermal decomposition of biguanide monosalt.

$$(C_6H_5NH\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX - \begin{cases} \nearrow (C_6H_5NH\cdot C(NH)\cdot NH_2)HX + NH_2\cdot CN \\ \searrow (NH_2\cdot C(NH)\cdot NH_2)HX + C_6H_5NH\cdot CN \end{cases}$$

If an amine salt should be existed in the reaction mixture, the cyanamides formed would react immediately to give corresponding guanidine salts. So, by the use of ammonium salt, the salt of phenylguanidine and guanidine may be formed.

$$NH_2\cdot CN + NH_3\cdot HX \rightarrow (NH_2\cdot C(NH)\cdot NH_2)HX$$
$$C_6H_5NH\cdot CN + NH_3\cdot HX \rightarrow (C_6H_5NH\cdot C(NH)\cdot NH_2)HX$$

Also by the use of aniline HCl, the formation of the salt of phenylguanidine and diphenylguanidine may be expected.

$$NH_2\cdot CN + C_6H_5NH_2\cdot HX \rightarrow (C_6H_5NH\cdot C(NH)\cdot NH_2)HX$$
$$C_6H_5NH\cdot CN + C_6H_5NH_2\cdot HX \rightarrow (C_6H_5NH\cdot C(NH)\cdot NHC_6H_5)HX$$

The latter two reactions were verified by the experiment. By the fusion of cyanamide (1 mol.) or phenylcyanamide (1 mol.) with aniline HCl (1 mol.), the salt of phenylguanidine or diphenylguanidine was obtained in yield as high as 96% and 92% respectively.

As the result of these successive reactions, a rough estimate of the ratio of the amount of phenylguanidine, guanidine and diphenylguanidine formed by the following reactions may be as follows.

(A) Thermal decomposition of phenylbiguanide-HCl.

(B) The reaction of phenylbiguanide-HCl with ammonium chloride.

(C) The reaction of phenylbiguanide-HCl with aniline HCl.

	Monophenylguanidine	Guanidine	Diphenylguanidine
(A)	1	1	0
(B)	2	2	0
(C)	2	1	1

The results shown in Table IV were in good agreement with this conclusion. But in the reaction (C), the amount of diphenylguanidine seemed to be somewhat larger than that of the other two guanidines. By referring the result of methylbiguanide described later, it is generally noticed that the proportion of different kinds of guanidines formed in these reactions may depend upon the substituent of biguanide as later indicated by Oxley and Short.[8]

If the sufficient amount of amine salt should not exist in the thermal decomposition of phenylbiguanide-HCl, the cyanamides formed might react together and form a mixture of melamine derivatives. Throughout the above three reactions, some amount of melamine derivatives could always be found in the reaction product as shown in Table IV. Melamine derivatives from the reaction (A) and reaction (B) were found to consist mainly of the same compound which was identified as 2.4-dianilino-6-amino-s-triazine (diphenylmelamine). This compound could be synthetized by the mutual reaction of phenylcyanamide and cyanamide.

2.4-dianilino-6-amino-s-triazine.

From the reaction A.

M.p. 201–205°C., m.p. of picrate: 272°C.

Found: C, 64.72, 64.78, H, 5.93, 5.54, N, 30.22

From the reaction B.

M.p. 208–210°C., m.p. of picrate: 272°C.

Found: C, 64.71, 64.76, H, 5.23, 5.58, N, 31.27

From the mutua! reaction of phenylcyanamide and cyanamide.

M.p. 197–202°C., m.p. of picrate: 272°C.

