THE ACTION OF SULFURIC ACID ON DICYANDIAMIDE.[1]

By TENNEY L. DAVIS.

In 1862 Haag[2] found that dicyandiamide, when boiled with acids, combines with water to form a base which he called dicyan-diamidine, and Baumann in 1874 showed[3] that this base is guanylurea. In 1913 Lidholm[4] studied the reaction, at 80° and at 100°, between equivalent quantities of dicyandiamide and 0.1 N sulfuric acid. He followed the progress of the reaction by titrating the reaction mixture with methyl orange and alkali, a procedure which the strongly basic character of guanylurea made applicable, and calculated the reaction constant for the second order reaction.[5]

$$NH = C(NH_2)NHCN + H_2O \longrightarrow NH = C(NH_2)NHCONH_2. \quad (I)$$
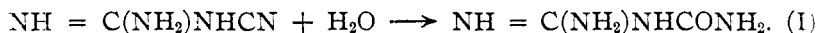
The same investigator found that strong sulfuric acid provokes the rapid evolution of carbon dioxide and carries the reaction further, converting the guanylurea into guanidine.

$$NH = C(NH_2)NH - CO - NH_2 + H_2O \longrightarrow$$
$$NH = C(NH_2)_2 + CO_2 + NH_3. \quad (II)$$
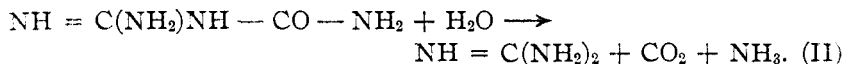
Since these reactions provide a ready means of preparing guanidine from an abundant source, we have undertaken a study of them in an effort to determine the conditions which will secure a maximum yield of product. Under the conditions which are necessary for the formation of guanidine from dicyan-diamide, the primary reaction leading to the formation of guanylurea is very rapid while the other reaction leading to the formation of guanidine is relatively much slower—and it was believed that the progress of the reaction could be studied satisfactorily by confining the attention merely to the rate of production of the products of the second and slower reaction.

With 61% sulfuric acid at 100° the production of guanidine is slow and a large amount of guanylurea survives after a heating of 6 hours. At higher temperatures the yield is better, and excellent yields can be obtained by 6 hours heating at 140°, 160° or 200°. At the high temperatures, a con-

[2] Haag, *Ann.*, **122**, 22 (1862).

[3] Baumann, *Ber.*, **7**, 1766 (1874).

[4] Lidholm, *ibid.*, **46**, 156 (1913).

[5] We find that the same reaction occurs in alkaline solution, and are now studying the matter in this laboratory.

siderable increase of temperature produces only a slight increase in the amount of product, and the yields at 140°, at 160° and at 200° are essentially the same. At the higher temperatures more carbon dioxide is produced than the formation of guanidine requires, a result which indicates that guanidine itself is destroyed by the strong sulfuric acid, presumably in accordance with the following equation.

$$NH = C(NH_2)_2 + 2H_2O \longrightarrow CO_2 + 3NH_3. \qquad (III)$$
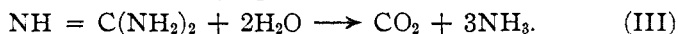
Discussion of Experiments.

In the first experiments dicyandiamide was heated with 4 times its weight of 61% sulfuric acid and portions of the reaction mixture were removed at intervals and analyzed for guanidine by precipitation with ammonium picrate according to the method of Vorzarik.[1] The precipitates were contaminated with varying amounts of guanylurea picrate, and results were erratic. Attempts to determine ammonia in portions of the reaction mixture were unsuccessful, for it was found that the alkali used to liberate the ammonia during the distillation process attacked the products of the reaction and caused falsely high results. Conditions were met by measuring the rate of production of carbon dioxide.

In a series of experiments, 8 g. of dicyandiamide and 32 g. of 61% sulfuric acid were heated together in the apparatus illustrated in Fig. 1.
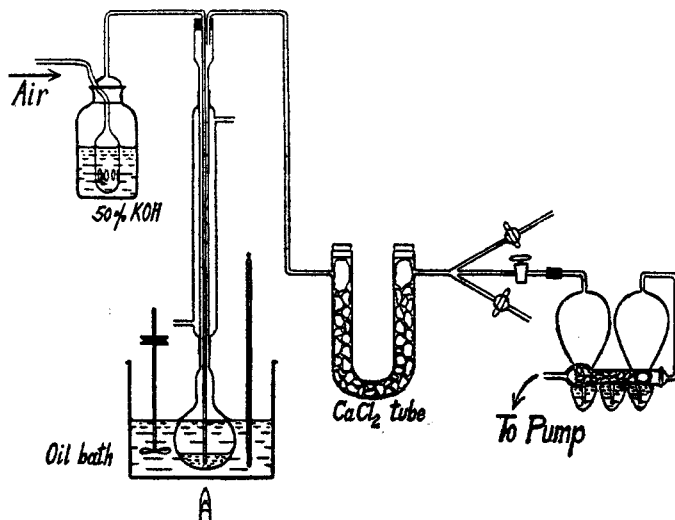

Fig. 1.—Apparatus for studying rate of hydrolysis of dicyandiamide.

The temperature was maintained constant within 1° above or below. The Geissler bulbs were changed at intervals of 30 minutes, and the carbon dioxide produced during the interval was weighed. At the end of

[1] Vorzarik, Z. angew. Chem., 15, 670 (1902).

6 hours, guanidine in the reaction mixture was determined by the method of Vorzarik. The experimental data are given in the accompanying table.

