

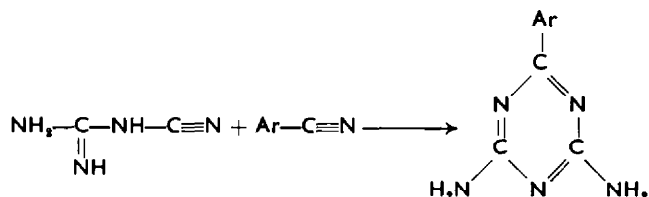
KINETICS OF THE FORMATION OF BENZOGUANAMINE FROM DICYANDIAMIDE AND BENZONITRILE

Y. OGATA, A. KAWASAKI and K. NAKAGAWA
Department of Applied Chemistry, Faculty of Engineering, Nagoya University,
Chikusa-ku, Nagoya, Japan

(Received 9 June 1964; in revised form 31 July 1964)

Abstract—The rates of the formation of benzoguanamine from dicyandiamide and benzonitrile in the presence of a basic catalyst, have been measured by means of UV spectrophotometry. The rate is expressed as $v = k \times [\text{dicyandiamide}] \cdot [\text{benzonitrile}] \cdot [\text{KOH}]$. Since the addition of a small amount of cyanamide retards the rate, cyanamide cannot be an intermediate. Application of the rate data observed with *p*-methyl-, methoxy-, and chlorobenzonitriles to the Hammett's equation gives a positive ρ value of +1.82. A probable mechanism involving a rate-determining attack of the conjugate base of dicyandiamide on benzonitrile is suggested and discussed.

BENZOGUANAMINE (2,4-diamino-6-phenyl-*s*-triazine), which constitutes one of the important materials for synthetic resins, coatings and drugs is prepared from dicyandiamide and benzonitrile.¹⁻³



Although no kinetic studies have been reported for this reaction, one of two mechanisms analogous to those for the formation of melamine⁴⁻⁷ may be possible. One, is the trimerization of cyano groups in benzonitrile and cyanamide dissociated from dicyandiamide,⁴ and the other the direct addition of dicyandiamide to benzonitrile.⁸ The present report summarizes the results of a kinetic study in the potassium hydroxide-catalysed formation of benzoguanamine in 2-methoxyethanol by means of UV spectrophotometry.

¹ J. Thurston, U.S. Patent 2,309,679 (1943); J. K. Simons and M. R. Saxton, *Organic Syntheses* Coll. Vol. IV; p. 78, J. Wiley, New York (1963).

² A. Ostrogovich, *Atti accad. Lincei* 20, I, 249 (1911); *Chem. Abstr.* 5, 2099 (1911).

³ R. D. Thrower and F. J. Pinchin, Brit. Patent 758,601 (1956); *Chem. Abstr.* 51, 10593 (1957).

⁴ K. Sugino, *Denki Kagaku* 11, 348 (1943); *Kogyo Kagaku Zasshi (J. Chem. Soc., Japan, Ind. Chem. Sect.)* 47, 877 (1944).

⁵ Y. Oshima, *Sci. Rep. of Research Inst., Tohoku Univ.* A3, 136 (1951).

⁶ M. Kurabayashi and K. Yanagitani, *Kogyo Kagaku Zasshi (J. Chem. Soc., Japan, Ind. Chem. Sect.)* 58, 750 (1955).

⁷ Ref. 19 in Ref. 6.

⁸ E. M. Smolin and L. Rapoport, *s-Triazine and Derivatives* p. 229. Interscience, New York (1959).

RESULTS AND DISCUSSION

Rate law. The rate was found to be first-order with dicyandiamide and first-order with benzonitrile as obvious from the constancy of second-order rate constants (k_2) in Table 1.

