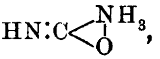
LXXVI.—*The Constitution of Carbamides. Part II. The Relation of Cyanamide to Urea. The Constitution of Cyanamide and the Mechanism of its Polymerisation.*

By Emil Alphonse Werner.

The constitution of cyanamide and its hydrolysis to urea have a special interest in connexion with the cyclic formula for the latter substance which has been proposed by the author (T., 1913, **103**, 1014, 2281). It was recently shown (T., 1914, **105**, 924) that urea assumes the "*iso*-carbamide" configuration in its reaction with methyl sulphate, this being derived from the structure:



$$\mathrm{HN{:}C}\!<\!\begin{matrix}\mathrm{NH_3}\\ |\\ \mathrm{O}\end{matrix},$$

which it is contended represents the true constitution of urea in the static condition, and when dissolved in a neutral solvent.

Whilst the main object of the present investigation was to obtain information regarding the structural relations of urea and cyanamide, the polymerisation of the latter has been incidentally examined, since this is a phenomenon which must be intimately associated with its constitution. A theory which explains the mechanism of the change, in complete agreement with all the observed facts, is now put forward, and is dealt with first, since it has a very important bearing on the main question under consideration.

The Polymerisation of Cyanamide.

Two papers on this subject have appeared recently, one by Grube and Krüger (*Zeitsch. physikal. Chem.*, 1913, **86**, 65), and the other by Morrell and Burgen (T., 1914, **105**, 576). Both investigations have shown that the well-known polymerisation of cyanamide to dicyanodiamide is greatly accelerated by the presence of alkalis, even in small amount, whilst Morrell and Burgen have also shown that an equally powerful accelerating effect is produced by acids.

The most interesting results which the latter investigators have brought to light are those dealing with the behaviour of cyanamide in the absence of either acid or base. They have shown that in a neutral aqueous solution cyanamide is remarkably resistant to polymerisation, a fact which is even more evident in the presence of alcohol, and, indeed, their results go to show that under such conditions cyanamide probably does not suffer polymerisation at all. Whilst the experimental results recorded in both investigations are beyond question, their interpretation and the conclusions drawn from them are certainly open to criticism.

An attempt has been made in both cases to explain the phenomenon of polymerisation by the aid of a purely ionic theory, which, as Morrell and Burgen freely admit, is not in harmony with all the observed facts, since they state that "a single explanation which will cover the accelerating action of both acids and bases cannot be put forward." Grube and Krüger (*loc. cit.*), who have only examined the influence of bases on the change, are satisfied with an ionic theory, and conclude that the course of the polymerisation proceeds according to the scheme:

$$CN{\cdot}NH_2 + \underset{\text{Cyan-amidion.}}{CN{\cdot}NH'} = \underset{\text{Dicyano-diamidion.}}{C_2N_2N_2H_3'},$$

an explanation which certainly throws very little light on either the cause or the mechanism of the change.

It must be remembered that cyanamide undergoes polymerisation when heated alone, in the absence of any solvent, and also when heated (at 150°) in solution in a non-ionising solvent, such as dry ether, as was shown long since by Drechsel (*J. pr. Chem.*, 1877, [ii], **9**, 284), and since there is no reason to conclude that the mechanism of the polymerisation under these conditions is different from that under the conditions just mentioned, it is obvious that an ionic theory which cannot include all the facts cannot be sound.

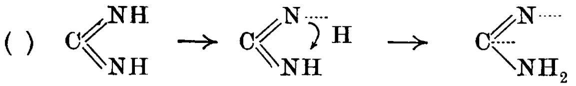
Curiously enough, in neither of the investigations has the primary question of the constitution of cyanamide itself been discussed; the structural formula, $CN{\cdot}NH_2$, has alone been considered to represent all the properties of the substance, a conclusion which has certainly helped greatly to obscure the meaning of the observed facts.

