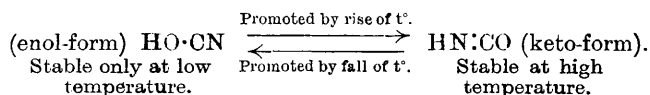


CXLVII.—*The Constitution of Carbamides. Part XIII.*
The Constitution of Cyanic Acid, and the
Formation of Urea from the Interaction of
Ammonia and Cyanic Acid at Low Temperatures.

By EMIL ALPHONSE WERNER and WILLIAM ROBERT FEARON.

THE theory which has been put forward by one of us to explain the constitution of urea, and the mechanism of its formation from ammonium cyanate (T., 1913, **103**, 1013, 2276; 1918, **113**, 84), is based, primarily, on the conception that cyanic acid, whether in the static condition or in solution, is an equilibrium mixture, represented thus:



Since cyanic acid is at all times very unstable, the stability referred to above is only relative. Permanent stability is only

attained by polymerisation, with the production of cyanuric acid from the keto-form and of cyamelide from the enol-form of the acid (*loc. cit.*).

Now, the ease with which ammonium cyanate is changed to urea is indicative of a close similarity in structure, and hence the constitution of cyanic acid is a question of paramount importance in solving the problem of the relation which exists between the two isomerides.

There are two reasons why previous investigators have given either little or no consideration to this important question, namely, the apparent uncertainty which has been assumed to exist as regards the nature of cyanic acid, and the general acceptance of the "carbamide" formula, which has all along masked the true relationship between urea and ammonium cyanate.

As a matter of fact, the constitution of cyanic acid is clearly indicated by (a) its polymerisation, and (b) its hydrolysis and behaviour towards ammonia at low temperatures.

(a) *Polymerisation of Cyanic Acid.*

Senier and Walsh (T., 1902, **81**, 290) showed that the spontaneous polymerisation of cyanic acid yielded a product which contained, in round numbers, 70 per cent. of cyanuric acid and 30 per cent. of cyamelide. This was the result of a single experiment, in which no particular effort was made to control the temperature at which polymerisation took effect.

If the theory of the polymerisation of cyanic acid which was propounded by one of us is sound (T., 1913, **103**, 1016),* and if cyanic acid is an equilibrium mixture, as indicated above, it follows that its composition at any particular temperature will be revealed by the relative proportions of the two polymerides formed. This inference, which was predicted when the theory was put forward, has now been verified by analyses of the products formed when liquid cyanic acid polymerised at different temperatures.

At zero the acid was stable for about four hours, provided it was not agitated, and it polymerised slowly. In order to obtain a reasonable control of the temperature at which polymerisation took place, only very small quantities of the acid were dealt with in each experiment (see experimental part).

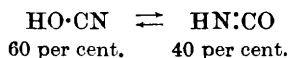
The results were as follows:

* For the sake of brevity, the theory is not reproduced here; in order to appreciate the significance of the results obtained it is necessary to consult the paper on the mechanism of the polymerisation of cyanic acid to which reference is made.

TABLE I.

Temperature of polymerisation (approximate).	Weight of polymeride.	Cyanuric acid found.	Percentage composition of polymeride.	
			Cyamelide.	Cyanuric acid.
0°	0.53 gram.	0.216 gram	59.25	40.75
5	0.42 "	0.174 "	58.58	41.42
10	0.105 "	0.045 "	57.27	42.73
20	0.24 "	0.136 "	42.92	57.08

In several experiments, where the acid polymerised when the containing vessel was plunged into water at 20°, the temperature rose suddenly to about 70°, and the proportions of cyanuric acid formed were from 70 to 80 per cent. Since the latter acid is almost the sole product found when polymerisation takes place at high temperatures, as, for example, when urea is heated above its melting point (132°) (T., 1913, **103**, 2276), it follows that, under such conditions, cyanic acid is liberated in the keto-form. Liquid cyanic acid, on the other hand, must be an equilibrium mixture, the composition of which is a function of the temperature; thus, at 0°, it may be represented as approximately

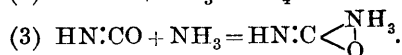


(b) *Hydrolysis of Cyanic Acid, and its Reaction with Ammonia at Low Temperatures.*

Whenever urea is formed in a reaction where cyanic acid and ammonia are concerned, it has always been assumed that it must originate from the transformation of ammonium cyanate produced in the first instance. Since the difference between the two isomerides is nothing more than that of the products of the union of ammonia with the enol- and keto-forms, respectively, of cyanic acid, it is obvious that the above assumption is superfluous.

