KINETICS OF THE FORMATION OF MELAMINE FROM DICYANDIAMIDE¹

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Abstract—The kinetics of the potassium hydroxide-catalysed formation of melamine from dicyandiamide in diethylene glycol monoethyl ether at 110–150° is expressed as: $v = k_1 K_2 \cdot [KOH] \cdot [dicyan$ $diamide]/(1 + K_2[KOH]), which is consistent with the rate of depolymerization of dicyandiamide to$ cyanamide. The addition of cyamamide to the reaction system causes a marked increase in the rate.The rate of formation of melamine from a mixture of dicyandiamide and cyanamide (1:1 in molarratio) is almost identical with that from cyanamide alone. These results suggest a mechanism involvinga rate-determining depolymerization of dicyandiamide to cyanamide followed by the condensationof the cyanamide produced with dicyandiamide leading to melamine by cyclization.

ALTHOUGH several mechanisms have been postulated for the formation of melamine from dicyandiamide, none seem to be conclusive.² One, involves the depolymerization of dicyandiamide to cyanamide followed by its trimerization.³ Another consists of the dimerization of dicyandiamide followed by the cyclization of the dimer and then cleavage forming melamine and cyanamide.⁴ A third involves the direct condensation of cyanamide with dicyandiamide followed by the cyclization of the condensate. The condensation product of cyanamide with dicyandiamide, cyanobiguanide (II), has been isolated from a dicyandiamide-acetone-hydrochloride complex.⁵ Cyanobiguanide may be an intermediate in the formation of melamine (Eq. 8) and the base-catalysed formation of benzo- or aceto-guanamine, by direct condensation of nitrile with dicyandiamide leading to cyclization has been suggested.⁶

The present paper describes the kinetics of formation of melamine (Eq. 1) in a homogeneous system (diethylene glycol monoethyl ether as a solvent), which involves the effect of base and cyanamide on the rate, and the rate of depolymerization of dicyandiamide to cyanamide. The rates were determined by following the formation of melamine by UV spectrophotometry.



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- ⁸ E. M. Smolin and L. Rapoport, s-Triazines and Derivatives p. 313. Interscience, New York (1959).
- * K. Sugino, Kogyo Kagaku Zasshi 47, 877 (1944).
- ⁴ M. Kurabayashi and K. Yanagitani, Kogyo Kagaku Zasshi 58, 750 (1955).
- ⁶ H. Beyer, H. Bieling and Th. Pyl, Z. Chem. 2, 310 (1962); M. Yamada, E. Ichikawa and K. Ohdo, Yuki Gosei Kagaku Kyokaishi 21, 946 (1963).
- Y. Ogata, A. Kawasaki and K. Nakagawa, Tetrahedron 20, 2755 (1964); Ibid. 22, 157 (1966).

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RESULTS AND DISCUSSION

Rate expression. The rate was found to be first-order with dicyandiamide (Fig. 1). This was confirmed by the constancy of the first-order rate coefficient (k) in one run and also in different runs with various initial concentrations of dicyandiamide. The kinetic data are shown in Table 1.

 TABLE 1. THE KINETIC DATA FOR THE FORMATION OF MELAMINE FROM DICYANDIAMIDE IN DIETHYLENE

 GLYCOL MONOETHYL ETHER.

 INITIAL CONC.:DICYANDIAMIDE, 0.135M

150° [KOH] <i>k</i> ⁴ × 10⁴		140° [KOH] <i>k</i> ª × 104	130° [KOH] <i>k</i> ª × 104	120° [KOH] <i>k</i> ª × 10	Energy of Activation E_a	
M	sec ⁻¹	M sec ⁻¹	M sec ⁻¹	M sec ⁻¹	kcal mole ⁻¹	
) 32 1·11	0.032 0.428	0.032 0.211	0.031 0.0763	29.4	
0.0	048 1.23	0.043 0.540	0.044 0.233	0.042 0.0924	28.5	
0.0	063 1.71	0.066 0.893	0.066 0.343	0.068 0.130	28.3	
_		0.090 0.875	0.091 0.377	0.096 0.162	27.3	
		0.123 1.10	0.140 0.506	0.131 0.206	27.1	
		(0·123 0·0116)°	(0·140 0·0122)°	(0·131 0·0117)°		
		0.211 1.41	0.209 0.640	0.200 0.274	26.4	
		0.294 1.55			Av. 27·8	

• The first-order rate constant.

