Electrolytic Reduction of Dicyandiamide

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This contribution is the abstract of my paper⁽¹⁾ already published in Japanese in the Journal of the Chemical Society of Japan in 1939. Some new and revised explanations are added.

For the structure of dicyandiamide, Bamberger[2] proposed cyanoguanidine formula $(NH_2 \cdot C(NH) \cdot NH \cdot CN)$ and with this, he could explain very smoothly the formation of guanidine and methylamine from dicyandiamide by the reduction with Zn and HCl (1893). Bell[3] (1926) however, repeated this experiment and he found that by hydration preceding the reduction (even in cold solution), guanylurea was formed instead and consequently he was led to adopt the original cyclic formula for dicyandiamide. So, it seemed to me that there were many problems regarding the reduction of dicyandiamide. For these reasons, an investigation was made to answer the following two questions.

1. Does dicyandiamide reduce directly ?
2. What kinds of products are given by the reduction ?

As the result of many experiments, it was found that dicyandiamide could be reduced directly only by the electrolytic reduction under special conditions (1% aq. solution of dicyandiamide acidified with H_2SO_4 amounting to 1%).

I. The case in which the electrolysis was stopped so as to let the catholyte remain acidic.

The conditions and the results obtained are shown in Table I.

A new compound (a base) was found to be formed by the following reduction.

$$C_2H_4N_4 + 4H \rightarrow C_2H_8N_4$$

This new compound seemed to be very unstable and could exist only in an acidic medium at room temperature. So, when the electrolysis was stopped so as to let the catholyte still remain acidic and a saturated solution of picric acid was added to the catholyte, the new compound could be precipitated as dipicrate.

Color: Light yellow (plate or needle)

m. p.: It has not the accurate melting point. It began to sinter at 180–200°C and decomposed at 220–230°C.

Found: C, 30.74, 30.62; H, 2.87, 2.70; N, 25.61, 25.62, 25.65.

Calc. for $C_{14}H_{14}N_{10}O_{14}$: C, 30.77, H, 2.56, N, 25.64%.

It was also observed that the dipicrate was easily hydrolysed to give guanidine picrate,

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[1] K. Sugino, *J. Chem. Soc. Japan*, **60**, 111, (1939); *C.A.*, **34**, 2795 (1940).

[2] Bamberger. *Ber.*, **26**, 1584, 1585 (1893).

[3] Bell, *Sci. Proc. Roy. Dublin Soc.*, **18**, 207–10 (1926); *C.A.*, **21**, 2444 (1927).

TABLE I

Catholyte			Electrode		Cathodic current density	Time	Temp.	Quantity of electricity consumed*	pH of catholyte after electrolysis	Reaction Product			
Dicyandiamide	H_2O	Conc. of H_2SO_4	Cathode	Anode						(1) Picrate of intermediate product weighed	(2)** Guanidine picrate obtained by the hydrolysis of catholyte	(3)** Picrate of intermediate product calculated from (2)	Yield of intermediate product (Aminomethylene guanidine)
(g.)	(cc.)	(%)			(A/dm²)	(hr.)	(°C)	(Ahr.)		(g.)	(g.)	(g.)	(%)
1.00	100	1	Hg	Pt	0.8–1.0	2.3	20–24	1.103	acidic	1.91	—	—	—
1.00	100	1	Hg	Pt	1.0	2.0	26	1.031	acidic	1.72	1.01	1.91	29
1.00	100	1	Pb	Pb	1.0	2.5	23	1.010	acidic	2.80	1.61	3.05	47
1.00	100	1	Pb	Pb	1.0	2.5	23	0.982	acidic	2.77	1.62	3.07	47

* Theoretical value for intermediate product. 1.243.
** (2), (3): Quantitative determination of the new compound. It was carried out as follows:
This compound was converted to guanidine by the hydrolysis according to the reaction (2) in the catholyte and resulting guanidine was weighed as picrate, by which the amount of picrate of original intermediate compound was calculated.