A quantitative study of the hydrolysis of cyanic acid has supplied convincing evidence that both isomerides are simultaneously formed when ammonia reacts with the acid at low temperatures. Not less than six consecutive changes are involved during the progress of this reaction, and these are conveniently divided into two groups, as follows:

Primary changes:



Secondary changes:

- (4) $\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} = \text{NH}_4\text{HCO}_3$.
 (5) Formation of biuret from interaction of urea and HNCO .
 (6) Production of cyamelide.

The main question was to prove the validity of reaction (3). This was successfully accomplished when an approximately *N*/4-solution of cyanic acid was allowed to hydrolyse at 0° . Under such conditions, the secondary changes were almost completely suppressed up to the point at which the primary changes were completed. A solution of cyanic acid was prepared by the addition of the theoretical amount (62.5 c.c.) of *N*-nitric acid to 5.05 grams of pure potassium cyanate dissolved in 187.5 c.c. of water. The solution (250 c.c.) was prepared at 0° , and maintained at this point during all the analyses.

The following results were obtained with 25 c.c., taken at intervals of fifteen minutes (Expt. II).

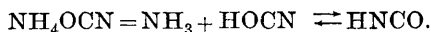
TABLE II.

Time in minutes.	Cyanic acid present (free, and as NH_4OCN). Gram.	Urea formed (theoretical). Gram.	Urea found. Gram.
—	0.230*	—	—
15	0.195	0.024	0.018
30	0.165	0.045	0.038
45	0.129	0.070	0.063
60	0.109	0.084	0.081
75	0.101	0.090	0.087
90	0.094	0.094	0.089
1230	0.061	0.118	not estimated.

* 0.267 Gram is the theoretical amount, from the weight of potassium cyanate taken. The deficiency found at the outset was due to: (a) loss by volatilisation—the solution had a very pungent odour; (b) time elapsed during addition of nitric acid, and impossibility of avoiding to a small extent the change $\text{HOCN} + \text{H}_2\text{O} + \text{HNO}_3 = \text{NH}_4\text{NO}_3 + \text{CO}_2$.

The theoretical values for urea formed were calculated from the amounts of cyanic acid which had disappeared after each interval on the basis $2\text{HNCO} \rightarrow \text{CON}_2\text{H}_4$.

It will be seen that, under the conditions stated, the hydrolysis of cyanic acid was comparatively slow; thus, about ninety minutes were required before all free acid had disappeared. At this stage the three primary reactions had been completed, hence there was no object in estimating urea formed beyond this point, since it could only then arise from the slow transformation of ammonium cyanate, as a result of its hydrolytic dissociation, thus:



This is strikingly shown by the last result, where, in the interval between 90 and 1230 minutes, only 0.033 gram of cyanic acid (as ammonium cyanate) had been removed, and when this is considered in connexion with the fact that in 75 minutes from the commencement of the change 0.313 gram of urea was formed, there can be no doubt that the latter can only have been produced as the direct result of reaction (3). Now, after 75 minutes, when the disturbing effects of reaction (4) were just noticeable,* half of the solution (125 c.c.) had been used, that is, 1.15 grams of cyanic acid, capable of yielding 0.8 gram of either urea or ammonium cyanate, had taken part in the completion of reactions (1), (2), and (3). Hence (0.8—0.313) 0.487 gram of ammonium cyanate was formed, which shows that cyanic acid, in aqueous solution at 0°, had reacted with ammonia as a mixture of $\text{HO-CN} = 60.9$ per cent. and of $\text{HNCO} = 39.1$ per cent., a result almost identical with that arrived at from the study of the polymerisation of the anhydrous acid at the same temperature.

