CVII.—Mechanism of the Transformation of Ammonium Cyanate into Carbamide, and of the Decomposition of Carbamide by Heat. The Polymerisation of Cyanic Acid.

By EMIL ALPHONSE WERNER.

THE interesting researches of Walker and his co-workers (T., 1895, 67, 746; 1897, 71, 489) have supplied us with most of our present knowledge regarding the phenomena which accompany the trans-

formation of ammonium cyanate into carbamide, both in the dry state and in aqueous or alcoholic solution.

The following are perhaps the most important established facts which support the views and experimental results that form the subject of the present communication: (1) The bimolecular order of the change. (2) The reversibility of the transformation. (3) The partial hydrolysis of ammonium cyanate with production of ammonium carbonate which accompanies the transformation; and (4) The greatly increased velocity of the change of ammonium cyanate into carbamide in an alcoholic, as compared with an aqueous, solution.

Quite recently Chattaway (T., 1912, 101, 170) has put forward a theory by the aid of which he proposes to explain, not only the probable changes which occur during the transformation of ammonium cyanate into carbamide, but also to account for the formation of biuret and cyanuric acid by the further action of heat on the amide. These changes, together with several related reactions in which cyanic acid and its esters are concerned, he considers may all be simply explained by the well known tendency

of the carbonyl group to add on other groups, such as ${}^{R}_{\nu}$ >NH or

R•OH, followed by a subsequent rearrangement involving the migration of a hydrogen atom from oxygen to nitrogen; thus the primary change of ammonium cyanate into carbamide is formulated as follows:

 $\mathrm{H_4N}\cdot\mathrm{N:C:O} \rightleftharpoons \mathrm{HN:C:O} + \mathrm{NH_3} \rightleftharpoons \mathrm{HN:C} {<_{\mathrm{NH_3}}^{\mathrm{OH}}} \rightleftharpoons \mathrm{H_2N}\cdot\mathrm{CO}\cdot\mathrm{NH_2}$

whilst the production of biuret is explained in accordance with the equation:

$$\begin{array}{ccc} \mathrm{NH}_{2} < & \mathrm{CO} \cdot \mathrm{NH}_{2} + \mathrm{OC}(\mathrm{NH}_{2})_{2} & \longrightarrow & \mathrm{NH} < & \mathrm{CO} \cdot \mathrm{NH}_{2} \\ & & \mathrm{CO} \cdot \mathrm{NH}_{2} + \mathrm{OC}(\mathrm{NH}_{2})_{2} & \longrightarrow \\ & & \mathrm{HN} < & \mathrm{CO} \cdot \mathrm{NH}_{2} \\ & & \mathrm{HN} + & \mathrm{NH}_{3} \end{array}$$

the amino-group of one molecule of carbamide reacting with the carbonyl group of another, the hypothetical intermediate product giving rise to biuret by loss of ammonia, and by a repetition of these changes, cyanuric acid is ultimately formed, no less than three hypothetical intermediate products being supposed to take part in the changes before the atomic complex, $HN < CO \cdot NH > CO$, is produced. Whilst this can scarcely be considered a simple explanation of the phenomena in question, this theory, as is pointed out in the following, is open to several serious objections, besides which it fails to explain some of the established facts connected with the

different changes, and in the present author's opinion does not possess the required agreement with experimental evidence to secure its general acceptance as a likely explanation of the well known reactions under consideration.

Commencing with the primary change, the first point subject to criticism is the constitution of ammonium cyanate itself. Chattaway considers this salt to be derived from the *iso*-, or, more correctly, the keto-form of the acid; and as dissociation proceeds with application of heat, the dissociated products re-unite to form carbamide, no change in the constitution of the cyanic acid being assumed to occur. Bearing in mind that the many reactions, attributed to the tendency of the carbonyl group to add on such groups as cited by Chattaway, take place readily at the ordinary temperature, it is difficult to understand why ammonium cyanate should be produced at all if cyanic acid is considered to be H·N:C:O only; for instance, there seems no reason why the two reactions:

and

(a)
$$NH_3 + HN:C:O = NH_4 \cdot N:C:O$$

(b)
$$NH_3 + HN:C:O = HN:C < _{OH}^{NH_2}$$

should take place at the same temperature (see Expts. 1, 2, 3, and 4), unless it be assumed that cyanic acid at low temperatures is predisposed to react in accordance with equation (a), since at 0° , for example, the product of the interaction is ammonium cyanate only. That a condition of equilibrium between the reaction products should be capable of arising from such a cause is very improbable.