TABLE 1. THE SECOND-ORDER RATE CONSTANTS FOR THE FORMATION OF BENZOGUANAMINE IN 2-METHOXYETHANOL AT 90°

Initial conc.		KOH	Rate constant	
Dicyandiamide	Benzonitrile		$k_1 \times 10^4$	$\frac{k_2}{[\text{KOH}]} \times 10^3$
M	M	N	M ⁻¹ sec ⁻¹	M ⁻² sec ⁻¹
0.69	0.69	0.131	1.87	1.43
0.60	0.60	0.131	1.78	1.36
0.62	0.42	0.141	1.77	1.25
0.60	0.20	0.127	1.67	1.31
0.40	0.60	0.129	2.87	2.06 ^a
0.20	0.60	0.129	4.26	3.30 ^a
0.20	0.20	0.134	2.62	1.95
0.40	0.40	0.139	2.69	1.93
0.80	0.81	0.132	1.62	1.23

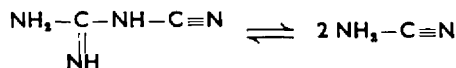
^a The deviation from constancy may be due to the decreased dissociation of dicyandiamide to cyanamide. See the text.

The rate constant, however, tends to decrease with increasing initial concentration of dicyandiamide. This tendency is probably due to the retarding effect of cyanamide existing in equilibrium with dicyandiamide, which will be discussed later. As shown in Fig. 1, the second-order rate constant (k_2) is proportional to the concentration of potassium hydroxide. Since addition of a small amount of water does not vary the rate, the effect is due to potassium hydroxide alone.

Therefore, the rate is expressed as:

$$v = k_3 [\text{dicyandiamide}] \cdot [\text{benzonitrile}] \cdot [\text{potassium hydroxide}]$$

The equilibrium between dicyandiamide and cyanamide. The presence of an equilibrium between dicyandiamide and cyanamide,



and the dimerization of cyanamide to dicyandiamide in an aqueous alkaline solution have been reported.⁹⁻¹¹ The rates of the depolymerization of dicyandiamide to cyanamide and the dimerization of cyanamide to dicyandiamide in 2-methoxyethanol containing 0.13M potassium hydroxide was measured at 90°. The forward (k_1) and the reverse (k_{-1}) rate constants were found to be $1.5 \times 10^{-6} \text{ sec}^{-1}$ and $5 \times 10^{-9} \text{ M}^{-1}\text{sec}^{-1}$, respectively; hence the equilibrium constant (k_1/k_{-1}) is $3 \times 10^{-4} \text{ M}$, i.e., the relative concentration of cyanamide vs. dicyandiamide should be very low.

The effect of addition of cyanamide on the rate. If cyanamide is an intermediate in

⁹ G. Grube and G. Motz, *Z. physik. Chem.* **118**, 147 (1925).

¹⁰ G. H. Buchanan and G. Barsky, *J. Amer. Chem. Soc.* **52**, 195 (1930).

¹¹ N. A. Gol'dberg and V. G. Golv, *Zh. Prikl. Khim.* **35**, 1592 (1962); *Chem. Abstr.* **57**, 12315 (1952).

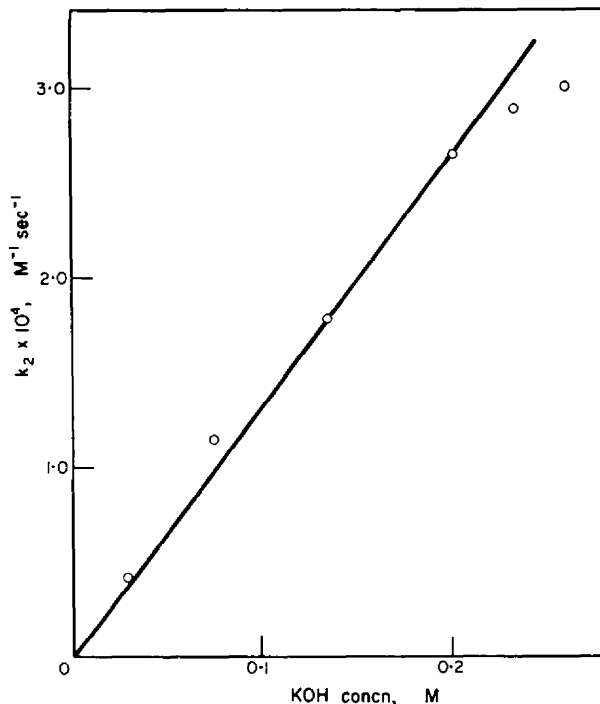


FIG. 1. Plot of the second-order rate constants vs. concentration of potassium hydroxide for the formation of benzoguanamine at 90°.