Now it must be conceded that the properties of cyanamide are in every sense characteristic of a tautomeric substance, and the constitution of the compound may be equally well expressed by the di-imino formula $C(NH)_2$; in the author's opinion both configurations of the molecule are present in a pure neutral solution, and the remarkable stability of cyanamide under such condition,* as shown by the experimental results of Morrell and Burgen, is very probably due to an electrostatic equilibrium between the two forms, which may be represented by the scheme:

$$\underset{\text{Acidic form }(-).}{(a).\ NH{:}C{:}NH.} \rightleftharpoons \underset{\text{Basic form }(+).}{CN{\cdot}NH_2\ (b).}$$

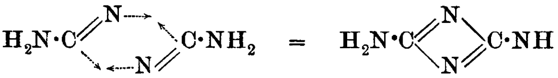
If this view be taken, the mechanism of the polymerisation may be easily explained by the aid of a theory similar to that put forward by the author to explain the polymerisation of the related cyanic acid (T., 1913, **103**, 1017), which will be found to cover all the observed facts.

Thus the addition of either an acid or a base to a neutral solution of cyanamide will disturb the above equilibrium, and polymerisation will soon commence as the result of an effort to maintain the equilibrium; for example, if a sufficiently strong acid be added to the solution it will at once exert a neutralising effect on the electropositive form (*b*), and will cause form (*a*) to change into form (*b*) in order to meet the new condition; polymerisation will then take effect, as illustrated in the following scheme:



(−.) (Phase 1) (Phase 2.)

the union of two molecules in phase (2) will give rise to the formation of dicyanodiamide, thus:



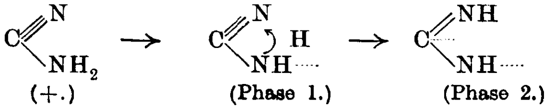
Hofmann's formula.

On the other hand, if a base be added to the solution it will

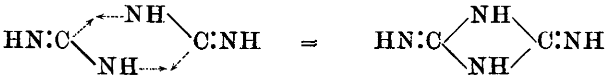
* The author has had in his possession an aqueous solution of pure cyanamide for more than four and a-half years, at the end of which time it still contained a large proportion of the unchanged substance.

neutralise the electronegative form (*a*), and (*b*) will then change in the following order:

(2)



and the union of two molecules in phase (2) will give rise to the formation of dicyanodiamide, thus:



Baumann's formula.

Dicyanodiamide, like cyanamide, is also a tautomeric substance, but, unlike cyanamide, is not capable of yielding salts with either acids or bases, and is, as Caro and Grossmann have shown (*Chem. Zeit.*, 1909, **33**, 734), a perfectly neutral substance; it can therefore be only a transition product formed from the cyanamide in its efforts to attain equilibrium (neutrality) with the base or acid present. In the latter case equilibrium is quickly reached by the hydrolysis of the dicyanodiamide to the strong base, the so-called dicyanodiamidine. As a matter of fact, the latter change appears to proceed with at least as great a velocity as the polymerisation of the cyanamide, since dicyanodiamidine can be detected in the solution as soon as the cyanamide commences to disappear. For this reason it has not been found possible to isolate any dicyandiamide from the product of the action of an acid on a solution of cyanamide.

In the case of the action of bases, dicyanodiamide can be easily obtained, this being the method commonly employed for its preparation; nevertheless, this does not represent final equilibrium under the conditions.

Dicyanodiamide is sensitive to hydrolysis by alkalis, a fairly strong acid, probably Hallwachs' amidodicyanic acid, being formed (ammonia and carbon dioxide being by-products), which ultimately neutralises the alkali. Whilst the velocity of this change is undoubtedly very much slower than the velocity of polymerisation of cyanamide in the presence of alkali, still its influence cannot be ignored, particularly in experiments where the heating at 100° was prolonged.

Morrell and Burgen have scarcely given this question the attention it deserves; it probably helps to explain the gradual decrease in the velocity of polymerisation which they observed. Their contention that during the course of the reaction the base (sodium hydroxide) is shared by the dicyanodiamide, and that this is dissociated primarily as a monobasic acid, is scarcely in agreement with the properties of the substance.

Whilst cyanamide affords a neutral solution, its acid character in so far as the production of metallic derivatives is concerned, is well known, and is very much more pronounced than the basic power; thus, according to Grube and Krüger, the salt NaN:C:NH in a molecular solution is dissociated only to the extent of about 3 per cent.

It seems evident, therefore, that a weak base should have a much greater disturbing effect on the equilibrium between the two forms of cyanamide than a correspondingly weak acid, and hence cause a much greater acceleration of the polymerisation.

In order to test this point, the behaviour of cyanamide in the presence of acetic acid has been examined; the results are given below, and for comparison a few values, calculated from Morrell and Burgen's experiments in the presence of ammonia, have been added.

