# XIII.—The Constitution of Carbamides. Part V. The Mechanism of the Decomposition of Urea when Heated in Solution with Alkalis and with Acids respectively. The Hydrolysis of Metallic Cyanates.

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WHEN urea, dissolved in a solution of barium hydroxide, was heated, ammonia was evolved as soon as the boiling point was reached, whilst several minutes elapsed before opalescence, due to separation of barium carbonate, appeared. This observation showed that carbon dioxide and ammonia were not simultaneously evolved at the outset of the decomposition, as indicated by the usual equation, adopted to express the change, namely,

 $\operatorname{CON}_{2}\operatorname{H}_{4} + \operatorname{Ba}(\operatorname{OH})_{2} = \operatorname{BaCO}_{3} + 2\operatorname{NH}_{3}.$ 

This fact was much more marked when a quantitative examination was made. Thus, when urea and barium hydroxide, in equal molecular proportions, were heated at  $100^{\circ}$  for two hours in aqueous solution at concentration N/7, the amount of ammonia evolved was equivalent to 20.5 per cent. of "hydrolysis," whilst the proportion of barium carbonate precipitated corresponded with only 12.5 per cent. of change, calculated on the basis of the above equation.

It is obvious that the usual interpretation of this reaction is an erroneous one, and it furnishes but another illustration of the manner by which a decomposition of urea has been accepted almost a priori on the basis of the carbamide configuration without a proper investigation of the change.

The expression 'hydrolysis of urea,' which is generally used with reference to the above decomposition, has been purposely avoided in giving a title to the present paper, since it has been clearly shown that urea was not directly hydrolysed when decomposed in the presence of acids or alkalis.

The relation which exists between urea and ammonium cyanate is a very simple one, namely, whilst the latter is produced from the union of ammonia with cyanic acid in the 'enol' form (HO·CN), urea is the result of the union of ammonia with cyanic acid in its 'keto' form (HN:CO) (T., 1913, **103**, 1013, 2276).

Herein lies the true difference between the two isomerides. When careful attention is given to the fact that dissociation into ammonia and cyanic acid is the first change which accompanies the action of heat on urea, all phenomena connected with its decomposition in solution, either alone or in the presence of acids or alkalis, are easily explained.

An isomeric transformation of urea, as a preliminary to its decomposition, as suggested by Fawsitt (*Zeitsch. physikal. Chem.*, 1902, **41**, 601) and by Burrows and Fawsitt (T., 1914, **105**, 609), is a quite unnecessary assumption.

## Decomposition of Urea in Aqueous Solution in the Presence of Acids.

This change is represented thus:

Phase I.  $HN:C <_{O}^{NH_{3}} + HCl = NH_{4}Cl + (HNCO \rightleftharpoons HOCN)$ 

Phase II.  $(HNCO \rightleftharpoons HO \cdot CN) + H_2O + HCl = NH_4Cl + CO_2$ .

Since cyanic acid is very rapidly hydrolysed, the velocity of the whole reaction will be regulated by the rate of dissociation of urea (at 100°), when both products of dissociation are removed practically as fast as they are generated.

The basic property of urea is much more pronounced than that commonly associated with acid amides, a fact which in itself may be used as an argument against such a structure,<sup>\*</sup> and when hydrochloric acid is added to an aqueous solution of urea, an equilibrium is established between the base and its hydrochloride. Thus, in a normal solution, Walker and Wood (T., 1903, **83**, 484) found that 45 per cent. of urea hydrochloride was undissociated, a condition

\* In this respect usea bears a much greater resemblance to the aminoacids, a type of constitution which is implied by the cyclic formula.

which, according to the author's views, is represented by the following equation:

 $\begin{array}{ccc} \mathrm{HN:C} <^{\mathrm{N}\,\mathrm{H}_3}_{\mathrm{O}} + \mathrm{HCl} & \xrightarrow{(\alpha)} & \mathrm{HN:C} <^{\mathrm{N}\,\mathrm{H}_2}_{\mathrm{OH}} \mathrm{HCl} \\ & \overbrace{55 \text{ per cent.}}^{(\alpha)} & 45 \text{ per cent.} \end{array}$ 

Now, since it is only 'free' urea which gives rise to the first phase of the decomposition, the velocity of the change might be expected to diminish with an increase in the concentration of hydrochloric acid. This, however, would be only slightly perceptible at all concentrations much below normal, since by far the greater part of the urea would be in the free state at the outset, and hence only a small amount of change in direction (b)would be involved throughout the whole progress of the reaction.