the formation of benzoguanamine, the addition of cyanamide to the reaction system would increase or change the rate only slightly. As shown in Table 2, addition of a small amount of cyanamide results in an apparent retardation of the rate, the retardation being increased with increasing concentration of added cyanamide. It is

TABLE 2. EFFECT OF CYANAMIDE AND *o*-CRESOL AT 90°
Initial conc.: dicyandiamide, 0.60 M; benzonitrile, 0.60 M, KOH, 0.13 M

Conc. of added cyanamide M	$k_2^a \times 10^4$ $M^{-1} \text{sec}^{-1}$	Conc. of added <i>o</i> -cresol M	$k_2 \times 10^4$ $M^{-1} \text{sec}^{-1}$
0	1.78	0	—
0.017	1.36	0	—
0.039	1.11	0.041	1.09
0.127	0.686	0.126	0.381
0.208	0.343	0	—

^a The second-order rate constant after 15 min.

probable that cyanamide acting as an acid consumes the catalysing hydroxide ion, since cyanamide ($pK_a^{25^\circ}$, 10.3)¹² is a stronger acid than dicyandiamide ($pK_a^{25^\circ}$, 14).¹³ It is of interest to note that the addition of *o*-cresol having a similar acidity ($pK_a^{25^\circ}$, 10.2)¹³ also retards the reaction. Furthermore, in one run with added cyanamide, the rate coefficient increased as the reaction proceeded, while in the other run with added

¹² N. Kameyama, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)* **24**, 1263, 1241 (1921).

¹³ D. R. Boyd, *J. Chem. Soc.* **107**, 1540 (1915).

TABLE 3. VARIATION OF RATE CONSTANT ON ADDITION OF
CYANAMIDE AT 90°
Initial conc. : dicyandiamide, 0.60M; benzonitrile, 0.60M; KOH, 0.13M

Time $t \times 10^{-2}$ sec	Addition of cyanamide (0.208M) $k_2 \times 10^4 M^{-1} \text{sec}^{-1}$	Addition of <i>o</i> -cresol (0.126M) $k_2 \times 10^4 M^{-1} \text{sec}^{-1}$
9	0.343	0.388
18	0.684	0.356
36	0.926	0.388
54	1.01	0.379
72	1.09	0.386
99	1.20	0.376
135	1.32	—
156	—	0.391
180	1.46	—
		Av. 0.381

o-cresol the rate coefficient did not vary with time (Table 3). This phenomenon may be explained by the rapid conversion of cyanamide to dicyandiamide with weaker acidity. Since an increase of the initial concentration of dicyandiamide results in an increase of the concentration of cyanamide in the solution, the rate coefficient decreases with increasing dicyandiamide (Table 1).

The effect of p-substituents in benzonitrile on the rate. As shown in Fig. 2, an electron-withdrawing group in benzonitrile increases, while an electron-releasing