Found: C, 64.75, 64.75, H, 5.50, 5.38, N, 29.69

Calc. for $C_{15}H_{14}N_6$: C, 64.74, H, 5.05, N, 30.21

By summarizing these observations, the author determined the mechanism of the reaction between dicyandiamide and aniline-HCl which are now believed to be as follows.

$$NH_2\cdot C(NH)\cdot NH\cdot CN + C_6H_5NH_2\cdot HX = (C_6H_5NH\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX \qquad (1)$$

$$(C_6H_5NH\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX - \begin{cases} \nearrow (C_6H_5NH\cdot C(NH)\cdot NH_2)HX + NH_2\cdot CN & (2) \\ \searrow (NH_2\cdot C(NH)\cdot NH_2)HX + C_6H_5NH\cdot CN & (2') \end{cases}$$

$$NH_2\cdot CN + C_6H_5NH_2\cdot HX = (C_6H_5NH\cdot C(NH)\cdot NH_2)HX \qquad (3)$$
$$(NH_2\cdot CN + NH_3\cdot HX = (NH_2\cdot C(NH)\cdot NH_2)HX)$$
$$C_6H_5NH\cdot CN + C_6H_5NH_2\cdot HX = (C_6H_5NH\cdot C(NH)\cdot NHC_6H_5)HX \qquad (3')$$
$$(C_6H_5NH\cdot CN + NH_3\cdot HX = (C_6H_5NH\cdot C(NH)\cdot NH_2)HX)$$

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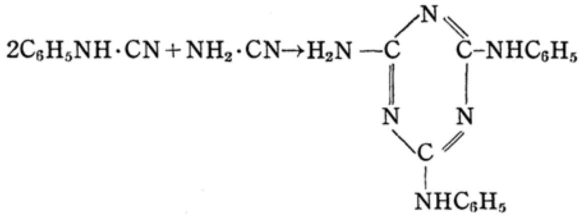
[8] Oxley and Short, *J. Chem. Soc.*, **1951**, 1252.


(4)

In the case of phenylbiguanide salt (a unsymmetrical biguanide), two reactions take place in the thermal decomposition. It is converted to (a) phenylguanidine salt and cyanamide and (b) guanidine salt and phenylcyanamide (2), (2′). The cyanamides formed in nascent state react immediately with amine salts and the corresponding salts of guanidines are formed (3), (3′). Some of the cyanamides react together and the phenyl derivatives of melamine (for example: 2.4-dianilino-6-amino-s-triazine (diphenylmelamine)) are obtained as byproducts (4).

III. Mechanism of the Reaction between Dicyandiamide and Methylamine Hydrochloride

The mechanism of the reaction between dicyandiamide and methylamine-HCl was also studied and was found to be almost the same as the case of aniline-HCl. For this purpose, a quantitative study of the following reactions was carried out just the same as in the case of the reaction between dicyandiamide and aniline-HCl.

1. The preparation of pure methylbiguanide-HCl.
2. The thermal decomposition of methylbiguanide-HCl.
3. The reaction between 1 mol. of methylbiguanide-HCl and 1 mol. of ammonium chloride.
4. The reaction between 1 mol. of methylbiguanide-HCl and 1 mol. of methylamine-HCl.
5. The reaction between 1 mol. of dicyandiamide and 2 mol. of methylamine-HCl.

The results obtained are summarized in Table VI.

TABLE VI

Methylbiguanide-HCl: 7.58 g. (molar ratio 1)

Conditions:* Temp. 190°C., Time 2 hrs.

Product / Reaction	Methylguanidine picrate		Guanidine picrate		Dimethylguanidine picrate	Insoluble residue of water extraction (100 cc.)	Picrate of melamines**
	Yield (g.)	Molar ratio	Yield (g.)	Molar ratio	Yield (g.)	Yield (g.)	Yield (g.)
(A) Thermal decomposition of methylbiguanide-HCl	7.47	0.49	5.46	0.38	—	0.24	0.84
(B) Reaction with ammonium chloride, 2.68 g. (Molar ratio 1:1)	13.09	0.87	12.18	0.85	—	trace	
(C) Reaction with methylamine-HCl, 3.38 g. (Molar ratio 1:1)	15.89	1.05	5.51	0.38	undetermined	nearly zero	
(D) Reaction of dicyandiamide (4.20 g.) with methylamine-HCl, 6.75 g. (Molar ratio 1:2)	17.87	1.18	3.55	0.25	undetermined	trace	

* After two hours and at that temperature, no methylbiguanide was present in the fused mass.