If a change in the configurations of the cyanic acid molecule from HO·C:N to HN:C:O with rise of temperature be admitted, all the phenomena connected with the transformation of ammonium cyanate into carbamide and of the decomposition of the latter by heat can be easily explained in a very simple manner, which is, moreover, shown in the following to be in complete accord with all the known facts.

It is only necessary to refer in general to the extensive work of E. Fisher on uric acid and its derivatives, and in particular to the interesting results of Hantzsch and Bauer (*Ber.*, 1905, **38**, 1005) and Hantzsch (*Ber.*, 1906, **39**, 139) on the constitution of the metallic salts of cyanuric acid and on the production of mixed *N*-alkyl and *O*-alkyl derivatives, to show that the formation of derivatives containing the complex $\mathbf{R}\cdot\mathbf{O}\cdot\mathbf{C}:\mathbf{N}\cdot$ from compounds containing the group $\cdot\mathbf{NH}\cdot\mathbf{CO}\cdot$ is determined by the electropositive character of the element or radicle taking part in the change.

It seems only natural to suppose that the group HN:CO, in the

free state, should behave in a similar manner, under the same influence. The experimental results, in fact, appear to favour the view that cyanic acid is capable of existing in equilibrium in the two forms, the relative proportions being a function of the temperature.

The two best known properties of ammonium cyanate, namely, its hydrolysis to ammonium carbonate, noticed by Walker (*loc. cit.*), and its transformation into carbamide are strong evidence in support of the constitutional formula $H_4N\cdot O\cdot CN$; thus, cyanic acid in its enolic form may be considered as "carbonicnitril," and the hydrolysis of the ammonium salt expressed as follows:

 $H_4N\cdot O\cdot C:N + H_2O \longrightarrow H_4N\cdot O\cdot CO\cdot NH_2 + H_2O \longrightarrow H_4N\cdot O\cdot CO\cdot ONH_4$, ammonium carbamate being, no doubt, an intermediate product. Assuming the formula $H_4N\cdot N:C:O,*$ the change by hydrolysis is by no means simple to follow, even admitting the presence of the ions H_4N and NCO in solution.

Being a weak acid in the enolic form (comparable to HOCl), cyanic acid would naturally yield a very unstable ammonium salt, easily dissociated by heat, both in the dry state and in solution, and transformable into carbamide according to the following scheme:

 $\begin{array}{cccc} & & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & &$

The formula $HN:C < \bigcup_{0}^{NH_3}$, which is used in the above to show the production of carbamide from the union of ammonia with H·N:C:O, is an extension of the formula recently proposed by the author to represent the constitution of thiocarbamide in the static condition (T., 1912, **101**, 2185): no particular stress is laid on its

acceptance in the above scheme until experimental evidence is forthcoming to support it, and whilst it helps to throw some light

* This constitution is based solely on analogy to KCNO; reactions of the type $KCNO + RX = R \cdot NCO + KX$ are no proof that the potassium salt must be KNCO; the constitution depends entirely on the electro-chemical nature of the element or radicle entering into the change; the properties of potassium cyanate are more in agreement with the constitution KOCN than KNCO.

† Since the group 'HN·CO' shows great analogy in its behaviour to the group 'CH₂·CO', the distinctive terms "enol" and "keto" are equally well applicable to the former group, and are used here in preference to the usual unsuitable terms "normal" and "iso" for the two forms of cyanic acid.

on the ultimate appearance of carbamide in either the symmetrical or unsymmetrical form, it is obvious that its removal from the scheme will not affect the meaning which this is intended to convey. Whilst carbamide is much more stable than ammonium cyanate, when it is heated above its melting point it also undergoes dissociation into ammonia and cyanic acid (chiefly in the keto-form), and gives a sublimate which, under ordinary conditions contains from 28 to 30 per cent. of ammonium cyanate, whilst if the vapours are artificially cooled, this may be increased to over 40 per cent. (see Experimental part); the rest of the sublimate is carbamide; if the vapour is kept warm, the sublimate, as might be expected, consists entirely of carbamide.

These results show that the dissociation product must contain cyanic acid both in the enol and keto-forms, the proportions varying with the temperature; the enol form, which is alone responsible for the presence of ammonium cyanate in the sublimate, is not capable of existing at the higher temperature.

The reversion of carbamide to ammonium cyanate first pointed out by Walker and Hambly (*loc. cit.*) is easily explained by the views embodied in the above scheme; it is evident that carbamide undergoes a certain amount of dissociation in aqueous solution, even at the ordinary temperature; under such conditions some of the cyanic acid will assume the enol form, and in presence of ammonia will give rise to the cyanate.