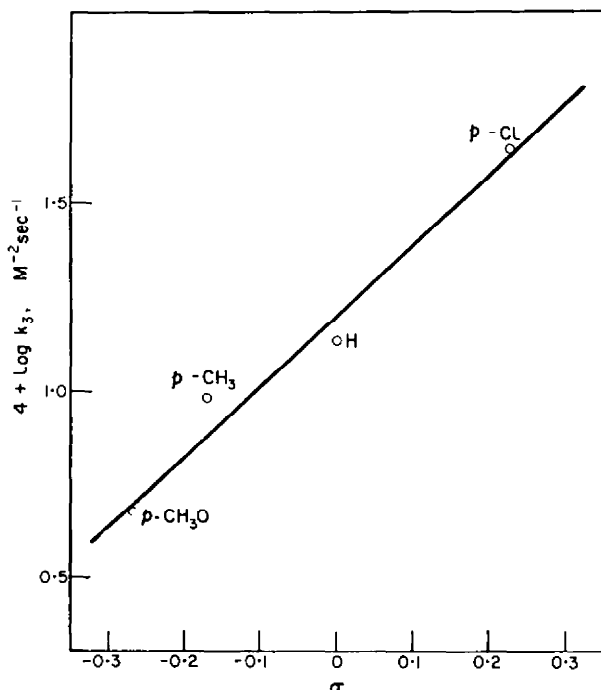
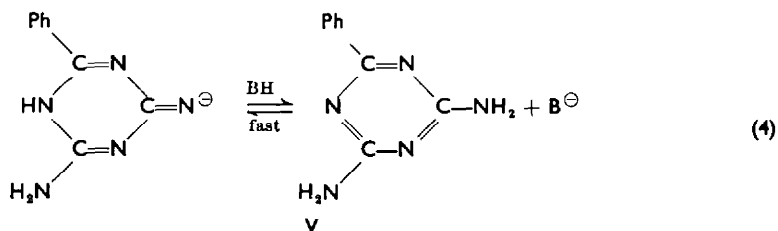
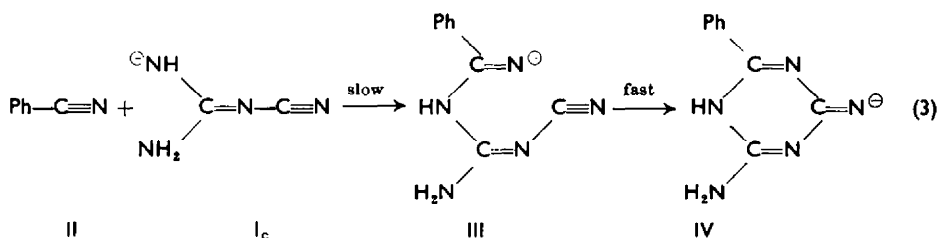
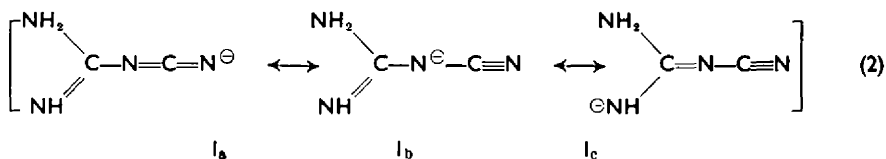
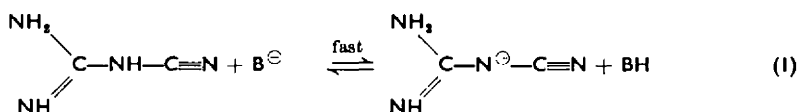


FIG. 2. Hammett relation plot of the third-order rate constants for the formation of benzoguanamine at 90°

group decreases the rate of reaction. *p*-Nitrobenzonitrile gives a product, not melting below 300° and with too low a solubility to purify by recrystallization. However, it was observed that it reacts faster than other benzonitriles.

A large positive ρ value (+1.82) suggests a rate-determining nucleophilic attack of the dicyandiamide anion at the cyano group in benzonitrile.

Reaction mechanism. These results suggest a probable mechanism for the reaction, where B^\ominus represents a base such as hydroxide ion or conjugate base of the solvent.