The concentration of cyanamide was approximately 2 per cent.

(*a*) Cyanamide heated in a water-bath at 100° for two hours:

	Per cent. of cyanamide polymerised.
In *N*/20-Acetic acid	6·3
„ *N*/10 „ „	8·8
„ *N*/4 „ „	16·3
„ *N*/2 „ „	21·9

(*b*) Cyanamide, heated as above in *N*/2-acetic acid, was polymerised as follows:

1. 3 hours, 28·8. 2. 4 hours, 33·8. 3. 5 hours, 38·1 per cent.

(*c*) Cyanamide heated in the presence of normal acetic acid for ten hours was polymerised to the extent of 63·5 per cent.

(*d*) Cyanamide heated as above in the presence of ammonia (M. and B.):

In *N*/70-Ammonia.		In *N*/7-Ammonia.	
Time.	Cyanamide polymerised.	Time	Cyanamide polymerised.
2·5 hours	28·0 per cent.	1 hour	80·1 per cent.
4·5 „	39·5 „	1·5 hours	92·4 „
8·5 „	52·0 „	3 „	100·0 „

It will be noticed that in order to obtain well-marked results with acetic acid it was necessary to start with a concentration of not less than *N*/20, and an inspection of the values obtained shows at once the enormously greater accelerating power of the weak base.

Thus the amount of polymerisation produced by *N*/2-acetic acid is only equal to that produced by *N*/70-ammonia under approximately the same conditions, whilst after five hours the effect of *N*/2-acetic acid is less than half that produced by *N*/7-ammonia in one hour. These results are quite in agreement with the equilibrium theory, bearing in mind the properties of cyanamide.

The accelerating effect of even a trace of alkali on the polymerisation was so great, as shown by the very careful experiments of Morrell and Burgen, that one might easily have arrived at the erroneous conclusion that cyanamide was more stable in the presence of acetic acid than in aqueous solution.

For example, the following results were obtained (*e*) after heating a solution of cyanamide (3 per cent. approximately) in ordinary distilled water at 100° in a soft glass tube, (*f*) after keeping the solution at the ordinary temperature:

(*e*) Time in hours.	Cyanamide polymerised
2	27·5 per cent.
4	33·2 ,,
9	56·8 ,,
16	86·5 ,,

(*f*) Time.	Cyanamide polymerised.
After 10 weeks	29·4 per cent.
,, 12 ,,	37·5 ,,
,, 11 months	81·8 ,,

These results, which are higher than those obtained by Morrell and Burgen, are entirely due to basic matter extracted from the glass, and they serve merely to illustrate how the acceleration of the change may vary according to the quality of the glass vessel employed.

In the experiments where a solution of cyanamide was heated at 100° for nine and sixteen hours respectively, a small quantity of a basic substance separated in each case; this proved to be neither melamine nor ammeline, and has not yet been identified.

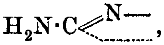
The polymerisation of cyanamide by heat alone, which is the chief factor in promoting the change, all other conditions being equal, can also be explained by the theory just described.

An increase in the vibratory motion within the molecule will naturally accompany a rise in temperature, and the stability of the cyanamide molecule will be thereby diminished, and the less stable form will tend to change into the more stable in accordance with one or other of the two schemes already given.

The direction of the change must depend on this relative stability of the two forms, and since the balance of evidence certainly favours the greater stability of the di-imino- or symmetrical form, the change will very probably take the course indicated in scheme (2).

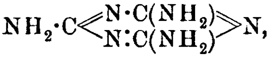
The more complex polymerisation of cyanamide at high temperatures (above 200°) with the production of the very strong base melamine is also in agreement with this view.

The sudden depolymerisation of dicyanodiamide by heat will give rise for the moment to cyanamide in the di-imino-form, the tendency to co-exist in equilibrium with the amino-form will persist, and by the union of three molecules in phase (2),



$$H_2N\cdot C{<}\begin{matrix}N—\\ \cdots\cdots\end{matrix},$$

scheme (1), the very stable, six-membered ring melamine,



$$NH_2\cdot C{<}\begin{matrix}N\cdot C(NH_2)\\ N{:}C(NH_2)\end{matrix}{>}N,$$

will be formed.

It may be added, in further support of the scheme (1), that a small quantity of melamine has always been detected in the product from the polymerisation of cyanamide in the presence of acids, but could not be found when bases were used.