If, on the other hand, most of the urea was 'fixed' at the outset as urea hydrochloride, the velocity of the change would be determined by the diminished rate of dissociation of free urea at low concentration, and this would be maintained fairly constant up to a certain point,<sup>\*</sup> since the change in direction (b) would only keep pace with the rate of disappearance of free urea.

The following results, which were obtained by heating solutions of urea with hydrochloric acid to the boiling point under reflux, will suffice to illustrate the points just mentioned.

#### TABLE I.

(I.) Urea, N/5; HCl, N/2.5. Molecular ratio, 1:2.

|     | Time. |    | Urea deco          | mposed. | [ | Ti   | me.  | $\mathbf{U}$ | rea decon                  | nposed.  |
|-----|-------|----|--------------------|---------|---|------|------|--------------|----------------------------|----------|
| 1 k | our   | -  | $21{\cdot}25$ per  | r cent. |   | 5 ho | ours |              | 63·75 pe                   | er cent. |
| 2 h | ours  | =  | 33·50 <sup>^</sup> | ,,      |   | 6    | ,,   |              | 68- <b>90</b> <sup>*</sup> | ,,       |
| 3   | ,,    | -  | 44.50              | ,,      |   | 7    | ,,   | =            | 78.50                      | ,,       |
| 4   | ,,    | == | 59.25              | ,,      | l | 8    | ,,   | =            | 79.25                      | ,,       |

(II.) Urea, N/5; HCl, N/5. (Equal mols.)

(III.) Urea, N/2.5; HCl, N/2.5.

| Time.       | U   | Trea decon  | nposed. | Time.                    | τ | rea deco | mposed. |
|-------------|-----|-------------|---------|--------------------------|---|----------|---------|
| 1 hour      |     | 22.0  per   | cent.   | l hour                   | = | 25.0 per | cent.   |
| 2 hours     | 212 | $34.5^{-1}$ | ,,      | 2  hours                 |   | 44.75    | ;,      |
| 3,,         | =   | 47.00       | ,,      | $145 \mathrm{\ minutes}$ |   | 50.0     | ,,      |
| 222 minutes | === | 50.0        | ,,      |                          |   |          |         |

A comparison of the results under (I) and (II) (urea = N/5) shows the effect of an increase in the concentration of hydrochloric

\* The neutralisation of free acid by ammonia would naturally exert a disturbing effect on the above equilibrium, which would be more marked at the higher concentration.

acid in lowering the velocity of the change; the difference was most marked during the third hour, that is, when the concentration of hydrochloric acid, in the case of (II), was very low as neutralisation was approached, since the maximum amount of urea that could be decomposed \* in the presence of one molecular proportion of hydrochloric acid is only half of the total present, on account of the simultaneous progress of the two phases of the reaction. The long period required to decompose urea when two molecular proportions of hydrochloric acid were present was due to the slow dissociation of urea as its concentration diminished, and the results show that the velocity of the change was determined solely by the concentration of 'free' urea. The results under (III) furnish additional proof of this; thus it will be noticed that the maximum amount of urea (N/2.5) was decomposed in 145 minutes, as compared with 222 minutes, which were required to effect the same amount of change when the concentration of urea at the outset was at N/5 (II).

Fawsitt found that it required 2600 minutes to decompose all urea in a solution which contained at the outset urea (N/8) and hydrochloric acid (N/2), that is, four molecules of acid to one of urea.

## Decomposition of Urea in Aqueous Solution in the Presence of Sodium Hydroxide.

Since the acidic property of urea is very feeble, when sodium hydroxide is added to its aqueous solution, an equilibrium represented as follows:

$$HN:C <_{O}^{NH_{g}} + NaOH \implies HN:C <_{ONa}^{NH_{2}} + H_{2}O,$$

would only obtain to a small extent when the concentration of both was very high. In solutions below normal, for example, it is certain that nearly if not all the urea would be in the free state. Therefore, according to the dissociation theory, the velocity of decomposition of urea in the presence of sodium hydroxide should be greater than in the presence of hydrochloric acid at all concentrations.