Production of Biuret and Cyanuric Acid from Carbamide.

The dissociation of carbamide by heat has not been considered by Chattaway in his explanation of the origin of biuret and cyanuric acid respectively by the decomposition of the amide, stress being laid solely on the evolution of ammonia, and both products are supposed to be formed by the mutual interaction of carbamide molecules in the manner already referred to.

All the experimental evidence, however, is in favour of the view that the cyanic acid set free by dissociation is responsible for the production of the biuret and cyanuric acid, the former resulting from its reaction with unchanged carbamide in the following manner:

$$\begin{array}{rcl} \mathrm{CO} <\!\!\!\! & \overset{\mathrm{NH}_2}{\underset{\mathrm{NH}_2}{}} \!\!\! + \mathrm{HN:} \mathrm{CO} &= & \mathrm{CO} <\!\!\!\!\! & \overset{\mathrm{NH}_2,\mathrm{HNCO}}{\underset{\mathrm{NH}_2}{\underset{\mathrm{Carbamide cyanate.}}{}} \!\!\! & \longrightarrow & \mathrm{CO} <\!\!\!\! & \overset{\mathrm{NH}\cdot\mathrm{CO}\cdot\mathrm{NH}_2}{\underset{\mathrm{NH}_2}{\underset{\mathrm{Biuret.}}{}} \!\!\! & \end{array} \end{array}$$

As is well known, when carbamide is heated alone the yield of biuret is very poor; the conditions are unfavourable for the realisation of the above reaction, much of the cyanic acid undergoes polymerisation to cyanuric acid at the high temperature, whilst another portion is volatilised along with ammonia.

Schiff's improved method for preparing biuret (*Ber.*, 1896, **29**, 298) by heating carbamide hydrochloride to a temperature not exceeding 130° , whereby a yield amounting to 45-50 per cent. of the carbamide taken may be easily obtained, is readily explained; the disturbing influence of the ammonia is removed by its conversion into ammonium chloride, whilst the low temperature retards the polymerisation of the cyanic acid.

The above reaction has, in fact, been realised long ago by Finckh (Annalen, 1861, **124**, 336), who showed that biuret may be prepared by passing the vapour of cyanic acid directly into carbamide heated to its melting point; moreover, in recent years several substituted biurets and thiobiurets have been prepared by analogous reactions.

When biuret is heated above its melting point (190°) it decomposes rapidly, giving off ammonia and cyanic acid; by artificially cooling the vapour a quantity of sublimate may be easily obtained; this was found in a single experiment to contain as much as 42-43 per cent. of ammonium cyanate, together with carbamide; the residue after heating was mainly cyanuric acid.

It is evident, therefore, that cyanic acid, as well as ammonia, is produced throughout the whole course of the changes, and since cyanuric acid, as pointed out by Hantzsch (*Ber.*, 1905, **38**, 1013), is a product of the polymerisation of cyanic acid at high temperatures, in contrast to cyamelide which is a product of an analogous change at low temperatures, it seems quite unnecessary to look outside this cause for the origin of cyanuric acid as a product of the decomposition of carbamide. It also explains why the polymeride appears at the very outset of the decomposition of carbamide, simultaneously with the biuret, and if any cyanuric acid is produced other than by polymerisation of HN:CO, it seems more likely to result from an interaction between biuret and cyanic acid on the same lines as in the last equation, rather than between biuret and unchanged carbamide, as suggested by Chattaway in his theory.

Constitution of Carbamide in the Static Condition.

It is rather remarkable that the dissociation of carbamide by heat, with formation of cyanic acid as a volatile product, has not received proper consideration; the general impression appears to be that carbon dioxide is one of the products which accompanies ammonia during the decomposition of carbamide by heat; even in such a recent work as "Organic Chemistry of Nitrogen" (Sidgwick, 1910, p. 186) the following statement occurs: "When urea is

strongly heated it breaks up with the formation of ammonia, carbon dioxide, biuret, and cyanuric acid," the latter being correctly attributed to the rapid polymerisation of cyanic acid as fast as it is set free. It is obvious that the formation of carbon dioxide would involve a secondary decomposition either between two molecules of carbamide, or one in which water is formed, which would then hydrolyse the cyanic acid with production of carbon dioxide.

