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THE HYDROLYSIS AND POLYMERIZATION OF CYANAMIDE

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The hydrolysis and polymerization of cyanamide in aqueous solutions have been the subject of many investigations, but an examination of the literature discloses a great diversity of opinion as to the nature of the reactions in the presence of acids and alkalies. While it is generally known that alkalies favor polymerization of cyanamide to dicyanodiamide, the simultaneous hydrolysis to urea appears to have been almost completely overlooked. Furthermore, in spite of the well-known fact that acids catalyze the hydrolysis of cyanamide to urea, a number of recent investigators have labored under the impression that polymerization also occurs in the presence of dil. acids.

The behavior of cyanamide in acid, alkaline and neutral solutions was investigated by Baumann,² who stated that water alone has no action on cyanamide, that urea is never obtained from cyanamide by the action of alkalies, and that urea is the main product of the action of acids, some dicyanodiamide being formed, the quantity of the latter being greatest in dil. acids. Baumann failed to note the formation of urea in alkaline solutions, and this error apparently influenced later investigators. Ulpiani states³ that cyanamide in an aqueous solution is unchanged by boiling for 50 hours, and submits evidence⁴ to show that in the presence of acids, cyanamide is hydrolyzed to urea without the formation of any dicyanodiamide.

The polymerization of cyanamide in the presence of ammonium, sodium, and potassium hydroxides has been investigated by Grube and Kruger.⁵ On the basis of their experiments they advanced the theory that polymerization of cyanamide in aqueous solution is the result of the union of free un-ionized cyanamide with the ion, HCN_2^- , these ions being present through the dissociation of a salt of cyanamide. Although the formation of urea, which undoubtedly occurred to some extent, was not taken into account, this does not invalidate their theory as will later be shown. The work of Morrell and Burgen⁶ on the polymerization of cyanamide, performed independently of Grube and Kruger, led to practically the same theory, although their conclusions are somewhat confused by their belief that acids even in minute quantities, as well as bases, cause polymerization of cyanamide. It would appear that Morrell and Burgen were influenced also by the statement of Baumann, to which they refer, namely, that no "urea is produced by the action of alkalies on cyanamide." In both of the investigations above mentioned the disappearance of cyanamide only was measured, the assumption being made in the latter case at least, that the decrease in concentration of this compound was due to polymerization alone.

¹ The authors are indebted to E. J. Fox for the analytical work presented in this paper.

² Baumann, *Ber.*, **6**, 1373 (1873).

³ Ulpiani, *Rend. soc. chim. di Roma*, **1906**, p. 4.

⁴ Ulpiani, *Gazz. chim. ital.*, **38**, [2] 358 (1908).

⁵ Grube and Kruger, *Z. physik. Chem.*, **86**, 65 (1913).

⁶ Morrell and Burgen, *J. Chem. Soc.*, **105**, 576 (1914).

In a paper dealing with the relation of cyanamide to urea, the constitution of cyanamide, and the mechanism of its polymerization, E. A. Werner,⁷ severely criticizes the ionic theory of polymerization above mentioned and puts forward a theory which he claims "explains the mechanism of the change, in complete agreement with all the observed facts." This theory postulates the existence of 2 tautomeric forms of cyanamide in "electrostatic equilibrium" and that on the addition of either an acid or a base the equilibrium is disturbed, resulting in polymerization by union of molecules in process of transformation from one form to the other. Werner furthermore concludes that cyanamide is remarkably resistant to hydrolysis in the presence of dil. acids or alkalies; that urea cannot be obtained from cyanamide in acid solution except as a salt of the acid and, therefore, in no greater quantity than the equivalent amount of acid present; and that "cyanamide has not been, and probably cannot be, directly hydrolyzed to yield urea in the free state."

It is seen from the preceding discussion that a considerable conflict of opinion exists even among the more recent investigators as to the nature and course of the transformation of cyanamide in acid and alkaline solutions. The investigation described in this paper was, therefore, made to obtain definite information on this subject.

Procedure.—The procedure in our experiments was to maintain a solution of cyanamide, containing acid or alkali, at a definite temperature and follow the course of the reactions by determining both cyanamide and urea and testing qualitatively for dicyanodiamide and guanylurea. In this way account was taken of all compounds which are significant in the interpretation of the results, thus avoiding the obvious error in previous investigations.