This has been found to be the case, which is contrary to the general result arrived at by Fawsitt (loc. cit.). The two phases

\* That is, within a comparatively short time, up to the point of neutralisation of the acid. Fawsitt found that in a solution of urea alone (N/2), decomposition to the extent of 98.9 per cent. required 450 hours at 99-100°.

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of this reaction, which were easily distinguished experimentally, may be represented as follows:

Phase I.  $HN:C < \stackrel{NH_3}{_O} + NaOH = NH_3 + NaOCN + H_2O.$ Phase II. (a)  $NaOCN + 2H_2O = NH_3 + NaHCO_8.$ 

In the first phase, cyanic acid is temporarily fixed as alkali cyanate; hydrolysis of the latter quickly follows, and the two phases continue to proceed simultaneously with velocities which vary as the conditions change during the progress of the reaction.

During the earlier stages, sodium cyanate accumulates in considerable quantity in solution, since the velocity of its formation in the first phase is much greater than the speed of its disappearance (by hydrolysis) in the second phase. As the concentration of urea diminishes, the velocity of its dissociation is exceeded by that of the hydrolysis of the alkali cyanate, and hence in the later stages the second phase becomes the predominant change.

The different results obtained after heating urea in solution with sodium hydroxide, under such conditions that ammonia was removed as it was evolved, whilst the concentration was maintained as nearly constant as was possible, are given in the following tables.

The proportion of change under phase I corresponds with the amount of alkali cyanate found in the cold solution at the end of an experiment, whilst phase II represents the amount of alkali cyanate which had been hydrolysed during the progress of the reaction, calculated from the amount of ammonia evolved, after the necessary correction, on the basis of equation (a), phase II.

### TABLE II.

Urea, N/5; sodium hydroxide, N/5. Molecular ratio, 1:1.

| Time.   |     |     | Phase I. |             | Phas     | e II.            | Urea decomposed. |                    |          |
|---------|-----|-----|----------|-------------|----------|------------------|------------------|--------------------|----------|
| l hour  | ••• |     |          | 17.7 p      | er cent. | 4·40 pe          | er cent.         | 22·10 p            | er cent. |
| 2 hours | ••• | ••• | •••      | $30.8^{-1}$ | ,,       | 9·0 <sup>1</sup> | ,,               | 39·80 <sup>*</sup> | ,,       |
| 3,,     | ••• | ••• | •••      | 36.0        | ,,       | 18.25            | ,,               | 54.25              | ,,       |

### TABLE III.

Urea, N/2.5; sodium hydroxide, N/2.5. Molecular ratio, 1:1.

| Time.   |       |       |     | Phase I.        | Phase II.      | Urea decomposed |  |
|---------|-------|-------|-----|-----------------|----------------|-----------------|--|
| 1 hour  | • • • | • • • |     | 21.25 per cent. | 4.15 per cent. | 25.40 per cent. |  |
| 2 hours | • • • | •••   |     | 32.00 ,,        | 10.00          | $42.00^{-1}$ ,  |  |
| 3 ,,    |       | • • • | ••• | 38.90 ,,        | 18.80 ,,       | 57.70 ,,        |  |
| 4·5 ,,  | •••   | •••   | ••• | 36.05 ,,        | 48.72 ,,       | 84.77 "         |  |

### TABLE IV.

Urea, N/5; sodium hydroxide, N/2.5. Molecular ratio, 1:2.

|         | Гime |     |     | Phas         | e I.     | Phas              | e II.    | Urea de | composed. |
|---------|------|-----|-----|--------------|----------|-------------------|----------|---------|-----------|
| 1 hour  |      | ••• |     | 19.05 pe     | er cent. | $4 \cdot 52 \ pc$ | er cent. | 23.57 p | er cent.  |
| 2 hours |      | ••• |     | $27.50^{-1}$ | ,,       | $13.12^{-1}$      | ,,       | 40.62   | ,,        |
| 3 ,,    | •••  | ••• | ••• | 35.35        | ,,       | 19.82             | ,,       | 55.17   | ,,        |
| 4,,     | •••  | ••• | ••• | 36.10        | ,,       | 28.95             | ,,       | 65.05   | ,,        |