^b The value calculated from the plot of 1/k vs 1/[KOH]. See Fig. 2.

• The first-order rate constant at 90° calculated from the above rate constants together with the energy of activation.



FIG. 1. First-order kinetics for the formation of melamine from dicyandiamide in diethylene glycol monomethyl ether at 148°.
●: a = 0.25M, ⊕: a = 0.15M, ○: a = 0.10M

Plot of the first-order overall rate constant (k) vs the concentration of potassium hydroxide [KOH] gives a curve passing through the origin. In contrast, the plot of the reciprocal of first-order rate constants vs the reciprocal of the concentration of



FIG. 2. Plot of 1/k vs 1/[KOH] for the formation of melamine from dicyandiamide in diethylene glycol monoethyl ether.

potassium hydroxide gives a straight line (Fig. 2). These results may be explained by the following scheme:

$$H_{s}NCNHCN + B^{\odot} \xrightarrow{K_{s}}_{mobile} N_{s}HCN^{\odot}CN + BH \qquad (2)$$

$$\| NH \qquad NH \qquad | NH \qquad (2)$$

$$H_{s}NCN^{\odot}CN \xrightarrow{k_{s}}_{slow} [I] \xrightarrow{h_{s}NCN} NH_{s} \qquad (3)$$

$$\| NH \qquad (2)$$

$$\| NH \qquad (2)$$

$$| NH \qquad (3)$$

$$\| NH \qquad (3)$$

Here, B^{Θ} and I represent a base and an active intermediate, respectively. The overall rate of reaction is expressed as:

$$v = \frac{k_3 K_2 [B^{\circ}]}{1 + K_2 [B^{\circ}]} \cdot [\text{dicyandiamide}]$$
(4)

Hence

$$\frac{1}{k} = \frac{1}{k_3 K_2} \cdot \frac{1}{[B^\circ]} + \frac{1}{k_3}$$
(5)

Eq. 5 agrees with the observed kinetic data as shown in Fig. 2, which gives the rate (k_3) and the equilibrium constants (K_2) from the intercept and slope of the line, respectively. Table 2 lists the values of k_3 and K_2 obtained by the least square method.

Temp	140° 2·32	130° 1·03	120° 0-392	E _a kcal mole ⁻¹ 28.7	Δ <i>S</i> ‡ e.u. -8·0
Rate constant $k_3 \times 10^4$, sec ⁻¹					
Equilibrium constant K_1 , M^{-1}	7.09	6.99	7.73		

TABLE 2. THE RATE (k_3) AND THE EQUILIBRIUM CONSTANTS (K_3) FOR THE FOR MATION OF MELAMINE FROM DICYANDIAMIDE IN DIETHYLENE GLYCOL MONOETHYL ETHER. SEE EQS 2 AND 3.

INITIAL CONC.: DICYANDIAMIDE, 0.135M

Rate-determining step. If cyanamide is an active intermediate, the rate of reaction should equal the depolymerization of dicyandiamide to cyanamide which determines the rate. Although the rate of depolymerization is difficult to measure in the present reaction system, it is available in an analogous solvent, 2-methoxyethanol, in the presence of 0.13M KOH at 90°, Eq. 6, $(k_{0}^{90} = 1.5 \times 10^{-6} \text{ sec}^{-1}).^{6}$

From the kinetic data in the presence of 0.13M KOH at $120^{\circ}-140^{\circ}$ together with the energy of activation, the first-order rate constant at 90° ($k^{90^{\circ}}$) in diethylene glycol monoethyl ether was calculated to be $1.2 \times 10^{-6} \text{ sec}^{-1}$ for the formation of melamine. This value is in good accord with the above rate constant (k_6), which supports the rate-determining depolymerization of dicyandiamide to cyanamide.

The rate constant for the formation of melamine (k) from dicyandiamide cannot always be identical with that of depolymerization of dicyandiamide (k_6) because of the faster reverse reaction (dimerization of cyanamide). However, at very low concentration of cyanamide and at higher concentration of dicyandiamide as in the present system, the rate constant for the dimerization of cyanamide (k_6) may be negligible compared with the rate of condensation of cyanamide with dicyandiamide.