Recrystallized cyanamide was used in all experiments. This material contained about 98.5% of H_2CN_2 , the impurities consisting mainly of moisture and ether, together with traces of urea. The solutions were placed in glass-stoppered bottles of 285 cc. capacity, which were sealed and then rotated in a thermostat at $50^\circ \pm 0.025^\circ$. This temperature was selected as one at which the reaction velocity was sufficiently high to afford measurable differences in reasonable lengths of time, and furthermore one which could be maintained accurately without great difficulty.

Samples of approximately 28 cc. each were withdrawn and the reaction arrested by transferring to small bottles immersed in an ice-bath. The temperature of the sample in each case was allowed to fall to 20° and the solution then diluted and analyzed immediately in order to avoid the changes which would undoubtedly take place even in the diluted samples if these should be allowed to stand.

Analytical Methods.—Total nitrogen was determined on aliquot portions of the sample by the standard Kjeldahl method. Cyanamide was precipitated with ammoniacal silver nitrate and the precipitate, after being washed free of all soluble nitrogen salts, was analyzed for nitrogen by the Kjeldahl method. Urea was determined by the urease method,⁸ which was found to be very reliable. Dicyanodiamide was not determined directly because an accurate method had as yet not been developed. In the few instances where figures for this compound are given, they were obtained by subtracting the sum of the cyanamide and urea nitrogens from the total nitrogen. Qualitative tests for dicyanodiamide and guanylurea were made by the nickel method.

⁷ Werner, *J. Chem. Soc.*, 107, 715 (1915).

⁸ Fox and Geldard, to be published later.

This method involves the hydrolysis of dicyanodiamide to guanylurea and the precipitation of the nickel salt of the latter.⁹

Effect of Acid Concentration on Rate of Hydrolysis.—The composition of the solutions in this experiment is given in Table I. The solutions were maintained at 50°, and samples were taken after 2, 4 and 24 hours.

TABLE I

EFFECT OF ACID CONCENTRATION ON RATE OF HYDROLYSIS OF CYANAMIDE

Composition of solns. Moles per liter	After 2 hours % of total nitrogen present as		After 4 hours % of total nitrogen present as		After 24 hours % of total nitrogen present as	
	Cyan. N	Urea N	Cyan. N	Urea N	Cyan. N	Urea N
1 H ₂ CN ₂ 0.01 H ₂ SO ₄	93.3	6.5	90.3	9.9	66.4	34.3
0.5 H ₂ CN ₂ 0.01 H ₂ SO ₄	93.5	7.3	89.7	10.6	62.8	37.2
0.5 H ₂ CN ₂ 0.1 H ₂ SO ₄	66.1	34.4	49.4	51.1	4.1	95.8
0.5 H ₂ CN ₂ 1 H ₂ SO ₄	1.6	99.2	None	100.2	None	100.0

In the case of molal sulfuric acid it will be noted that the cyanamide has been *completely* hydrolyzed to urea in less than 4 hours. Qualitative tests on the final solution failed to show the presence of either dicyanodiamide or guanylurea. The practically negligible effect on the percentage conversion, in a given time interval, produced by doubling the concentration of cyanamide is shown in the experiments in which *M* and 0.5 *M* cyanamide were employed in identical acid concentrations. This fact shows that the hydrolysis is a monomolecular reaction, as opposed to the contention of Werner that hydrolysis could only proceed to the formation of a salt of urea. It should also be noted that in only one case, that of *M* acid, was there sufficient acid present to combine in molar proportion with the urea formed. In all other cases the urea was greatly in excess of the acid which would be required to combine with it. This is also contrary to Werner's statements.

Order of Hydrolysis Reaction.—To establish further the order of the hydrolysis reaction the following experiment was made. A solution was made up with a concentration 0.5 *M* cyanamide and 0.06 *M* sulfuric acid and immediately analyzed. It was then maintained at 50° and samples were taken at short intervals of time and analyzed for total nitrogen and urea nitrogen. The results are shown in Table II together with the calculated velocity constant.