### TABLE V.

Urea, N/5; sodium hydroxide, N. Molecular ratio, 1:5.

| 7       | l'ime. |     |     | Phas     | se I. | Phase   | e II.    | Urea de | composed. |
|---------|--------|-----|-----|----------|-------|---------|----------|---------|-----------|
| 1 hour  | •••    |     | ••• | 20.0 per | cent. | 6·75 pe | er cent. | 26·75 p | er cent.  |
| 2 hours | •••    | ••• | ••• | 28.9     | ,,    | 16.55   | ,,       | 45.45   | ,,        |
| 3,,     | •••    | ••• | ••• | 34.2     | ,,    | 27.65   | ,,       | 61.89   | ,,        |

When the above results are compared with those recorded under table I, it will be seen that the proportion of urea decomposed was greater in the presence of sodium hydroxide than in the presence of hydrochloric acid at similar concentrations.

Whilst the foregoing results are in perfect agreement with the dissociation theory of the mechanism of the change, they appear as a contraversion of the conclusions arrived at by Fawsitt (*loc. cit.*), who found that unless the concentrations of alkali was very high (and that of urea relatively so), the velocity of the change was greater in the presence of hydrochloric acid than in the presence of sodium hydroxide.

All Fawsitt's experiments were made in sealed tubes, and herein lies the cause of the discrepancy, which supplies further evidence in support of the present theory. It is obvious that accumulation of ammonia in solution under pressure would seriously check the dissociation of urea, and so retard the change to an extent which would have no parallel in the case of the decomposition in the presence of an acid, where both dissociation products were removed as fast as they were generated. Thus, when urea and sodium hydroxide, in equal molecular proportions and at concentration N/5, were heated for three hours at 100° in a sealed tube, only 33 per cent. of urea was decomposed, as against 54.25 per cent. (exp. 3, table II) when the experiment was performed in an open vessel, all other conditions being equal. It should be noticed that the amount of urea decomposed in the former case is also considerably less than that decomposed in the presence of hydrochloric acid (N/5) in an open vessel [table I, (II)].

When the relative effects of acids and alkalis on the velocity of the decomposition of urea are considered, there can be no doubt that in Fawsitt's experiments, on account of the use of sealed tubes, a departure from comparable conditions was quickly brought about.

As a matter of fact, Fawsitt showed that the decomposition of urea was retarded by the presence of ammonium hydroxide or ammonium chloride, whilst such salts as sodium chloride and potassium chloride, although they had but little effect in very dilute solutions, produced a marked increase in the speed of decomposition at normal concentration. Other 'catalysts,' including platinum-black, were found to be without effect, and in the obscure light of the isomeric transformation theory, no explanation could be offered.

The effects in question are obviously in complete agreement with the dissociation theory, which they help to confirm.

## Decomposition of Urea in Aqueous Solution in the Presence of Barium Hydroxide.

This reaction was originally proposed by Bunsen as a method for the estimation of urea, based on the amount of barium carbonate formed. As is well known, severe conditions are required to complete the change, namely, very prolonged heating, a high temperature ( $180-200^{\circ}$ ), and an excess of barium hydroxide.

It is curious, in view of the above, that the progress of this decomposition has apparently not been investigated.

The two phases of the reaction are represented thus:

Phase I. 
$$2\text{HN:C} < \bigcirc_{0}^{NH_3} + B_4(OH)_2 = B_4(OCN)_2 + 2NH_3 + 2H_2O.$$
  
Phase II.  $\begin{cases} (b) & Ba(OCN)_2 + 3H_2O = BaCO_3 + 2NH_3 + CO_2, \text{ and} \\ (c) & Ba(OCN)_2 + 2H_2O = BaCO_8 + CON_2H_4. * \end{cases}$ 

The following results were obtained when urea and barium hydroxide in equal molecular proportions were heated at 100° in aqueous solution, and whilst ammonia was removed as it was evolved.