TABLE II

Catholyte			Electrode		Cathodic current density	Time	Temp.	Quantity of electricity consumed	pH of catholyte after electrolysis	Reaction Product			
Dicyandiamide	H_2O	Concentration of H_2SO_4	Cathode	Anode						Guanidine picrate*		Amine-HCl** (mainly ammonium chloride)	
(g.)	(cc.)	(%)			(A/dm²)	(hr.)	(°C)	(Ahr.)		(g.)	(g.)	(g.)	(%)
1.01	100	1	Hg	Pt	1.0–0.46	—	20–23	2.66	alkali	1.56	46	Undetermined	—
1.00	100	1	Hg	Pt	1.0	7.6	20–23	3.76	alkali	1.31	38	0.40	62
1.01	100	1	Pb	Pb	1.0	6.3	20–23	2.96	alkali	0.89	26	0.88	138

* m.p. 320°C.
Found: N, 29.28.
Calc. for $C_7H_8N_6O_7$: N, 29.16%.
** m.p. above 250°C.
The existence of methylamine was verified by its characteristic odour and also the positive result for chloranil test.

ammonium picrate and formaldehyde almost quantitatively when its aqueous solution was boiled or made alkaline at room temperature.

Guanidine picrate: Yield: 94–120% of the theoretical value* m.p.: 320°C Found: C, 29.50; H, 2.77; N, 29.37 Calc. for $C_7H_8N_6O_7$: C, 29.17; H, 2.80; N, 29.16%.

Ammonium picrate: Long needle, m.p. 280°C (decomp.), Ammonia was evolved quantitatively by heating its aqueous solution with caustic alkali.

Formaldehyde: Yield, 93% of the theoretical value* (determined by the iodometric titration)

The compound itself, in the catholyte, was also found to be hydrolysed to give the same products when the catholyte was treated in the same manner as described above. From these observations, it was concluded that this compound has the constitution of amino-methylene guanidine.

$$NH_2\cdot C(NH)\cdot NH\cdot CH_2\cdot NH_2$$

The hydrolysis of the compound (and its dipicrate) may be represented by the following reaction.

$$NH_2\cdot C(NH)\cdot NH\cdot CH_2\cdot NH_2+H_2O= NH_2\cdot C(NH)\cdot NH_2+NH_3+CH_2O \quad \cdots\cdots(2)$$

$$C_2H_8N_4\cdot 2C_6H_2(NO_2)_3OH+H_2O= CH_5N_3\cdot C_6H_2(NO_2)_3OH+ NH_3\cdot C_6H_2(NO_2)_3OH+CH_2O \quad \cdots\cdots(2')$$

II. The case in which the electrolysis was continued till the catholyte became alkaline.

When the electrolysis was continued till the catholyte became alkaline, reaction (2) occurred spontaneously and guanidine, ammonia and formaldehyde were obtained as the final products. But a small part of $C_2H_8N_4$ was reduced to guanidine and methylamine.

$$C_2H_8N_4+2H=NH_2\cdot C(NH)\cdot NH_2+CH_3\cdot NH_2 \quad \cdots\cdots(3)$$

An example of the results is shown in Table II.

In the high acid concentration of the catholyte, dicyandiamide was first hydrated to guanylurea, which was hardly further reduced in the acidic medium.

From the results of the author, he is induced to think that Bell's conclusion is erroneous and he agrees with Bamberger's one that dicyandiamide is directly reduced. But the author's final reduction products were entirely different from Bamberger's one. And the author's results showed that dicyandiamide should have both guanidine group and N-CN linkage, the latter of which behaves somewhat differently from usual nitrile. By referring the result of Hughe's X-ray analysis later published[4] (1940), the structure of dicyandiamide may be represented as guanylcyanamide rather than cyanoguanidine.

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* Refer to the reaction (2).

[4] Hughes, *J. Am. Chem. Soc.*, **62**, 1258 (1940).