The presence of traces of melamine and dicyanodiamidine in solutions containing an excess of cyanamide or dicyanodiamide may be easily recognised by the aid of picric acid.

Melamine picrate forms characteristic, tangled masses of extremely delicate, hair-like threads of a pale yellow colour, which decompose, without melting, at about 268°; dicyanodiamidine picrate separates slowly from solution in the form of nodules, or small rosettes of stout prisms of a dark yellow colour, which melt at 265°.

Interaction of Cyanamide and Nitrous Acid.

The behaviour of cyanamide towards nitrous acid does not appear to have been hitherto examined. A few quantitative experiments have supplied what appears to be conclusive evidence in favour of the views already expressed regarding the constitution of cyanamide in solution.

The experiments were carried out in a nitrometer, and the details are described in the experimental part of the paper.

The main facts observed may be stated as follows:

(1) Cyanamide and nitrous acid (liberated from sodium nitrite by an excess of acetic acid) showed practically no signs of interaction, so far as the evolution of gas was concerned, even after one hour.

Such a negative result could scarcely have been expected if cyanamide was wholly present in the form $CN\cdot NH_2$.

(2) In the presence of sulphuric acid there was an immediate brisk evolution of gas (almost entirely nitrogen), which, after an interval of two minutes, amounted to half the theoretical volume required by the equation:

$$CN\cdot NH_2 + ON\cdot OH = N_2 + H_2O + CN\cdot OH.$$

This was followed by a very slow and continuous evolution of gas largely composed of carbon dioxide, and therefore mainly due to the gradual hydrolysis of the cyanic acid generated in the first stage. An interval of one hour was required for the evolution of a volume of gas equal to that set free in the first few minutes. An examination of the residual liquid at this point showed that slightly over half of the cyanamide was still unchanged, whilst there was much nitrous acid present (see Expt. I).

(3) When the reaction was allowed to proceed for twenty minutes, nearly 60 per cent. of the cyanamide was unchanged, and in a final experiment, where the reaction was allowed to continue for twenty hours, nearly 13 per cent. of the cyanamide was still undecomposed (see Expts. II and III).

In spite of the secondary change introduced by the continuous decomposition of cyanic acid, the results have shown that the course of the reaction is in perfect harmony with the equilibrium theory; thus whilst all the cyanamide present at the outset in the amino-form is rapidly decomposed by nitrous acid in the usual manner, the more stable imino-form at the ordinary temperature changes very slowly into the amino-form, which is then attacked by nitrous acid as fast as it is generated. The results also indicate that in a normal solution of cyanamide the equilibrium mixture is approximately 60 per cent. $C(NH)_2$ and 40 per cent. $CN{\cdot}NH_2$ (Expt. II).

The Formation of Urea by the Hydrolysis of Cyanamide.

A study of the constitution of cyanamide was a necessary preliminary to an examination into the mechanism of its hydrolysis. The formation of urea from cyanamide was originally shown many years ago by Baumann (*Ber.*, 1873, **6**, 1373), but the exact conditions under which the hydrolytic change takes place have not, in the author's opinion, been properly appreciated. Thus Baumann showed that whilst very concentrated acid was necessary to obtain urea (as a salt) from cyanamide, this was always accompanied by more or less dicyanodiamidine, the proportion of the latter increasing with the dilution of the acid, and Drechsel (*J. pr. Chem.*, 1880, [ii], **20**, 77) has pointed out that the compound

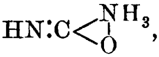
$$CN{\cdot}NH_2,2HCl,$$

when decomposed by water, did not afford urea, but only dicyanodiamidine.

The usual equation, $CN{\cdot}NH_2 + H_2O = H_2N{\cdot}CO{\cdot}NH_2$, so freely expressed in text-books and works of reference, and commonly accompanied by the simple statement that cyanamide readily combines with water to form "carbamide," besides being misleading when the real facts are considered, has led to the impression that cyanamide is a substance easily hydrolysed. This is not the case.

Whilst cyanamide is readily polymerised when heated in the presence of dilute acids or alkalis, it is remarkably resistant to hydrolysis, as is shown by the fact that not a trace of urea can be detected in the products after heating solutions of cyanamide for various intervals of time under the aforesaid conditions.

