Polymerization of Cyanamide to Dicyanodiamide

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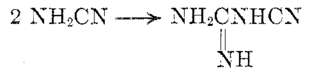
The method of polymerization of cyanamide to dicyanodiamide has been improved by the subjection of concentrated cyanamide solutions containing relatively small amounts of ammonia to a higher temperature in an open system, whereby a yield of 98 per cent or better is obtained. In addition to yield, it is superior to previously described methods with respect to cost, simplicity, and rapidity of operation.

DICYANODIAMIDE has potentialities as an industrial chemical in the preparation of synthetic resins (*3*) and pharmaceuticals (*2*). Ever since the development of the cyanamide process for the fixation of atmospheric nitrogen, numerous investigators have been engaged in attempting to improve the existing methods for the polymerization of cyanamide to dicyanodiamide:



$$2\ NH_2CN \longrightarrow NH_2\underset{\underset{NH}{\|}}{C}NHCN$$

The more important observations obtained in previous studies (*1, 4, 5, 8–12, 14*) may be summarized as follows: (*a*) The polymerization of cyanamide in aqueous solution involves a reaction of cyanamide with the cyanamide ion, the latter being present through the dissociation of a salt of cyanamide. The dicyanodiamide ion thus formed combines with a hydrogen ion, yielding dicyanodiamide which is only slightly ionized. (*b*) The rate of polymerization is a function of the hydrogen-ion concentration. It reaches a maximum at pH 9.6 and decreases rapidly below and above this value; above 12, cyanamide is hydrolyzed to urea. (*c*) A relatively small amount of melamine is formed.

A few years ago two papers appeared showing the importance of hydrogen-ion concentration in the polymerization of cyanamide. Cochet (*5*) found that a 10 per cent cyanamide solution having a pH of 9.9 yields about 85 per cent conversion at room temperature and that equilibrium is attained at the end of 165 hours. Buchanan and Barsky (*4*) obtained 88.5 and 88.6 per cent conversion of cyanamide into dicyanodiamide in 2 per cent solutions having an average pH of 9.0 and 9.6, respectively, after 72 hours heating at 50° C.

Grube and Nitsche (*10*) studied the polymerization of cyanamide in dilute solutions (0.5 to 2 *N* cyanamide) in the presence of ammonia and obtained yields of 84 to 85 per cent after 4 hours of heating at 60° C. They concluded that optimum conditions are attained when the concentration of ammonia is half of the cyanamide expressed in terms of normality.

It was felt that the yield could be improved and the rate of polymerization increased by operating at a higher temperature with a weakly alkaline solution. It seemed that the ideal conditions for the polymerization of cyanamide would be the use of a highly concentrated solution of cyanamide with a low ammonia concentration in an open system in which the decrease of ammonia through volatilization would take place simultaneously with the polymerization. A series of experiments was therefore designed to study the influence of the factors mentioned in the foregoing.

The cyanamide used in the following experiments was obtained from crude calcium cyanamide by a method already described (*13*). The analytical methods used in this investigation are those developed in this laboratory: cyanamide by Pinck (*15*), dicyanodiamide by Garby (*7*), and urea by Fox and Geldard (*6*). Total nitrogen was obtained by the Kjeldahl method.

Preliminary experiments were run on cyanamide solutions made up by adding large amounts of cyanamide to aqua ammonia. These solutions were heated in glass evaporating dishes on a steam bath until practically all the water was driven off. The residue was then dried at 125° C. and analyzed for total nitrogen and dicyanodiamide; found 95 to 97 per cent conversion.

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A series of experiments was then performed under similar conditions, but on solutions of known composition. The concentration and relative proportions of cyanamide and ammonia were varied to afford some indication of the influence of these factors. The analyses of the initial solutions and of the final residues are presented in Table I.

TABLE I. POLYMERIZATION OF CYANAMIDE TO DICYANODIAMIDE

	Concn. of Initial Soln.		Analysis of Product			
Expt. No.	Cyanamide %	NH_3 %	Total N %	Dicyanodiamide N %	Dicyanodiamide %	Urea[a] %
1	41.7	16.6	65.25	63.90	98.0	...
2	29.4	11.7	65.55	62.90	96.2	0.3
3	26.4	21.0	65.45	64.10	98.0	...
4	22.7	9.0	66.22	63.25	95.6	0.4
5	20.9	16.6	65.40	62.30	95.3	...
6	19.4	23.0	65.88	62.75	95.2	...

[a] Determined only in experiments 2 and 4.

These results show that a conversion of cyanamide to dicyanodiamide higher than that recorded in the literature is obtainable, and moreover, the extent of polymerization is not appreciably affected by the variation of the cyanamide concentration in aqueous solutions of cyanamide and ammonia of these high concentrations.

Effect of Concentration of Cyanamide and Ammonia

To determine the minimum amount of ammonia necessary for conversion in the presence of various concentrations of cyanamide, a series of experiments was carried out in which these factors were varied, the solutions being heated for a period of 15 minutes. The composition of the solutions and analyses of the products are shown in Table II.

The results of these and subsequent experiments indicate that a maximum conversion of cyanamide to dicyanodiamide is obtained in solutions containing at least 20 per cent cyanamide and 2 per cent ammonia. The maximum yield of dicyanodiamide is not affected when higher concentrations of either cyanamide or ammonia are used. It was also observed that cyanamide is quantitatively polymerized to dicyanodiamide in liquid ammonia solution upon spontaneous evaporation of the solvent.