Addition of cyanamide. Although the addition of cyanamide retarded the rate of formation of benzoguanamine,⁶ the addition of cyanamide in the present reaction should increase the rate as it is an active intermediate formed in the rate-determining step. As shown in Fig. 3, the rate increases sharply on addition of cyanamide at 148° and then decreases gradually to the original rate.

When the reaction was started with an equimolar mixture of dicyandiamide and cyanamide, the rate was faster than with dicyandiamide alone, although the initial concentration of dicyandiamide in the former ($[DD]_0 = 0.121M$) is lower than in the latter ($[DD]_0 = 0.181M$).

These results suggest that cyanamide is an active intermediate. Since added cyanamide may be consumed both by the formation of melamine and by the dimerization to dicyandiamide then depletion of cyanamide 20 min after the reaction is started, may be due to the fast dimerization of cyanamide $(k_{-6}^{90^\circ} = 5 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1})^6$ as will be shown later.

Formation of melamine from cyanamide. Since cyanamide is an active intermedate, the following two mechanisms may be considered. One is the direct trimerization of cyanamide, the rate being expressed as:

$$v = k \, [H_2 NCN]^3$$

The other is the condensation of cyanamide with dicyandiamide, the rate being:

$$v = k [H_2NCN] \cdot [H_2NCNHCN]$$

$$\|$$
NH

As shown in Fig. 4, the rate of formation of melamine from cyanamide alone is faster than that from dicyandiamide alone, but is almost identical with that from an equimolar mixture of cyanamide and dicyandiamide even at early stages of reaction where the concentration of cyanamide is lower. These facts imply that the direct condensation of cyanamide with dicyandiamide is preferred to the trimerization of cyanamide for the formation of melamine.



Time, min

The melamine formation from an equimolar mixture of cyanamide and dicyandiamide is insignificant without KOH. Therefore, cyanamide as its anion should attack dicyandiamide forming cyanobiguanide (II).

$$H_{1}HCN + B^{\Theta} \rightleftharpoons NH^{\Theta}CN + BH$$
(7)



FIG. 4. Comparison of the rate of formation of melamine from an equimolar mixture of cyanamide and dicyandiamide with that of cyanamide alone at 110°. Initial conc.:*a*, dicyandiamide, 0·120M; *b*, dicyandiamide, 0·125M; c, cyanamide, 0·125M; *c*, cyanamide, 0·375M.

Reaction mechanism. The above discussion suggests a mechanism involving a rate-determining depolymerization of dicyandiamide to cyanamide followed by the condensation of cyanamide with dicyandiamide. The overall process may be represented as follows:

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$$H_{a}NCN^{\underline{0}}CN \xrightarrow{\text{slow}} H_{a}NCN + HN^{\underline{0}}CN \qquad (6')$$

$$\begin{array}{c} \text{mobile} \\ \text{H}_{a}\text{NCN} + \text{B}^{\odot} & \longrightarrow \\ \text{HN}^{\odot}\text{CN} + \text{BH} \end{array}$$
(7)

$$\begin{array}{ccc} & \text{fast} \\ \text{H_*NCNHC} + \text{HN}^{\underline{\circ}}\text{CN} & \xrightarrow{\text{fast}} & \text{H_*NCNHCNHC} \\ \parallel & \parallel & \parallel & \parallel \\ \parallel & \parallel & \parallel & \parallel \\ \text{NH} & \text{N} & \text{NH} & \text{N}^{\underline{\circ}} & \text{N} \end{array}$$
(8a)

$$\begin{array}{c} \text{fast} \\ \text{H}_{s}\text{NCNHCNHC} + \text{BH} \xrightarrow{\text{fast}} \begin{bmatrix} \text{H}_{s}\text{NCNHCNHC} \\ \parallel & \parallel \\ \text{NH} & \text{N}^{\odot} & \text{N} \end{bmatrix} + B^{\odot} \\ \begin{bmatrix} \parallel & \parallel & \parallel \\ & \text{NH} & \text{NH} & \text{N} \end{bmatrix} \end{array}$$
(8b)

$$\begin{bmatrix} H_3NCNHCNHC \\ \parallel & \parallel & \parallel \\ & NH & NH & N \end{bmatrix} \xrightarrow{\text{fast}} \text{Melamine}$$
(9)
(II)

The mechanism of depolymerization of dicyandiamide (Eqs 2 and 6') is the reverse of dimerization of cyanamide.⁷

The observed entropy of activation (-8 e.u.) is very small for the first-order decomposition reaction.⁸ The negative charge in dicyandiamide anion (III) may delocalize on all six carbon and nitrogen atoms, whereas the delocalization of negative charge at the transition state should be limited to three N-C-N atoms (IV). Therefore, the solvation of alcohol is probably much stronger at the transition state than in the original anion, which causes the observed small entropy of activation.