Negative results, so far as the hydrolysis to urea was concerned, were also obtained after heating cyanamide with water alone for several hours at 100°, and after heating in a sealed tube at 120—130° for three hours.

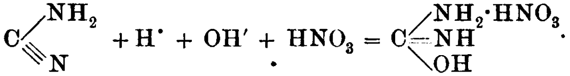
A comparison of the urea formula,  $HN{:}C{<}\begin{array}{l}NH_3\\ \,|\\ O\end{array}$, with either of the two formulæ of cyanamide shows that the relation between the two compounds is evidently not the simple one so generally supposed, namely, that of nitrile and amide.

By the addition of nitric acid (D 1·42) to a solution of cyanamide in moist ether, Baumann (*loc. cit.*) obtained urea nitrate together with more or less of the nitrate of dicyanodiamidine, but the production of urea in the free state directly from cyanamide by hydrolysis has not yet been accomplished.

A quantitative study of Baumann's experiment has shown that whilst the proportion of water present may be more than sufficient to hydrolyse all the cyanamide in solution, the amount of urea nitrate formed is determined by the quantity of nitric acid added. When the latter was insufficient in amount to form urea nitrate from all the cyanamide present, the excess of this remained unchanged; it was not polymerised, since the nitric acid was removed from solution by the urea generated, and the equilibrium of the remaining cyanamide was not further disturbed (see Expts. IV and V). When, on the other hand, the amount of water present was sufficient (without being in very great excess) to bring about the complete dissociation of the salt of urea, if formed, then no urea was generated, and the cyanamide was slowly polymerised with the subsequent production of dicyanodiamidine.

These results, which are in marked contrast to those commonly associated with the hydrolysis of nitriles or amides, may be readily explained if the mechanism of the change be carefully considered, and supply, in the author's opinion, an interesting confirmation of his views regarding the constitution of urea in the static condition and in the presence of an acid.

The conditions show that cyanamide must have assumed the amino-form before hydrolysis, and since the ions $H^{\bullet}$ and OH' are undoubtedly the active agents which take part in the change, this may be represented by the following equation:



$$\mathrm{C}\begin{array}{l}\diagup \mathrm{NH_2}\\ \equiv \mathrm{N}\end{array} + \mathrm{H}^{\bullet} + \mathrm{OH}' + \mathrm{HNO_3} = \mathrm{C}\begin{array}{l}\diagup \mathrm{NH_2\cdot HNO_3}\\ = \mathrm{NH}\\ \diagdown \mathrm{OH}\end{array}.$$

This reaction, which is analogous to the formation of *iso*carbamides from cyanamide and alcohols in the presence of hydrogen chloride, shows that urea, when generated, has the *iso*carbamide configuration, which is retained only in the salt and in the presence of a small quantity of water.

Now the hydrolysis of cyanamide is a rapid change which proceeds at the ordinary temperature, in contrast to polymerisation, which is a very slow change unless aided by heat; therefore, the formation of urea nitrate must be the outcome of a rapid effort to attain more stable equilibrium under the disturbing influence of the strong acid. This stability can only be attained provided the conditions are such that a salt of urea can be formed, because the *iso*carbamide configuration of the urea molecule is too unstable to exist in the static condition, and hence urea can only be generated in quantity sufficient to form a salt with the particular amount of acid present. It follows, therefore, that if the salt cannot exist even though acid be present, a condition brought about, for example, by the presence of too much water, no urea can be formed, which, as the experiments have shown, was actually the case. In further confirmation of this, it may be mentioned that fuming hydrochloric acid was added to cyanamide dissolved in moist ether, and after keeping for twenty-four hours, practically all the cyanamide was found unchanged (Expt. VI).

Apart even from the remote relationship between cyanamide and urea, as indicated by the cyclic structure of the latter, the fact that cyanamide has not been, and probably cannot be, directly hydrolysed to yield urea in the free state, is in perfect agreement with the above explanation of the mechanism of the change.

Thus whilst it is true that urea in its static condition is a more stable compound than cyanamide, it is equally true that the latter must be much more stable than urea when this is in its tautomeric or *iso*carbamide configuration, and hence the more stable compound cannot be produced through the intermediary of a substance less stable than cyanamide itself.