\* See page 94

## TABLE V1.

| Urea, | N/8; | barium | hydroxide, | N | /8. |
|-------|------|--------|------------|---|-----|
|       |      |        |            |   | 4   |

Calculated on the usual equation.

|         |     |              |           |                     |                                      | 1                           |
|---------|-----|--------------|-----------|---------------------|--------------------------------------|-----------------------------|
| Time.   |     | Phase I.     | Phase II. | Urea<br>decomposed. | BaCO <sub>3</sub> pre-<br>cipitated. | NH <sub>3</sub><br>evolved. |
|         |     | Per cent.    | Per cent. | Per cent.           | Per cent.                            | Per cent.                   |
| 1 hour  |     | 16.0         | 3.0       | 19.0                | 6.0                                  | 11.0                        |
| 2 hours |     | $23 \cdot 9$ | 8.55      | $32 \cdot 45$       | 12.5                                 | 20.5                        |
| 3       |     | 28.7         | 15.15     | 43.85               | 18.5                                 | 29.5                        |
| 4 ,,    | ••• | 29.9         | 17.55     | 47.45               | $22 \cdot 5$                         | 32.5                        |

The numbers in the two last columns are given to prove the fallacy underlying the usual interpretation of the change. Thus, after one hour, whilst the amount of barium carbonate formed indicated the decomposition of only 6 per cent. of the urea originally present, the ammonia evolved was equal to the decomposition of 11 per cent.; in reality, the amount of urea which had been decomposed was equal to 19 per cent., that is, 8 per cent. of the nitrogen of urea was present in solution as barium cyanate.

In these experiments, phase II commenced (judged from the sudden appearance of opalescence) about seven minutes after phase I had been in progress. Since one molecular proportion of barium hydroxide can theoretically complete the decomposition of two molecular proportions of urea, the results of the two phases should be compared with those under table IV. When the true mechanism of the change is brought to light, it can be readily understood why such severe conditions have been found necessary in order to estimate urea by means of this reaction.

## The Stability of Urea in Aqueous Solution and in the Presence of Acid, and of Alkali in the Cold.

After a solution of urea has been heated for a few minutes at  $90-100^{\circ}$  and subsequently cooled, the presence of the cyanate radicle can be readily proved on addition of silver nitrate. This well-known fact is not explained by the usual ionic theory. Fawsitt found that 450 hours were required to decompose and hydrolyse 98.9 per cent. of the urea originally present in a semi-normal solution at 99°.

If the dissociation products could persist at a constant temperature an equilibrium, represented thus,

$$\begin{array}{c} \mathrm{NH}_{8} \\ \swarrow & \swarrow \\ \mathrm{HN:C} \overset{\mathrm{NH}_{8}}{\rightleftharpoons} \rightleftharpoons \mathrm{HN:CO} \rightleftharpoons \mathrm{HO\cdot CN} \rightleftharpoons \mathrm{NH}_{4} \cdot \mathrm{OCN} \end{array}$$

would obtain, and the decomposition of urea and of ammonium cyanate would be completely arrested. The velocity of the change is determined by the very slow hydrolysis of cyanic acid under highly unfavourable conditions, whilst dissociation of urea is checked in consequence.

The progress of the change may be mentally compared to the working of a syphon in which the flow of liquid through the downward tube is seriously checked by a very narrow outlet.

Since urea is not dissociated in solution at the ordinary temperature, an equilibrium between it and ammonium cyanate can only arise on the application of heat. Judging from certain statements in the literature of the subject, the views on this point do not appear quite clear, since it is sometimes stated that the equilibrium is independent of the temperature.

In order to settle the question, a solution of pure urea (N/2) in distilled water sterilised by saturation with toluene was tested from time to time with silver nitrate and with barium hydroxide respectively. After nine months, the solution was still neutral, and a negative result was obtained with each reagent.

A similar solution of urea in non-sterilised water gave a marked opalescence with the respective reagents after fourteen days. At the end of six months, the solution contained ammonium carbonate, but no ammonium cyanate, since, after precipitation with barium hydroxide, the carefully neutralised filtrate gave no precipitate on the addition of silver nitrate. This latter result is of interest, since the decomposition of urea in this case was unquestionably brought about, through the agency of urease, by micro-organisms \* which had developed in the solution.

A solution of urea (N/2) in pure sodium hydroxide (N/2) solution, after remaining at the laboratory temperature for five months, showed no change; at the end of twelve months a trace of the cyanate radicle was detected.

A solution of urea in the presence of hydrochloric acid under similar conditions remained unchanged.

Urea therefore does not undergo an isomeric change until the temperature of its dissociation is reached.