When the structural formula for carbamide suggested by the writer is considered, there appears no reason why the decomposition by heat should not be a simple and straightforward change, thus:

$$HN:C <_{O}^{NH_{3}} = \stackrel{NH_{3}}{+} \stackrel{\rightarrow}{\leftarrow} HOC:N,$$

in which no secondary products are formed, so far as the volatile substances are concerned. This view has been confirmed by direct experiment, the results of which prove conclusively that carbon dioxide is not a product of the decomposition by heat of pure dry carbamide. The change is a simple case of dissociation, and, as indicated by the above equation, ammonia and cyanic acid are the sole volatile products, the presence of the latter being, no doubt, responsible for the erroneous idea that carbon dioxide is one of the decomposition products.

Experimental evidence in support of the constitution of carbamide here proposed is deferred to a future communication.

The Formation of Cyamelide and Cyanuric Acid from Cyanic Acid.

The polymerisation of cyanic acid at low temperatures, with production of cyamelide, has an important bearing on the views put forward by the writer regarding the relations of the two forms of cyanic acid. Van't Hoff ("Chemical Dynamics," p. 110) has shown that the change of cyanic acid to cyamelide is no doubt a termolecular reaction; Hantzsch (*Ber.*, 1905, **38**, 1016), from a study of its chemical properties, has proposed a constitutional formula for cyamelide which is in all probability a correct representation of the structure of the compound. It is concluded that cyamelide cannot contain either the group HO·CN or the group HN·C·O, and is hence very likely a polymeride resulting from the union of three molecules of cyanic acid through the intervention of oxygen, thus:

$$\mathbf{NH:C} \underbrace{\langle \mathbf{O} \cdot \mathbf{C}(:\mathbf{NH}) \rangle }_{\mathbf{O} \cdot \mathbf{C}(:\mathbf{NH})} > \mathbf{O}$$

and comparable to paracetaldehyde:

 $CH_3 \cdot CH < \stackrel{O \cdot CH(CH_3)}{O \cdot CH(CH_3)} > 0,$

Hantzsch's conclusion that cyamelide must be considered as a condensation product derived from ψ -cyanic acid, that is, the keto-form, HN:C:O, does not necessarily follow from the above formula, and is open to criticism, since it still leaves unanswered the question: "Why is cyamelide formed along with cyanuric acid under the conditions stated."

When cyanic acid undergoes polymerisation, the change, as well known, is very rapid, and is accompanied by much development of heat, and the product is a mixture of the two polymerides; in the particular experiment recorded by Senier and Walsh (T., 1902, **81**, 290), as much as 70 per cent. of the product was found to be cyanuric acid. Hantzsch's experiments (*loc. cit.*) have shown that the conditions favourable to the formation of cyamelide are slow polymerisation and a low temperature; and Walker's observation of the production of some cyamelide during the slow transformation of ammonium cyanate into carbamide at 61° is of particular interest in this connexion.

The mechanism of the formation of cyamelide and cyanuric acid becomes intelligible if the tendency of the two forms of cyanic acid to co-exist in equilibrium be taken into consideration, and may be explained as follows. Cyanic acid represents an unstable group of atoms, which is incapable of assuming a simple * molecular configuration which can give rise to a condition of static equilibrium, an end which is only attained by polymerisation to a six-membered ring, the most stable form of cyclic molecules.

The enol-form of the acid is apparently the less stable, and tends to change to the more stable keto-form, thus:

Since an interval of time must elapse, while the hydrogen atom has migrated from oxygen to nitrogen, either a valency of the oxygen atom becomes momentarily free (a), followed immediately by a momentary liberation of a carbon valency (b) when the hydrogen atom unites with nitrogen, or when the hydrogen atom has attained a position as represented in (a) a simultaneous liberation of the respective valencies occurs, their union within the molecule giving rise to the keto-form of the acid. Since this is also an unstable configuration, it is natural to conclude that the chief result will be the formation of cyamelide by the union of three molecules when in the state represented by phase (b), the free valency of the oxygen

* Neither fulminic acid, C:NOH, nor formonitrile oxide, CH:N, has been isolated.

atom of one molecule uniting with the free valency of the carbon atom of another, thus:



According to this theory, cyamelide is not the result of the polymerisation of cyanic acid pre-existing in the keto-form (ψ -acid of Hantzsch), but is the product of the natural tendency to stable equilibrium formed while the acid is in the act of changing from one form to the other. It also explains a third condition which is necessary in order that cyamelide may be formed, namely, that the cyanic acid must be primarily in the enol form.