The acidity of the solution decreased during the run from 0.120 *N* to 0.116 *N*. This fact may be attributed to the decomposition of urea

⁹ A quantitative method based on this procedure will be described in a forthcoming paper from this Laboratory.

to ammonium sulfate and probably explains the falling value of the constant which was obtained. Since the progress of the reaction was followed by analyzing for urea, the figures given should be corrected by allowing for the urea decomposed by the acid. To estimate this correction, the

TABLE II
HYDROLYSIS OF CYANAMIDE BY SULFURIC ACID. ORDER OF REACTION

Time Min.	Cyan. N as % of total N $\frac{A-X}{A}$	$K = 2.3 \frac{1}{t} \log \frac{A}{A-X}$	Time Min.	Cyan. N as % of total N $\frac{A-X}{A}$	$K = 2.3 \frac{1}{t} \log \frac{A}{A-X}$
0	98.11 (A)	115	78.31	0.00196
25	93.19	235	63.55	0.00184
55	87.91	0.00199	355	52.00	0.00179
86	82.73	0.00197	1080	14.30	0.00178
					Av. 0.00189

acidity was determined on the sample taken after 1080 minutes. Calculating from this the urea decomposed, the corrected value for the constant at the end of this period becomes 0.00184.¹⁰

We may definitely conclude that the hydrolysis of cyanamide in the presence of sulfuric acid is a monomolecular reaction in which the acid plays the role of catalyst.

In support of his theory of polymerization of cyanamide, Werner describes an experiment in which solutions of cyanamide with various concentrations of acetic acid were heated at 100° for periods ranging from 2 to 10 hours. The disappearance of cyanamide was measured and attributed entirely to polymerization. As it is our belief that urea is the primary product under these conditions and that dicyanodiamide is not formed at all, an experiment was made in which a solution having a concentration of 0.5 *M* cyanamide and *M* acetic acid was heated for 4 hours at 100°. Careful qualitative tests on the resulting solution showed the complete absence of dicyanodiamide or guanylurea. Urea was present to the extent of approximately 30% of the total nitrogen. The solution contained some ammonium acetate, derived doubtless from the decomposition of urea.

The preceding experiments all point to the conclusion that hydrolysis of cyanamide is catalyzed by the hydrogen ion. To confirm this view an experiment was made in which a solution of cyanamide containing the acid salt ammonium dihydrogen phosphate was heated for several hours at 100°. About 20% of the nitrogen in the final solution was present as urea and none as dicyanodiamide.

Hydrolysis and Polymerization in the Presence of Sodium Hydroxide.—Experiments on the behavior of cyanamide in the presence of sodium hydroxide were made using solutions 0.5 *M* with respect to cyanamide

¹⁰ No allowance need be made for the decrease in rate of reaction due to the 4% decrease in acid concentration, since the data given in Table I show this to be negligible.

and 0.01, 0.1 and 1 *M* with respect to sodium hydroxide. Samples were taken after 1, 2, 3 and 20 hours.

TABLE III
HYDROLYSIS AND POLYMERIZATION OF CYANAMIDE IN THE PRESENCE OF SODIUM HYDROXIDE AT 50°

Concn. of NaOH Moles per liter	After 1 hr.			After 2 hrs.			After 3 hrs.			After 20 hrs.		
	% of total nitrogen present as			% of total nitrogen present as			% of total nitrogen present as			% of total nitrogen present as		
	Cyan. N	Urea N	Dicyan. N ^a	Cyan. N	Urea N	Dicyan. N ^a	Cyan. N	Urea N	Dicyan. N ^a	Cyan. N	Urea N	Dicyan. N ^a
0.01	92.1	2.9	5.0	90.4	3.3	6.3	85.8	3.3	10.9	47.2	4.9	47.9
0.1	69.6	3.2	27.2	55.6	3.8	40.6	44.4	4.1	51.5	14.1	10.1	75.8
1.0	94.0	5.0	1.0	92.3	7.0	0.7	89.3	8.3	2.4	62.7	34.4	2.9

^a Dicyanodiamide values obtained by difference.