As regards the secondary changes, the production of biuret confirms reaction (3), since it must be a sequence of it (compare Werner, T., *loc. cit.*; P., 1914, **30**, 262), and whilst its formation does not affect the above result as regards the proportion of cyanic acid which reacted as HN:CO , its presence was mainly responsible for the low values found for urea formed in the early stages of the reaction. In agreement with theory, the formation of biuret was largely confined to this period.

The production of a trace of cyamelide in these experiments proves that cyanic acid was liberated in the enol-form, since the generation of this polymeride takes effect from the change $\text{HO-CN} \rightarrow \text{HNCO}$. When a solution of ammonia in pure ether at -8° was gradually added to a similar solution of cyanic acid, the crystalline product which immediately separated was found to be a mixture of ammonium cyanate and urea in the proportion of 6 to 2.6 respectively.

Note on the Xanthhydrol Test for Urea.

The use of xanthhydrol for the detection and estimation of urea depends on the formation of a very sparingly soluble condensation product. Fosse (*Compt. rend.*, 1907, **145**, 813; 1913, **156**, 1938) recommends pure acetic acid as the solvent in applying the test. This introduces certain limitations, and where the detection of a

* For this reason, 75 minutes must be taken as the limit up to which the change had proceeded undisturbed in accordance with the primary reactions.

trace of urea in a relatively large volume of water is desired, the process is tedious.

As a matter of fact, xanthhydrol is not a test for "free" urea; thus, in alcoholic solution, no reaction was effected, even after heating at 100° in a sealed tube for several days. After the addition of one drop of concentrated hydrochloric acid, the condensation product was precipitated, and its formation was completed within ten minutes. The solubility of dixanthylurea in pure alcohol at 15° was equal to 0.009 gram in 100 c.c.

A salt of urea must be formed in order to bring about the necessary configuration of the urea molecule before it can react with xanthhydrol, and, in accordance with this view, the test can be applied as follows.

A saturated aqueous solution of xanthhydrol (containing 0.13 gram in 1000 c.c. at 15°) is readily prepared by adding the reagent, previously dissolved in 2 c.c. of alcohol, to a litre of boiling water. The cold solution (filtered, if necessary), when added in considerable excess (not less than 6 vols. to 1) to an aqueous solution containing urea to which a few drops of hydrochloric acid have been added, will reveal 1 part in 10,000 within fifteen seconds, whilst 1 part of urea in 800,000 can be detected in about ten minutes.

The solution of xanthhydrol loses its sensitiveness after about a week, on account of gradual oxidation to xanthone.

EXPERIMENTAL.

I. *Polymerisation of Cyanic Acid.*—The results given in table I were obtained as follows: cyanic acid was prepared from pure, dry cyanuric acid, which was heated electrically in a hard glass tube so arranged that the heating could be continued right up to the neck of the receiver. The construction of the latter was such that liquid cyanic acid collected in the narrow space between an inner and an outer vessel, each of which was kept at 0°. A relatively large surface of the acid was thus maintained at a constant temperature, and by careful avoidance of agitation, which was found to be a great promoter of the change, polymerisation was allowed to proceed as slowly as possible. The ice in the outer vessel only was displaced by water at the temperature at which it was desired to bring about polymerisation; in this way only was it possible to control, within reasonable limits, the temperature at which the change took effect.

A weighed quantity of the polymeride was extracted with hot water; the cyanuric acid present was estimated by titration with *N*/10-sodium hydroxide, using phenolphthalein as indicator.

Whilst it was necessary to prepare small portions of cyanic acid for each experiment, the values given represent the mean of many more experiments than are recorded.

II. *Formation of Urea at 0°.*—Cyanic acid was estimated by precipitation with an excess of silver nitrate, and the silver cyanate, dissolved in dilute nitric acid, was titrated by Volhard's method. The filtrate, freed from the excess of silver, was rendered just alkaline by addition of pure lime, and, after the removal of all traces of ammonia, urea was estimated in the residue by (a) the "hypobromite" method, (b) decomposition by urease, and (c) precipitation with xanthhydrol. The presence of biuret was proved by the copper test.

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UNIVERSITY CHEMICAL LABORATORY,
TRINITY COLLEGE, DUBLIN.

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