In conclusion, it may be added that if cyanamide is related to urea, as nitrile to amide, and if urea has the "carbamide" structure both in the free state and as a salt, as is generally supposed, the facts observed become unintelligible, and there appears no reason why cyanamide should not be hydrolysed in the normal manner, and be capable of directly furnishing urea whether a certain fixed quantity of acid were present or not.

The converse change, namely, the production of cyanamide from urea, will form the subject of another communication. It may be stated here that the facts hitherto recorded regarding the formation of cyanamide by the removal of the elements of water from urea, have not been confirmed.

EXPERIMENTAL.

Polymerisation of Cyanamide in the Presence of Acetic Acid.

The estimations of cyanamide were made by precipitation with an excess of $N/10$-ammonio-silver nitrate solution, the excess of silver being estimated by Volhard's method. The details and precautions recommended by Morrell and Burgen were carefully adhered to, and in some cases the estimations were checked by a direct weighing of the precipitated silver cyanamide previously dried at 100°.

In view of the work already published by the above-mentioned investigators, the following few results will suffice to illustrate how the values already given were obtained.

Five c.c. of the cyanamide solution used required 53·3 c.c. $N/10$-$AgNO_3$ (1 c.c. = 0·0021 gram CN_2H_2); the concentration of cyanamide was therefore 2·24 per cent. After heating for two hours at 100° under a reflux condenser, the values obtained were:

Acetic acid		$N/10$-$AgNO_3$ required, c.c.		CN_2H_2 unchanged.
In $N/20$	=	50	=	93·7 per cent.
„ $N/10$	=	48·6	=	91·2 „
In $N/4$	=	44·6	=	83·7 per cent.
„ $N/2$	=	41·6	=	78·1 „

Fifty c.c. of cyanamide solution in normal acetic acid after boiling for ten hours under a reflux condenser required for 5 c.c., 19·6 c.c. $N/10$-$AgNO_3$; unchanged cyanamide = 36·5 per cent.; this result represents the maximum change reached in the experiments in the presence of acetic acid.

In referring to the stability of cyanamide in the solid state, Morrell and Burgen have shown that a specimen after six months still contained 91·1 per cent. of the substance unchanged. A specimen of cyanamide, crystallised from ethereal solution, has given the author, after ten months, the following result:

0·1165 required 51·75 c.c. $N/10$-ammonical silver nitrate; cyanamide = 93·28 per cent.

It is evident, therefore, that the pure substance is much more stable in the solid state than is generally supposed. On the other hand, a 4 per cent. aqueous solution, after keeping for the same period in a stoppered bottle of clear, white glass, was found to have developed a distinct alkaline reaction towards phenolphthalein, and contained only 20·2 per cent .of the cyanamide unchanged, whilst a few crystals of dicyanodiamide (m. p. 205°) had separated. A determination of the solubility of dicyanodiamide in water at 15° gave 2·56 grams in 100 c.c.

Action of Nitrous Acid on Cyanamide.

The experiments were made in a Lunge nitrometer. A normal solution of cyanamide was used, since on the basis of the equation:

$$CN{\cdot}NH_2 + HNO_2 = N_2 + H_2O + HCNO$$

1 c.c. should be capable of giving 22·36 c.c. of gas at 0° and 760 mm.

Expt. I.—One c.c. of the cyanamide solution and 0·069 gram of sodium nitrite,* dissolved in 0·5 c.c. of water, were introduced into the nitrometer over mercury, and 1 c.c. of dilute sulphuric acid (1:10) was added. Gas was rapidly evolved, which amounted to 12 c.c. at 18° and 769 mm. after two minutes; at the end of this short interval the evolution of gas diminished considerably, and after one hour 23·8 c.c. were obtained at the same temperature and pressure. The composition of the gas was N = 64·8; CO_2 = 26·4; NO = 8·8 per cent.

An analysis of the gas evolved in the first two minutes showed the presence of 86·3 per cent. of nitrogen.

Since, on account of the hydrolysis of the cyanic acid produced, no useful information was to be obtained by correcting the gas to the normal temperature and pressure, this was not done.

In a repetition of the experiment the residual solution, after the expulsion of the evolved gas, required 10·7 c.c. *N*/10-ammoniacal silver nitrate; cyanamide = 53·3 per cent. of that originally present.

Expt. II.—Same proportion as in the previous experiment, but the reaction was allowed to proceed for only twenty minutes.

Volume of evolved gas = 16 c.c. at 15° and 763 mm.; this was not analysed, and was expelled from the nitrometer.