Half hour period.	At 100°.		At 120°.		At 140°.		At 160°.		At 200°.	
	During interval.	Total.	During interval.	Total.	During interval.	Total.	During interval.	Total.	During interval.	Total.
First	0.1333	0.1333	0.7734	0.7734	1.5220	1.5220	1.7575	1.7575	2.1985	2.1985
Second	0.1702	0.3035	0.6013	1.3747	0.8229	2.3449	0.8615	2.6190	0.7260	2.9245
Third	0.1595	0.4630	0.4394	1.8141	0.4717	2.8166	0.4573	3.0763	0.3977	3.3222
Fourth	0.1644	0.6274	0.3291	2.1432	0.2867	3.1033	0.2793	3.3556	0.2253	3.5475
Fifth	0.1525	0.7799	0.2367	2.3799	0.2080	3.3113	0.1705	3.5261	0.1505	3.6980
Sixth	0.1500	0.9299	0.1867	2.5666	0.1535	3.4648	0.1138	3.6399	0.0877	3.7857
Seventh	0.1450	1.0749	0.1445	2.7111	0.1055	3.5703	0.0872	3.7271	0.0454	3.8311
Eighth	0.1304	1.1053	0.1210	2.8321	0.0796	3.6459	0.0550	3.7821	0.0391	3.8702
Ninth	0.1207	1.2260	0.0923	2.9244	0.0670	3.7129	0.0360	3.8181	0.0301	3.9003
Tenth	0.1104	1.3364	0.0762	3.0006	0.0470	3.7599	0.0255	3.8436	0.0184	3.9187
Eleventh	0.0850	1.4214	0.0544	3.0550	0.0442	3.8041	0.0167	3.8603	0.0130	3.9217
Twelfth	0.0405	1.4619	0.0617	3.1167	0.0260	3.8301	0.0105	3.8708	0.0090	3.9307
Carbon dioxide, % of theory.		34.8		74.5		91.3		92.4		93.8,
Guanidine by analysis.		1.97		3.84		4.76		4.80		4.83
Guanidine, % of theory.		35.1		68.3		84.7		85.4		85.9

Fig. 2, the graph of these data shows that the variation in the amount of produced carbon dioxide is remarkably regular, but the fact, brought out by the analysis, that the amount of carbon dioxide in certain cases is in excess of the amount of guanidine, probably renders impracticable the calculation of a velocity constant.
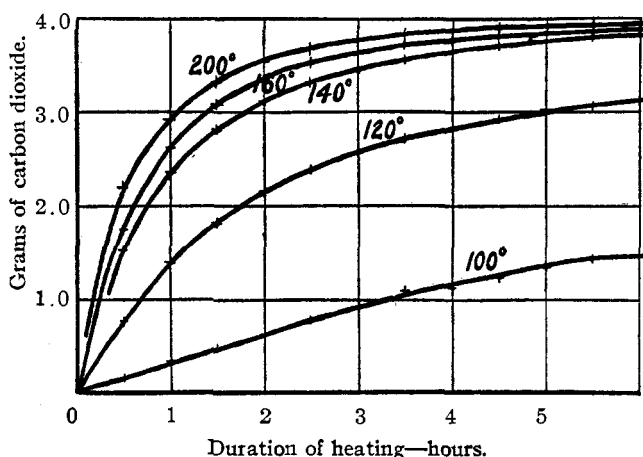

Fig. 2.—Rate of production of carbon dioxide from dicyandiamide by heating with 61% sulfuric acid.

In the 100° run the apparent amount of guanidine as indicated by analysis is larger than that which corresponds to the amount of carbon dioxide, a result which can lead only to the inference that the precipitated picrate was contaminated with picrate of guanylurea and to the conclusion that the figure for carbon dioxide is probably fairly representative of the actual amount of guanidine. In the other runs at higher temperatures, the carbon dioxide exceeds the guanidine. But the reactions (II and III above) which lead to the formation of guanidine and to the destruction of guanidine each produce one mol-equivalent of carbon dioxide. The actual amount of guanidine, therefore, which is produced during the reaction (and in part destroyed) is represented by the arithmetical mean between the value given by analysis and that indicated by the carbon dioxide. Dicyandiamide heated for 6 hours with 4 times its weight of 61% sulfuric acid actually produces at 100° about 34.8%; at 120°, 71.4%; at 140°, 88.0%; at 160°, 88.9% and at 200°, 89.9% of the theoretical amount of guanidine.

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BUTYL- AND ISOBUTYL-CYANO-ACETIC ACIDS.[1]

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In continuation of the work already done on the alkylation of cyano-acetic acid ethyl ester, the authors have carried out the Conrad-Limpach reaction with *iso*-butyl alcohol as the solvent and have determined that the *iso*-butyl and di-*iso*-butylcyano-acetic esters formed were *iso-butyl* esters rather than *ethyl* esters. The present paper also describes a number of salts of *iso*-butyl and di-*iso*-butyl-cyano-acetic acids, as well as the preparation of *normal* butyl-cyano-acetic acid and ester and a number of their derivatives.

I. **Action of Cyano-acetic Acid Ethyl Ester with Sodium *Iso*-Butylate and *Iso*-Butyl Iodide in *Iso*-Butyl Alcoholic Solution.**—A solution of sodium *iso*-butylate was prepared from 6.6 g. of sodium and 185 cc. of absolute *iso*-butyl alcohol. The solution solidified when cold. It was treated with 32.4 g. of cyano-acetic acid ethyl ester dissolved in 65 cc. of absolute *iso*-butyl alcohol, and the mixture was warmed slightly until the solid sodium salt went into solution. The solution was then cooled and 55 g. of *iso*-butyl iodide was added. This is an excess of 2 g.

The solution gradually assumed a deep-red color. After 40 hours the solution was heated to boiling until it was neutral to litmus. The *iso-*