When cyanic acid is generated at a high temperature, as during the dissociation of carbamide by heat, it is liberated solely in the keto-form, which polymerises at once to cyanuric acid, no cyamelide being formed. In this case the polymerisation originates as follows:

$$C \ll_{O}^{\mathbf{NH}} \longrightarrow C \ll_{O-}^{\mathbf{N}} H \longrightarrow C \ll_{OH}^{\mathbf{N}}$$

Keto. Intermediate phase (a). Enol.

the conditions being altogether unfavourable for the existence * of HO·C:N; the latter cannot be formed by union of the momentary free valencies of the carbon and nitrogen atoms within the molecule itself, and hence a state of stable equilibrium is attained by the union of three molecules in phase (a) to form cyanuric acid the moment the hydrogen atom has entered into union with oxygen, thus:



Cyanuric acid (enol form).

It is obvious that cyamelide cannot be formed in the above reaction; on the other hand, cyanuric acid is largely formed during the production of cyamelide (Senier and Walsh, *loc. cit.*), a fact which the present theory is capable of predicting, namely, since the keto-form of cyanic acid is produced simultaneously with the cyamelide, in accordance with the first scheme, and also in consequence, simultaneously with the disappearance of the enol acid, it

^{*} Although HO CN cannot exist free at the temperature, the tendency of HN:CO to co-exist in equilibrium with it would still persist, from which cause the polymerisation takes effect.

(the keto-acid) becomes immediately polymerised to cyanuric acid in an endeavour to restore equilibrium by giving rise to more of the enol form, in accordance with the second scheme.

There is little doubt that the thermal effect which accompanies the polymerisation of liquid cyanic acid must have an important influence on the relative proportions of the two polymerides produced in a given experiment, and it is very likely that if cyanic acid were allowed to undergo slow polymerisation at a very low temperature a much larger proportion of cyamelide would be produced than was found by Senier and Walsh in the single case recorded by them.

The production of a small quantity of cyamelide from ammonium cyanate at 61° (Walker, *loc. cit.*) confirms the view that cyanic acid in the form HO·C:N results from the dissociation of the ammonium salt.

The theories which have been put forward in the present communication to explain the several phenomena discussed can lay claim to be in complete agreement with all the experimental facts, and no series of hypothetical intermediate compounds is introduced to hamper their simplicity. All the different changes can be referred to the two fundamental causes:

(1) Dissociation, and (2) the reversible reaction:

$HO \cdot C:N \rightleftharpoons HN:CO.$

In the face of all the evidence, Chattaway's conclusion that "the oldest and best-known instance of isomeric change is not a case of isomeric change at all" is not justifiable; there exists no reason for removing Wöhler's historical discovery from its time-honoured position of being the first example of isomeric change on record.

Experimental.

Qualitative experiments have shown that when carbamide or biuret are decomposed by heating in a long test-tube the sublimate formed consists of ammonium cyanate and carbamide, the proportions of which vary with the temperature and rate of heating.

Soluble cyanates can be rapidly estimated with a fair degree of accuracy by direct titration with N/10-silver nitrate, using neutral chromate as indicator; the estimation is not interfered with by the presence of carbamide in excess.

Example I: 0.098 KOCN (Kahlbaum) dissolved in 20 c.c. of water.

N/10-AgNO₃ required = 11.2 c.c.; KOCN = 92.5 per cent.

Example II: 0.1935 KOCN (freshly prepared by action of

potassium hydroxide on urethane in alcoholic solution; Mulder, Rec. trav. chim., 1888, 6, 170) dissolved in 40 c.c. of water.

N/10-AgNO₃ required = 23.4 c.c.; KOCN = 98.07 per cent.

In all the following experiments 4 grams of well-dried powdered carbamide were heated in a dry test-tube 2.5 cm. wide and 18 cm. long, closed with a cork carrying a piece of narrow glass tubing about 15 cm. to exclude moisture from the air during the heating. The tube was held in a nearly horizontal position.

Expt. 1.—Carbamide heated at a moderate rate until the liquid just became opalescent. Tube quickly cooled under the water tap, and the greater part of the sublimate removed by means of a steel spatula, and at once analysed.

Sublimate = 0.0241.

N/10-AgNO₃ required = 1.2 c.c.; NH₄OCN = 29.8 per cent.

Expt 2.—Same as above.

Sublimate = 0.09.

N/10-AgNO₃=4.4 c.c.; NH₄OCN=28.8 per cent.