If vigorously digested, the rate of polymerization is more rapid and the final conversion is greater than with gentle boiling.

Table II. Polymerization of Cyanamide Solutions with Varying Concentrations of Cyanamide and Ammonia

	Concn. of Initial Soln.		*Analysis of Product*			
Expt. No.	Cyanamide	NH_3	Total N	Ammonia N	Dicyanodiamide N	Conversion
	%	%	*Grams*	*Gram*	*Grams*	%
7	38.0	0.6	1.446	0.001	0.766	53.0
8	38.0	1.1	1.114	0.001	0.784	70.5
9	38.0	2.4	1.294	0.004	1.228	95.2
10	38.0	3.6	1.216	0.006	1.154	95.3
11	38.0	4.5	1.252	0.009	1.195	96.2
12	21.7	0.6	0.734	0.001	0.381	51.9
13	21.7	1.1	0.749	0.002	0.569	76.2
14	21.7	2.4	0.708	0.003	0.680	96.6
15	21.7	3.6	0.640	0.003	0.625	98.2
16	21.7	4.5	0.700	0.004	0.671	96.5
17	10.0	0.6	0.351	0.003	0.039	10.8
18	10.0	1.1	0.298	0.003	0.060	20.4
19	10.0	2.4	0.365	0.004	0.110	30.6
20	10.0	3.6	0.435	0.006	0.212	49.4
21	10.0	4.5	0.395	0.006	0.204	52.3[a]

[a] Cyanamide nitrogen, 0.182 gram or 46.8 per cent.

Rate of Polymerization

After the concentration of cyanamide and ammonia and the conditions of heating most favorable for the polymerization were determined, its rate in a solution containing 23.6 per cent cyanamide and 2.4 per cent ammonia was studied. The results are shown in the following table:

		Analysis of Product			
Expt. No.	Time of Digestion	Total N	Ammonia N	Dicyanodiamide N	Conversion
	Min.	*Gram*	*Gram*	*Gram*	%
22	5	0.801	0.014	0.342	42.3
23	10	0.790	0.004	0.569	72.4
24	15	0.777	0.003	0.758	98.0

In the foregoing experiments there remained as a source of error the possibility that some cyanamide might have been lost by volatilization (*11*). The efficiency of the process was therefore determined by basing the yield on an accurately determined amount of starting material. A 20 per cent (approximate) cyanamide solution was made up, and an aliquot was analyzed and found to have the following composition: total nitrogen, 0.6745 gram; cyanamide nitrogen, 0.6465 gram; dicyanodiamide nitrogen, 0.0265 gram. The polymerization product of a similar aliquot containing 2.5 per cent ammonia gave the following analyses; total nitrogen, 0.6730 gram; cyanamide, nitrogen, 0.0070 gram; dicyanodiamide nitrogen, 0.6653 gram. It is evident that no cyanamide was lost by evaporation, for the final crop of dicyanodiamide and cyanamide was equivalent to 99.7 per cent of the initial total nitrogen. It is noteworthy that 98.9 per cent of the cyanamide was converted into dicyanodiamide.

Polymerization in a Closed System

Polymerization was also studied in a closed system by carrying out a number of experiments in sealed tubes. The data are as follows:

				Analysis of Product[a]	
Expt. No.	Cyanamide Concn.	NH_3 Concn.	Time of Heating	Cyanamide	Didyanodiamide
	%	%	*Min.*	%	%
25	10.0	0.5	15	3.0	90.1
26	10.0	0.5	25	4.3	92.7
27	17.2	2.4	15	3.6	94.1

[a] Urea was not determined but may be estimated by difference.

Although fairly satisfactory results were obtained in the closed system, it was believed that near the end of the reaction when there would be a deficiency of cyanamide with respect to ammonia, the consequently higher hydroxl-ion concentration would bring about some hydrolysis of cyanamide to urea. This conjecture was confirmed by an experiment in which a 5 per cent solution of cyanamide containing 0.4 per cent ammonia was heated at 100° C. in a closed system. The reaction product yielded 6.4 per cent of the total nitrogen in the form of urea and still had 5.5 per cent unconverted cyanamide.

In order to determine the applicability of the new method to a somewhat larger scale, the following experiment was performed: Three liters of a 20 per cent cyanamide solution were made ammoniacal to the extent of 2.4 per cent by the addition of 380 cc. aqua ammonia. The solution was transferred to a steam-jacketed Elyria kettle (2-gallon or 7.6-liter capacity) and heated at a temperature ranging between 98° and 104° C. for 25 minutes. The product was collected and dried in an oven at 100°. A yield of 97.9 per cent dicyanodiamide was obtained.

Suggested Method for the Preparation of Dicyanodiamide

A neutral aqueous solution of cyanamide, or a solution made very slightly alkaline with ammonia, is evaporated at reduced pressure to a concentration of at least 20 per cent cyanamide. While the solution is still hot (70° C. or thereabout), ammonia, either gaseous or in the form of aqua ammonia, is added in quantity sufficient to bring its concentration within the range of 2.0 to 4.5 per cent. The temperature is then raised as rapidly as possible until the reaction mixture boils vigorously, and the heating is continued until the cyanamide has been completely converted, as shown by a qualitative test with ammoniacal silver nitrate. The ammonia may be recovered and stored for use in subsequent batches or it may be found desirable to pass it directly into one or more converter units in series, before final recovery. The charge may be evaporated practically to dryness without loss or decomposition.

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Received January 30, 1935.