The dicyandiamide anion, in mobile equilibrium (1) has been assumed in the formation of dicyandiamide from cyanamide.¹⁰ Of the canonical forms I_a , I_b and I_c , form I_c is the most suitable for the formation of benzoguanamine. According to X-ray diffraction,¹⁴ dipole moment,¹⁵ IR spectrum¹⁶ and molecular orbital theory,¹⁷ dicyandiamide has a planar structure with π -electrons delocalized over all carbon and nitrogen atoms and hence the hybridization of forms I_a , I_b and I_c has been suggested. The base-catalysed reactions of dicyandiamide with malonic esters or with malononitriles leading to cyclic compounds^{18,19} supports the amino structure, I_c , as the

¹⁴ E. W. Hughes, *J. Amer. Chem. Soc.* **62**, 1258 (1940).

¹⁵ W. C. Schneider, *J. Amer. Chem. Soc.* **72**, 761 (1950).

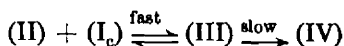
¹⁶ W. J. Jones W. J. Orville-Thomas, *Trans. Farad. Soc.* **55**, 193 (1959).

¹⁷ A. J. Owen, *Tetrahedron* **14**, 237 (1961).

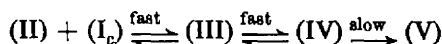
¹⁸ F. Pohl, *J. Prakt. Chem.* [2] **77**, 542 (1908).

¹⁹ M. Boëtius, B. Marchand and G. Dietz, *J. Prakt. Chem.* **7**, 135 (1958).

attacking anion. This mechanism is supported by the observed kinetics of the reaction and the large positive ρ value. The other mechanisms



or



seem less probable, because there is no indication of the presence of III or IV as a stable intermediate and also no rapid disappearance of benzonitrile was observed by UV spectrophotometer on admixture of benzonitrile (II) and dicyandiamide (Ic).

The Arrhenius plot with k_3 gave apparent energies of activation for the reactions of substituted benzonitriles. p -Substituent and E_a (kcal/mole) were as follows: methoxy, 22.4; methyl, 23.8; unsubstituted, 23.6; chloro, 22.7. Enthalpies and entropies of activation calculated from the data are shown in Table 4. These values of energy of activation are smaller than that in the formation of melamine (30 kcal/mole),⁷ corresponding to the fact that the formation of melamine requires more drastic conditions than those for benzoguanamine.

TABLE 4. ENTHALPIES AND ENTROPIES OF ACTIVATION FOR THE FORMATION OF BENZOGUANAMINES

p -Substituent in benzonitrile	Rate constant, $k_3 \times 10^4$ $M^{-2} \text{sec}^{-1}$				Enthalpy of activation ΔH^\ddagger , kcal mol ⁻¹	Entropy of activation ΔS^\ddagger , e.u.
	70°	80°	90°	100°		
Cl	—	20.7	44.0	121	22.0	— 8.8
H	1.75	5.06	12.3	31.2	22.9	— 8.9
CH ₃	—	3.59	9.68	21.5	23.1	— 8.8
CH ₃ O	—	2.08	4.75	11.0	21.7	—14.1

EXPERIMENTAL

Materials. Dicyandiamide, m.p. 210°, with purity over 99.4% purchased from Nippon Carbide Co. was used without further purification. Commercial benzonitrile was dried with P₂O₅ and distilled. Substituted benzonitriles were prepared from the corresponding anilines by the Sandmeyer reaction.²⁰ p -Substituents and m.p. (or b.p.) of these benzonitriles were as follows: unsubstituted, (186–187°); methyl, (82.5–84.5°/9mm); methoxy, 59°; chloro, 93°. Cyanamide, m.p. 42°, was prepared from an aqueous solution of calcium cyanamide.²¹ Commercial 2-methoxyethanol and ethanol were distilled and they had no absorption at wave length higher than 220 $m\mu$.

Products. Benzoguanamine and p -substituted benzoguanamines were prepared from dicyandiamide and p -substituted benzonitriles in 80–90% yield.¹ p -Substituents and m.p. of benzoguanamines were as follows: unsubstituted, 229–231°; methyl, 242–244°; methoxy, 233–235°; chloro, 248–250°. The yield of melamine formed under these conditions was less than 5%.