An attempt to isolate cyanobiguanide (II) as a complex with cupric ion⁵ was unsuccessful probably because of its low concentration.

As stated above, cyanamide anion should be a stronger nucleophile than dicyandiamide anion because of the higher delocalization of negative charge, hence an attack of cyanamide anion on cyano group of dicyandiamide is preferred to that of dicyandiamide anion, and hence the increased rate on addition of cyanamide.

The depolymerization of dicyandiamide may be suppressed by ammonia whereas the dimerization of cyanamide or condensation of cyanamide or dicyandiamide with ammonia may be observed in the autoclave reaction.⁹ Cyanamide is surely an active intermediate at least under the present conditions, and the addition of cyanamide accelerates the reaction.

The rate of cyclization of cyanobiguanide⁵ or triguanide¹⁰ have been reported as very fast or spontaneous processes.

EXPERIMENTAL

Materials. Dicyandiamide, m.p. 210°, with purity over 99.4% purchased from Nippon Carbide Co. was used without further purification. Cyanamide, m.p. 42°, was prepared from calcium cyanamide.¹¹ Commercial diethylene glycol monoethyl ether was purified, after standing for one day in the presence of NaOH, by vacuum distillation, b.p. 66–67°/4.5 mm.

Analysis of melamine. The UV spectra of 0.1N HClaq. containing dicyandiamide and melamine corresponding to 0, 20, 40, 60, 80 and 100% conversions for the formation of melamine are shown in Fig. 5. The plot of extinctions of mixtures at 236 m μ vs concentration of melamine gave a straight line. Extinction at isoabsorptive point 227 m μ gives the sum ([dicyandiamide] + $\frac{3}{2}$ [melamine]). ε^{236} for melamine, 1.02 × 10⁴ (lit.¹³ 1.0 × 10⁴); ε^{236} for dicyandiamide, 6.2 × 10³. The concentration of melamine in mixtures was determined from the extinction at 236 m μ .

- ⁷ G. H. Buchanan and G. Barsky, J. Amer. Chem. Soc. 52, 195 (1930).
- ⁸ L. L. Schaleger and F. A. Long, *Advances in Physical Organic Chemistry* (Edited by V. Gold) Vol. I, p. 1. Academic Press, New York (1963).
- * P. P. McClellan, Ind. Eng. Chem. 32, 1181 (1940).
- ¹⁰ F. Kurzer and E. D. Pitchfork, J. Chem. Soc. 3459 (1964).
- ¹¹ L. A. Pinck and J. M. Salisbury, Inorganic Syntheses Vol. III; p. 41. McGraw-Hill (1950).
- ¹⁸ I. M. Klotz and T. Askounis, J. Amer. Chem. Soc. 69, 801 (1947).

A typical procedure for kinetic measurements. A mixture of 0.125M dicyandiamide and 0.13M KOH in dicthylene glycol monoethyl ether was kept in a polyethylene glycol bath at ca. 154°. After 10 min when the solution reached thermal equilibrium, the first aliquot (at time t_0) was diluted 1000-



FIG. 5. Ultraviolet spectra of a mixture of dicyandiamide and melamine in 0·1N HClaq. corresponding to the formation of melamine from dicyandiamide (7·5 × 10⁻⁴M). Melamine (%):a, 100; b, 80; c, 60; d, 40; e, 20; f, 0.

fold with 0.1N HCl. The extinction at 227 m μ and 236 m μ was measured by a Shimadzu SV50A spectrophotometer. Aliquots (at t) were periodically worked up analogously. The overall first-order rate constant (k) was calculated by the following equation:

$$k = \frac{2 \cdot 303}{t - t_0} \log \left(\frac{a - \frac{1}{2} x_0}{a - \frac{1}{2} x} \right)$$

Here, a is the initial concentration of dicyandiamide, x_0 and x are the concentrations of formed melamine at time t_0 and t, respectively.

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