SHORT COMMUNICATIONS

Formation of Formoguanamine by the Reaction between Cyanamid and a Reduced Compound of Free Guanidine (Studies on Some Derivatties of Cyanamide XLV**)*

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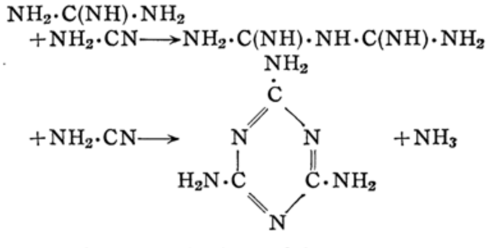
It seemed to us that the reaction between cyanamide and free guanidine in alcoholic solution has hitherto not been studied. So, an investigation was made in order to clarify the products of this reaction.

First, the authors expected biguanide as a primary reaction product and melamine as a final product. But it was found that entirely different products were obtained in accordance with different procedures of the preparation of free guanidine. When a solution of free guanidine in ethanol was prepared by adding an equivalent amount of guanidine salt (for example, guanidine hydrochloride) to a sodium ethylate solution, it reacted with cyanamide to give biguanide just as we expected. But the reaction was found to proceed very slowly, so that only a trace of biguanide was formed even when the mixture was heated at 70–80°C for two hours[1]. And biguanide itself was found to give melamine when it was treated with cyanamide in ethanol. These reactions can be represented as follows.



But when a solution of free guanidine was prepared by adding an equivalent amount of metallic sodium to a solution of guanidine salt in ethanol, it reacted with cyanamide to give formoguanamine in a fair yield. This reaction seemed to be very rapid as compared with the formation of biguanide from guanidine.

For a typical run, 47.77 g. (0.50 mole) of thoroughly dried guanidine hydrochoride was dissolved in 250 cc. of absolute ethanol and 11.50 g. (0.50 mole) of clean sodium cuttings was added piece by piece with agitation, keeping the temperature at 20–30°C. A small quantity of ammonia was evolved during the dissolution of sodium (refer to Fig. 1). In the resulting solution, about 75% of guanidine used was found to remain as free base, but about 25% of it was supposed to be converted to a reduced form which could not be precipitated as picrate. 11.05 g. (0.25 mole) of cyanamide crystal (purity 95% was added to this solution without separating sodium chloride and the mixture was warmed gradually under reflux on the steam bath with slow stirring. When the temperature reached about 40°C, the reaction began to occur with the evolution of ammonia The reaction mixture was continued to heat till the temperature reached 80°C and maintained at that temperature for 30 minutes. (total reaction time: 3 hours and 20 minutes). In Fig. 1, are plotted the quantity of ammonia evolved and the reaction temperature against time which shows the proceeding of the over-all reaction accurately.

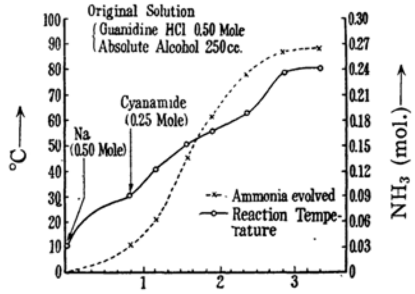
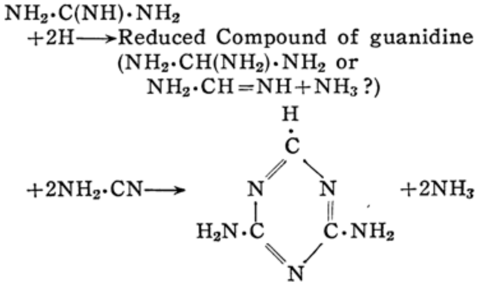


Fig. 1.

After the reaction, the solid (36.50 g.) was filtered off and treated with 100 cc. of water to dissolve sodium chloride only. The residue, washed with water and ethanol, dried, and weighed 7.00 g. (0.063 mole), m.p. 309–312°C, m.p. 316–7°C after crystallization from hot water. A mixture melting point with pure formoguanamine prepared from biguanide[2] showed no depression. Found: N, 62.73. Calcd. for $C_3H_5N_5$: N, 63.04%. The picrate melted at 248°C.

In the mother solution, about 58% of guanidine and 25% of cyanamide were found to remain unchanged together with a trace of biguanide formed[3]. Of course, a part of cyanamide was converted to dicyandiamide.

From these results, it was concluded that, in the latter case, guanidine was probably reduced to give an unstable reduced compound (triaminomethane (a part, formamidine $+NH_3$) ?) and it reacted with cyanamide to give formoguanamine according to the following formula.



$$NH_2 \cdot C(NH) \cdot NH_2 + 2H \longrightarrow \text{Reduced Compound of guanidine } (NH_2 \cdot CH(NH_2) \cdot NH_2 \text{ or } NH_2 \cdot CH{=}NH + NH_3\,?)$$

$$+2NH_2 \cdot CN \longrightarrow \text{(formoguanamine)} + 2NH_3$$

The formation of formoguanamine was an unexpected result and seemed to be very interesting, because the possibility of the reduction of guanidine itself was proved.

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[**] XLIV, K. Shirai, *J. Chem. Soc. Japan.*, Industrial Chemistry Section, 58, 343 (1955).

[1] Under these conditions, cyanamide itself was converted in a considerable yield to dicyandiamide in the presence of guanidine.

[2] This sample was prepared by Mr. M. Yamashita according to his procedure (*J. Chem. Soc. Japan*, Industrial Chemistry Section, 54, 786 (1951)) m.p. 318°C.

[3] After standing for several months, the authors found a small amount of melamine crystallized out in the mother solution of this experiment.