Analysis of products. The UV spectra of ca. $5.5 \times 10^{-6}M$ ethanolic solutions of dicyandiamide, benzonitrile or benzoguanamine are shown in Fig. 3. The absorption maximum of benzoguanamine was 244 $m\mu$ ($\epsilon_{244} = 1.83 \times 10^4$; lit.²² 1.86×10^4), the absorptions of dicyandiamide and benzonitrile being negligible at this wave length. Mixtures of dicyandiamide, benzonitrile and benzoguanamine of known concentrations corresponding to 0, 20, 40, 60, 80 and 100% conversions were prepared and a plot of extinctions at 244 $m\mu$ vs. concentrations of benzoguanamine gave a straight line. The amount of benzoguanamine in mixtures were determined from the extinctions at 244 $m\mu$ with precision

²⁰ H. T. Clarke and R. R. Read, *Organic Syntheses* Coll. Vol. I, p. 514. J. Wiley, New York (1941).

²¹ L. A. Pinck and J. M. Salisbury, *Inorg. Synth.* Vol. III, p. 41. McGraw-Hill (1950).

²² F. C. Nachod and E. A. Steck, *J. Amer. Chem. Soc.* 70, 2819 (1948).

of $98.0 \pm 0.9\%$. For *p*-methyl-, *p*-methoxy- and *p*-chlorobenzoguanamines, the extinctions at 256, 270, and 254 $m\mu$ were employed, respectively.

A typical procedure for the rate measurement. A 1.2M solution of benzonitrile in 2-methoxyethanol containing 0.27M KOH (25 ml) and a 1.2M solution of dicyandiamide in 2-methoxyethanol

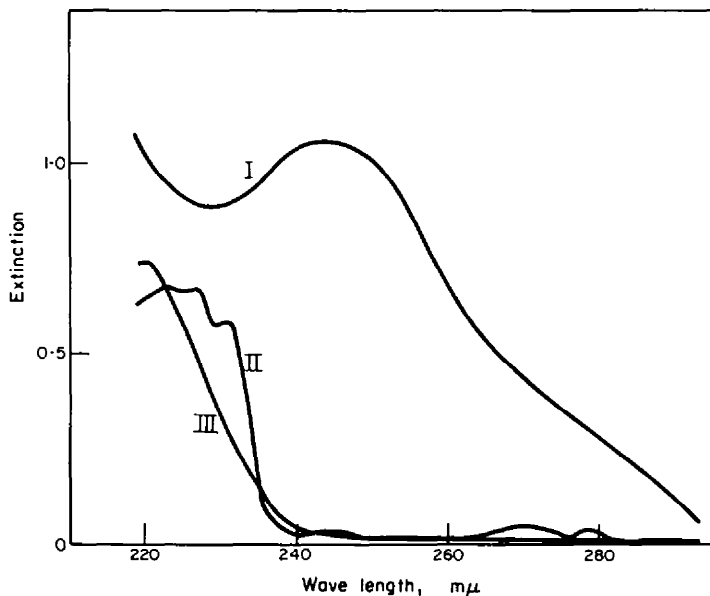


FIG. 3. Ultraviolet spectra of 5.5×10^{-5} M benzoguanamine (I), benzonitrile (II), and dicyandiamide (III) in ethanol.

(25 ml), both of which had previously been brought to thermal equilibrium ($90.0 \pm 0.3^\circ$), were mixed in a 100 ml flask. Aliquots were periodically withdrawn and diluted to 10,000 fold ethanolic solution. Their extinctions at 244 $m\mu$ were measured by a Shimadzu SV50A automatic spectrophotometer or a Hitachi EPU-2A spectrophotometer at room temp. Cyanamide was estimated by a silver nitrate procedure.²³

Acknowledgment—The authors wish to thank Nippon Carbide Co. and Nissan Chemical Co. for their gift of materials.

²³ G. Grube and J. Krüger, *Z. Angew. Chem.* 27, 326 (1914).