** M.p. 282°C.

The preparation of methylbiguanide-HCl was carried out as follows.

$$\left.\begin{array}{l}\text{Dicyandiamide (1 mol.)}\\ \text{Methylamine-HCl (1 mol.)}\end{array}\right\rangle \xrightarrow{\text{fused at 120-130°C, for 1 hr.}}$$

$$\text{—dissolved in hot water—}\left\langle\begin{array}{l}\text{Insoluble matter}\\ \text{Filtrate — CuCl}_2\text{ (or}\end{array}\right.$$

$$\text{CuCl) NH}_3\text{ soln. was added—}\left\langle\begin{array}{l}\text{Filtrate}\\ \text{Pink colored precipitate}\end{array}\right. \xrightarrow[\text{treated with H}_2\text{S}]{\text{dissolved in HCl soln.}} \left\langle\begin{array}{l}\text{CuS}\\ \text{Filtrate}\end{array}\right. \xrightarrow{\text{evaporated}} \text{Crude}$$

$$\text{Methylbiguanide-2HCl} \xrightarrow{\text{recrystallization from 80-90\% alcohol}}$$

$$\text{Pure Methylbiguanide-2HCl} \text{ — dissolved in water and neutralized with equiv. amount of NaOH } \left\langle\begin{array}{l}\text{NaCl}\\ \text{Methylbiguanide-HCl}\end{array}\right. \xrightarrow{\text{extracted with abs. alcohol}} \text{Pure Methylbiguanide-HCl.}$$

The separation of methylguanidine and guanidine from the reaction mixture could be performed successfully by using the difference of the order of precipitation of those picrates. By adding a saturated solution of ammonium picrate in the reaction mixture, guanidine picrate was first precipitated and when the precipitation of guanidine picrate was almost completed, methylguanidine picrate began to precipitate. So, by carrying out the precipitation cautiously and also recrystallizing, those two picrates could be separated almost completely.

The results seemed to be very similar to that of the reaction of phenylbiguanide-HCl. First, methylbiguanide-HCl also yielded both the salt of methylguanidine and guanidine by the thermal decomposition in fused state just the same as in the case of phenylbiguanide-HCl. Cyanamide and methylcyanamide which were supposed to form at the same time reacted together to give melamine derivatives. By the presence of a suitable amount of an amine salt in the reaction mixture, these cyanamides, if they existed, must be converted to corresponding guanidines. In the case of NH_4Cl, therefore, guanidine and methylguanidine may be obtained and in the case of methylamine-HCl, methylguanidine and sym-dimethylguanidine may also be expected to form. So, similar to the case of phenylbiguanide, a rough estimate of the ratio of the amount of methylguanidine and guanidine formed by the following reactions may be expected as follows:—

(A) The thermal decomposition of methylbiguanide-HCl.

(B) The reaction between methylbiguanide HCl and ammonium chloride.

(C) The reaction between methylbiguanide HCl and methylamine-HCl.

	Methylguanidine	Guanidine
(A)	1	1
(B)	2	2
(C)	2	1

The results shown in Table VI were in good agreement with this assumption. The result of the reaction between 1 mol. of dicyandiamide and 2 mol. of methylamine HCl (D) was found to be almost the same as that of the reaction (C), but the amount of methylguanidine was somewhat larger than in the latter case.

About sym-dimethylguanidine, its confirmation was not carried out in the above experiment. But now, Mr. R. Kitawaki of my laboratory, has again been studying the same reaction in order to confirm this compound in the reaction product. He succeeded in isolating about 9.0 g. of N, N′-dimethylguanidine picrate from the reaction product obtained by the fusion of 21.0 g. of Dicyandiamide with 33.8 g. of methylamine-HCl at 190°C for 1 hr*.

