

Studies on Melamine. IV : The Reaction Mechanism of the Formation of Melamine from Dicyandiamide

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The Reaction Mechanism of the Formation of Melamine from Dicyandiamide

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I. Introduction

In the case of preparing melamine from dicyandiamide by the fusion method, Sugino⁽¹⁾ perceived the dissociation of dicyandiamide into cyanamide as suggested by Werner and Bell⁽²⁾ and assumed that the coexisted potassium hydroxide accelerated the dissociation and pushed the dissociation-equilibrium to the side of cyanamide by fixing the latter and then he presented the following mechanism for the formation of melamine from dicyandiamide:



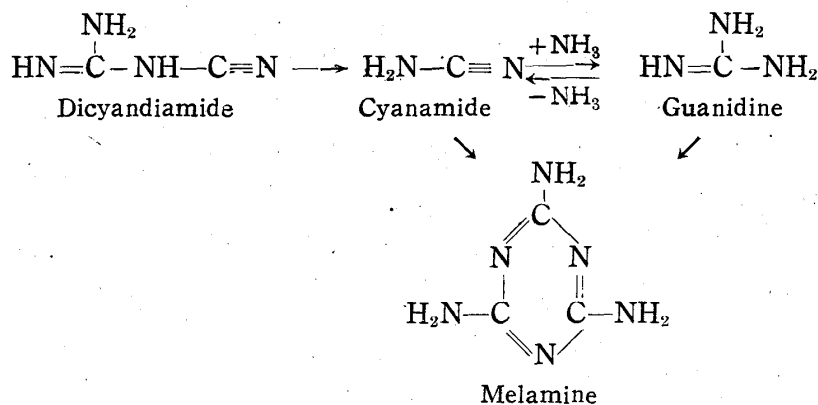
On the solvent method of preparing melamine from dicyandiamide, no report on the reaction mechanism of which was found. In the method using benzyl alcohol as the solvent, the present author⁽³⁾ isolated cyanamide in the form of its hydrochloride as an intermediate product in the reaction, finding that dicyandiamide dissociated into cyanamide in an early stage of the reaction and assumed that the coexisted potassium hydroxide acted as the case of the fusion method.

In preparing melamine from dicyandiamide in presence of liquid ammonia under pressure, Scholl and Davis⁽⁴⁾ perceived qualitatively the presence of guanidine in the reaction product by the method of Buchanan,⁽⁵⁾ but did not isolate guanidine. The present author isolated guanidine in the form of its picrate as an intermediate product in the pressure method, using dicyandiamide and liquid ammonia. The reaction mechanism of the reaction will be discussed.

In the early stage of the reaction in the pressure method using dicyandiamide and liquid ammonia, an autoclave, in which the reaction was conducted, was cooled quickly from outside. Guanidine was isolated as the picrate from the reaction product. It was therefore assumed that dicyandiamide dissociated into cyanamide in the reaction, which formed guanidine with the coexisting ammonia and the resulted compound changed into melamine.⁽⁶⁾ The author proved the

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- (1) Sugino, *J. Soc. Chem. Ind. Japan*, 47 (1944) 887.
 - (2) Werner and Bell, *J. Chem. Soc.* 117, (1920) 1133.
 - (3) Oshima, *J. Soc. Chem. Ind. Japan*, 53, (1950) 135.
 - (4) W. Scholl and R. O. E. Davis, *Ind. Eng. Chem.* 29, (1937) 202.
 - (5) Buchanan, *Ind. Eng. Chem.*, 15, (1923) 637.
 - (6) Krall, *J. Chem. Soc.*, 107, (1914) 1396.

formation of guanidine in the early stage of the reaction, while Scholl and Davis in the last stage, respectively. Therefore, ammonia not only kept down the evolution of ammonia by mutual action of melamine, but also changed cyanamide into guanidine. Melamine was therefore assumed to be formed by the polymerization of the three moles of cyanamide or by the action between cyanamide and dicyandiamide:



II. Experimental part

(1) Preparation of guanidine picrate from guanidine nitrate.

One gram of guanidine nitrate (m p 209-212°C) was dissolved in 25 cc of about 95 per cent alcohol in a beaker of 250 cc capacity, to which 35 cc of about 15 per cent alcoholic ammonia were added and then 25 cc of alcoholic solution containing 2 grams of picric acid (m p 121-121.5°C). A light orange yellow precipitate was collected, washed with 50 cc of about 95 per cent alcohol and dried at 100-110°C, melting point of which was 318-319°C (decomposed) and the yield 1.5 grams. It was recrystallised from 300 cc of water, obtaining guanidine picrate (1) as orange yellow needles, melting point, 325-326°C (decomposed). Analysis of 1 gave the following result:

Sample 1	2.346 mg.	N ₂	0.596 cc (22°C, 764.5 mm)
	Measured	N	29.57 %
	Calculated as C ₇ H ₈ O ₇ N ₆	N	29.17 %

As melting point of guanidine picrate, Lidholm⁽⁷⁾ adopted 333°C, Kutscher and Schenk⁽⁸⁾ 318°C and Sugino⁽⁹⁾ 320°C (decomposed), but they did not analyse the sample. The author obtained 325-326°C (decomposed) as the melting point and the analytical result was almost coincidental with the theoretical value.

(2) Isolation of guanidine during the formation of melamine from dicyandiamide. Ten grams of dicyandiamide (dried at 100-110°C, m p 206°C) were put in

(7) Lidholm, Ber., 46, (1913) 160.

(8) Kutscher und Schenk, Ber., 38, (1905) 458.

(9) Sugino and Yamashita, The Synthetic Method of Organic Compounds. Vol. 2, Page 92 (1950).

an autoclave, into which 20 cc of liquid ammonia were introduced and heated in an electric furnace. After 70 minutes, the outside temperature rose to 185°C (45 atmospheres). The autoclave was quickly cooled by dipping it into an ice water. After expelling off ammonia, the autoclave was opened and the content was crushed with a metallic rod and treated with 100 cc of ether (cyanamide is soluble in ether) and filtered. The undissolved solid was thoroughly agitated with 100 cc of absolute alcohol at room temperature and filtered. To the filtrate, 10 cc of 95 per cent alcohol containing 0.4 gram of picric acid and filtered quickly. Light orange yellow precipitate (m p 222-235°C) obtained from the filtrate standing for long time was recrystallised twice from water, obtaining about 20 milligrams of orange yellow needles (2), melting point of which was 323-325°C (decomposed). When 2 was compared with 1, they are similar in color, crystalline form and melting point, and analytical value of nitrogen coincided with that of guanidine picrate.

Sample 2.	1.354 mg	N 0.341 cc (22°C, 764.5 mm).
	Measured	N 29.31 %
	Calculated as C ₇ H ₈ O ₇ N ₆	N 29.17 %

It was therefore proved that 2 was guanidine picrate and the substance dissolved in the alcohol was guanidine.

Summary

(1) In the case of preparing melamine from dicyandiamide in presence of liquid ammonia under pressure, the formation of guanidine as an intermediate product was proved by isolating it as its picrate.

(2) In the above case, dicyandiamide was therefore dissociated into cyanamide, which was fixed as guanidine by coexisting ammonia. The formation of melamine was assumed to be due to the polymerization of the three moles of cyanamide produced through guanidine or to the combination of cyanamide and dicyandiamide.

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