Eapt. 3.--Carbamide heated slowly, front of tube, to extent of 8 cm., surrounded by a coil of narrow lead piping carrying a current of cold water.

Sublimate = 0.1215.

N/10-AgNO₃=7.4 c.c.; NH₄OCN=36.5 per cent.

Expt. 4.—Carbamide heated very rapidly, vapour cooled as in Expt. 3.

Sublimate = 0.151.

N/10-AgNO₃=10.4 c.c.; NH₄OCN=41.3 per cent.

Thus the artificial cooling of the vapour, as was to be expected, increased the proportion of ammonium cyanate in the sublimate. Since the rate of heating might be expected to have an influence on the proportion of cyanic acid that would escape polymerisation, the following two experiments were made. Hantzsch has shown that cyanuric acid may be accurately titrated with sodium hydroxide solution, using phenolphthalein as indicator; it then behaves as a monobasic acid, $H(H_2C_3N_3O_3)$.

Expt. 5.—Carbamide heated very slowly, vapour not artificially cooled.

Sublimate = 0.0786.

N/10-AgNO₈=3.8 c.c.; NH₄OCN=29 per cent.

Residue = 2.44 dissolved in water. N-NaOH = 2 c.c. Cyanuric acid = 10.57 per cent.

Expt. 6.—Carbamide heated very rapidly, as in Expt. 5.

Sublimate = 0.0955.

N/10-AgNO₃=5.6 c.c.; NH₄OCN=35.18 per cent.

Residue=2.34. N-NaOH=2.6 c.c. Cyanuric acid=14.33 per cent.

Whilst the polymerisation increases with the rate of heating, more cyanic acid is able to escape during the rapid heating, and hence the larger proportion of ammonium cyanate in the sublimate.

Expt. 7.—Biuret (2 grams) heated in test-tube until fluid commenced suddenly to thicken. Vapour artificially cooled.

Sublimate = 0.066.

N/10-AgNO₃=4.7 c.c.; NH₄OCN=42.7 per cent.

Expt. 8.—Biuret heated as above. Sublimate examined under microscope had characteristic fern-leaf-like formation (due to NH₄OCN); the tube was now immersed to the neck in boiling water for a few minutes; the sublimate changed in appearance, and under the microscope was seen to consist of well-defined, broadangled prisms. The solution of the crystals in water gave no precipitate with silver nitrate; some of the solution gave, with nitric acid in excess, characteristic crystals of carbamide nitrate. Α similar result can be obtained with carbamide; the sublimate in the first instance, if dissolved in water, gives a copious precipitate with silver nitrate; after warming and then dissolving in distilled water a solution is obtained, which gives at most only a faint opalescence with silver nitrate. As both experiments can be performed in a few minutes, they form the subject of an interesting and instructive lecture demonstration to support the theories Further experiments are in progress over a more put forward. extended series of conditions.

Examination of the Gaseous Products Evolved during the Decomposition of Carbamide by Heat.

Expt. 9.—Five grams of finely powdered and well-dried carbamide were heated in a dry test-tube (2.5 cm. by 18 cm.), provided with a delivery tube dipping to the bottom of 50 c.c. of absolute alcohol contained in a flask immersed in ice-cold water. The carbamide was heated rapidly until the liquid became suddenly opalescent, indicating separation of cyanuric acid, whilst the tube was maintained in an almost horizontal position. A crystalline precipitate formed in the alcoholic solution, whilst the latter contained much free ammonia. The solution was poured off from the crystals, which were rapidly washed with a small quantity of fresh alcohol.

The solution of the crystals in water, and also the alcoholic solution, gave the following reactions:

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(1) Addition of calcium chloride solution---no immediate precipitate in the cold; slight opalescence after ten minutes; a copious precipitate of calcium carbonate on warming.

(2) A portion of each solution was heated in a test-tube immersed in boiling water for five minutes, and then cooled; on addition of calcium chloride a faint opalescence was obtained, which was not sensibly increased by warming.

This last result could not be obtained if either ammonium carbamate or carbonate * was present in the crystals or in the alcoholic solution; the absence of a precipitate of calcium carbonate in the second case being due to the disappearance of the ammonium cyanate by its conversion into carbamide on heating.

Expt. 10.—Carbamide was heated as before; the gas evolved was collected over mercury after expulsion of all the air; 50 c.c. of gas so obtained was found to be completely dissolved by 2 c.c. of water, and the solution gave no opalescence with calcium chloride.

These results prove that ammonia and cyanic acid are the only volatile products, and no carbon dioxide is present when dry carbamide is heated.

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