M. p. 159–160°C.

After recrystallization: m. p. 172–4°C.

m. p. of N, N′-dimethylguanidine-HCl derived from the purified picrate: 151–2°C.

m. p. of the mixture of these samples with the same salts of N, N′-dimethylguanidine prepared by the reaction of methylamine with iodocyan or of monomethylcyanamide with methylamine. HCl.*

	Known sample	Mixture
picrate	177°C	175°C
hydrochloride	154°C	153–4°C

As the result of these observations, the mechanism of this reaction could also be formulated as follows.

$$NH_2\cdot C(NH)\cdot NH\cdot CN + CH_3NH_2\cdot HX$$
$$= (CH_3NH\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX \qquad (1)$$

$$(CH_3NH\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX$$
$$\nearrow (CH_3NH\cdot C(NH)\cdot NH_2)HX + NH_2\cdot CN \qquad (2)$$
$$\searrow (NH_2\cdot C(NH)\cdot NH_2)HX + CH_3NH\cdot CN \qquad (2')$$

$$NH_2CN + CH_3NH_2\cdot HX$$
$$= (CH_3NH\cdot C(NH)\cdot NH_2)HX \qquad (3)$$
$$(NH_2CN + NH_3\cdot HX = (NH_2\cdot C(NH)\cdot NH_2)HX)$$

$$CH_3NH\cdot CN + CH_3NH_2\cdot HX$$
$$= (CH_3NH\cdot C(NH)\cdot NHCH_3)HX \qquad (3')$$
$$(CH_3NH\cdot CN + NH_3\cdot HX$$
$$= (CH_3NH\cdot C(NH)\cdot NH_2)HX)$$

Mutual reaction of cyanamides
→Melamine derivatives (4)

In this case, the thermal decomposition of methylbiguanide hydrochloride takes place mainly to the side of methylguanidine formation (2), (This may be the influence of CH_3-group discribed above.) therefore the reaction product consisting of mainly methylguanidine-HCl and the amount of guanidine-HCl seemed to be relatively small. Also, a small amount of N, N′-dimethylguanidine was successifully found in it.

In 1922 Werner[9] also had carried out the reaction between dicyandiamide and methylamine-HCl. He supposed that methylguanidine was only the reaction product according to his supposed mechanism.

$$\begin{array}{c} C_2H_4N_4 \rightleftharpoons 2NH_2CN \\ \underline{2NH_2CN + 2CH_3NH_2\cdot HX = 2(CH_3NH\cdot C(NH)\cdot NH_2)HX} \\ C_2H_4N_4 + 2CH_3NH_2\cdot HX = 2(CH_3NH\cdot (NH)\cdot NH_2)HX \end{array}$$

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* Unpublished papers of R. Kitawaki,

[9] Werner, *J. Chem. Soc.*, **121**, 1790 (1922).

He obtained a picrate which melted at 285°C. and supposed it to be methylguanidine picrate. But the melting point of methylguanidine picrate is about 200°C according to many other researches.[10] This erroneous observation induced the following two erroneous explanations of other investigators. Schenck[11] supposed the picrate obtained by Werner to be ethylenediguanidine picrate and also Kapeller[12] supposed the same picrate to be a mixture of dicyandiamide and picric acid. These observations, of course, were also erroneous. This question continued to be unsolved till 1943, when the author has again studied this reaction.

The author also obtained a picrate melted at 285°C in the reaction product of this reaction. According to the author's mechanism, it was obviously certain that this picrate was a mixture of a large amount of guanidine picrate and a small amount of methylguanidine picrate. It was first formed by adding the picrate solution in the solution of reaction product due to the difference of precipitation velocity of two picrates.

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[10] Phillips, Clarke, *J. Am. Chem. Soc.*, **45**, 1756 (1923).
[11] Schenck, *Z. physiol. Chem.*, **155**, 306 (1926).
[12] Kapeller, *Ber.*, **59**, 1652 (1926).