The residual solution required 11·8 c.c. *N*/10-ammoniacal silver nitrate; cyanamide = 59 per cent. of that originally present.

Thus approximately 60 per cent. of the cyanamide was unchanged after the completion of the first stage of the decomposition. Whilst this is apparently finished after two or three minutes, the reaction was allowed to continue for twenty minutes

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* The specimen of sodium nitrite used was assayed; 0·072 gram was found to be equivalent to 0·069 gram of the pure salt.

on account of the secondary change which no doubt accompanies the primary to a small extent.

Expt. III.—Same proportions as before, but the reactions were allowed to proceed for twenty hours.

Volume of gas evolved = 38·8 c.c. at 16° and 763 mm.

Composition: N = 55; CO_2 = 40·1; NO = 4·9 per cent.

The large increase in the proportion of carbon dioxide shows that the cyanic acid generated was hydrolysed as fast as cyanamide was being attacked by the nitrous acid, after the first rapid decomposition had been completed.

The residual liquid required 2·55 c.c. *N*/10-ammoniacal silver nitrate; cyanamide = 12·7 per cent. of that originally present. The remarkable resistance of cyanamide to further attack by nitrous acid, after the first rapid action has been completed as shown by these experiments, suggests that the change $C(NH)_2 \longrightarrow CN{\cdot}NH_2$ must proceed at a very slow rate at the ordinary temperature even in the presence of a dilute mineral acid.

The possible formation of a nitroso-derivative as an intermediate product has yet to be investigated.

The Hydrolysis of Cyanamide.

A 4·25 per cent. solution of cyanamide in ether saturated with water, after keeping for three weeks at the ordinary temperature, and after heating at 100° for ten hours in a sealed tube of soft glass, was found to have suffered no change. After the addition of a few drops of concentrated nitric acid crystals of urea nitrate were slowly deposited. In order to examine the course of this change, the following experiments were made.

Expt. IV.—To 15 c.c. of the moist ethereal solution of cyanamide (0·638 gram CN_2H_2), 1·5 grams of nitric acid (D^{15} 1·425) were added. This was slightly more than sufficient to form urea nitrate by the hydrolysis of all the cyanamide present. After two hours crystals commenced to separate, and the product was kept for twenty hours.

Weight of crystals deposited = 1·9 grams. Theory for urea nitrate = 1·87 grams. All the cyanamide had disappeared from the ethereal solution. The hydrolysis was therefore complete, although it should be mentioned that the crystals contained a small quantity of dicyanodiamidine nitrate.

Expt. V.—The last experiment was repeated, but only 1 gram of nitric acid was added.

Weight of crystals deposited after twenty hours = 1·57 grams.

The residual ethereal solution was shaken with 400 c.c. of distilled water, and then required 63 c.c. *N*/10-ammoniacal silver nitrate for the complete precipitation of the remaining cyanamide, which is thus found to be 20·7 per cent. of the amount originally present.

Thus whilst all the nitric acid was removed as urea nitrate, the excess of cyanamide remained unchanged, although there was more water present than was necessary to effect its complete hydrolysis.

The remarkable stability of cyanamide and its indifference towards hydrolysis were shown by the following striking and conclusive result.

Expt. VI.—0·42 Gram of cyanamide was dissolved in 20 c.c. of moist ether, and 1 c.c. of fuming hydrochloric acid (D=1·16) added; the mixture was repeatedly shaken in a small stoppered separating funnel during an interval of six hours, and was then kept until the following morning. The small aqueous layer was removed, and after neutralisation with an excess of aqueous ammonia, the cyanamide was precipitated in the form of its silver salt.

Weight of Ag_2CN_2 obtained$=1·742$; $CN_2H_2=0·2856$.

The ethereal solution required 46·1 c.c. $N/10$-ammoniacal silver nitrate; $CN_2H_2=0·0968$. Hence 0·3824 gram, or 91·04 per cent. of the cyanamide originally taken, was unchanged.

Thus, whilst in this experiment the amount of hydrochloric acid present was sufficient to form urea hydrochloride by the hydrolysis of the cyanamide, the amount of water present was too great to allow the undissociated urea salt to separate, and hence very little, if any, hydrolysis of cyanamide took place. A small quantity of dicyanodiamidine was found in the aqueous layer.

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