The point of greatest interest is the remarkably low value for dicyanodiamide, and the correspondingly high value for urea, in *M* sodium hydroxide after 20 hours. Less than 3% of the cyanamide had been polymerized while over 30% had been hydrolyzed. This is in striking contrast to the belief commonly held¹¹ as to the behavior of cyanamide in alkaline solution. It is seen that the disappearance of cyanamide was most rapid and proceeded to the greatest extent in 0.1 *M* sodium hydroxide solution and that dicyanodiamide formation accounts for about 75% of the total nitrogen. Since of the 3 solutions, this one contained free and combined cyanamide most nearly in the proportion of 1:1, which according to the ionic theory of Grube and Kruger is the optimum condition for polymerization, the results further substantiate their theory for the polymerization of cyanamide.

Grube and Kruger⁵ do not mention the formation of urea in alkaline cyanamide solutions. The fact that hydrolysis does occur, however, does not invalidate their polymerization theory but rather may be readily interpreted in conjunction with it. When sodium hydroxide is added to a solution of cyanamide the principal ionic relations are expressed by the reaction $\text{H}_2\text{CN}_2 + \text{Na}^+ + \text{OH}^- \rightleftharpoons \text{Na}^+ + \text{HCN}_2^- + \text{HOH}$. The equilibrium is such that the reaction proceeds to the right nearly to completion, hydrolysis of the salt, NaHCN_2 , in molal solution being of the order of 3% at 25°, according to Grube and Kruger.

If we consider that the hydrolysis in the presence of alkalis is catalyzed by the hydroxyl ion we should expect the rate of reaction to increase with increasing concentration of this ion. That this is the case is shown in Table III. In these experiments relatively small amounts of urea were formed in the two solutions containing 0.01 and 0.1 *M* sodium hydroxide, but in the case of *M* sodium hydroxide hydrolysis proceeded practically to the exclusion of polymerization.

In interpreting these results it should be pointed out that the amount of

¹¹ Compare Ref. 6.

the catalytic agent, hydroxide ion, present is determined solely in the first two experiments by the hydrolysis of the salt, sodium acid cyanamide, in accordance with the equation, $\text{Na}^+ \text{HCN}_2^- + \text{H}_2\text{O} = \text{Na}^+ + \text{OH}^- + \text{H}_2\text{CN}_2$. In the case of 0.01 *M* alkali this condition prevailed throughout the experiment and we find but little urea formed. The excess of cyanamide was not so great in 0.1 *M* alkali and we would therefore have more free sodium hydroxide in solution, with a corresponding increase in hydrolysis. In the third run, however, where there was at all times an actual excess of sodium hydroxide, the high concentration of hydroxyl ion would increase the velocity of the hydrolysis reaction, and consequently the free cyanamide in solution would be transformed very largely into urea. The concentration of free cyanamide at any instant would be low, however, and hence the disappearance of cyanamide would be slower than in the other two experiments as is seen to be the case.

From these experiments it is seen that the hydrolysis of cyanamide in alkaline solutions is catalyzed by the free alkali (hydroxyl ion). It is seen that the reaction is analogous in several respects to the hydrolysis in the presence of acids. On the other hand, a velocity constant is not to be expected, since the hydroxyl-ion concentration is a variable, increasing as the alkali is released from combination with cyanamide.

Summary

1. The behavior of cyanamide in both acid and alkaline solution has been studied and the course of the reactions followed by determinations of both cyanamide and urea.
2. Cyanamide is hydrolyzed in sulfuric acid solutions to urea without the formation of dicyanodiamide. This appears to be the effect of the hydrogen ion since mineral and organic acids and acid salts produce similar results.
3. The hydrolysis of cyanamide in acid solution is a monomolecular reaction. The velocity of hydrolysis increases with increasing acid concentration within the limits studied.
4. Polymerization of cyanamide in aqueous solution cannot be explained by the equilibrium theory advanced by Werner, since the presence of acids does not cause polymerization.
5. Our results on the polymerization of cyanamide in aqueous solutions can be readily interpreted on the basis of the ionic theory suggested by Grube and Kruger.
6. This investigation shows conclusively that cyanamide in alkaline solutions is hydrolyzed to urea, as well as polymerized to dicyanodiamide, the hydrolysis probably being due to the catalytic influence of the hydroxyl ion.