## Note on the Decomposition of Urea by Urease.

The ease with which urea is decomposed by urease, even at  $15-20^{\circ}$ , is in striking contrast to its stability in the presence of acids or of alkalis at the same temperature, or when heated alone

<sup>\*</sup> The mycelium of a specific mould was observable in the solution.

in solution. When the remarkable\* 'selective' action of the enzyme is remembered (Armstrong and Horton, *Proc. Roy. Soc.*, 1912, **85**, 109), this fact must be considered as additional evidence in favour of a molecular structure of urea peculiar to itself, as shown by the cyclic formula.

It seems probable that the zymolysis of urea is a true case of direct hydrolysis, independent of dissociation as a preliminary to the change. Urease was not found to have an accelerating effect on the hydrolysis of potassium cyanate, nor has it been found possible, so far, to detect the cyanate radicle during the decomposition of urea by the enzyme. The suggestion put forward by Armstrong and Horton (*loc. cit.*) that urease, the solution of which they noted was acid to phenolphthalein, probably acts by combining with urea in virtue of the basic character of the latter, is open to doubt. Urease is markedly amphoteric, a fact which, so far as the author is aware, has not been generally recognised. The alkalinity of a solution of the enzyme towards methyl-orange was found to be greater than its acidity towards phenolphthalein.

## The Decomposition of Urea in the Presence of Alcohol.

Burrows and Fawsitt (*loc. cit.*) found that the addition of alcohol to a solution of urea (N/10) + hydrochloric acid (N/10) produced a marked decrease in the velocity of decomposition. This result, they state, "was not exactly what we anticipated," since "alcohol increases the velocity of transformation of ammonium cyanate into urea, and the decomposition of urea is closely related to its formation." The latter remark, of course, is only true so far as the change (dissociation) which gives rise to the first phase of its decomposition is concerned.

The addition of alcohol should undoubtedly produce an increase in the velocity of the decomposition of urea if this is solely dependent on its dissociation and all other conditions are the same. A consideration of the conditions implied by the equilibrium scheme just given will show why this result is not effected. Since alcohol promotes the dissociation of ammonium cyanate, it must also inhibit to a corresponding degree any tendency to its formation at all temperatures above its dissociation point, and hence its presence brings about a limitation on one side which counterbalances its promotive effect on the other. The ulterior effect of

<sup>\*</sup> The behaviour of urease towards seventeen different amino- and iminocompounds, presumably more or less related to urea in constitution, has been examined. In no case was there evidence of decomposition.

alcohol will therefore depend on its power of facilitating or retarding the removal of one or other of the dissociation products, and since a check on the rate of hydrolysis of cyanic acid will be the effect, as suggested by Burrows and Fawsitt from a somewhat different point of view, the velocity of the decomposition of urea will be retarded in consequence. The increased pressure produced by alcohol, particularly at high concentration, and at the higher temperature (98.2°), would also check dissociation of urea.

In the conversion of ammonium cyanate into urea, the promotive effect of alcohol is in no way interfered with, since both dissociation products are removed with great rapidity by the formation of urea at a temperature much below its dissociation point, and hence there is little or no opportunity for hydrolysis of cyanic acid.

It is interesting to note the very much greater velocity of decomposition of urea at  $98.2^{\circ}$  as compared with that at  $71.25^{\circ}$  and at  $61.05^{\circ}$  found by Burrows and Fawsitt. The respective values are represented by the ratios 83.6, 2.77, and 0.715. The fact that urea only commences to dissociate in solution at a fair degree of rapidity above  $90^{\circ}$  explains the cause of this wide difference.

## Mechanism of the Formation of Urea during the Hydrolysis of Metallic Cyanates.

O. and J. Masson (*Zeitsch. physikal. Chem.*, 1910, **70**, 290) have shown that the hydrolysis of potassium cyanate at  $80^{\circ}$  was completed, in accordance with the equation:

(d) 
$$4$$
KOCN +  $6$ H<sub>2</sub>O =  $2$ K<sub>2</sub>CO<sub>3</sub> + (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> + CON<sub>2</sub>H<sub>4</sub>

whilst in the case of barium cyanate the whole of the nitrogen appeared in the form of urea, as represented by equation (c) (p. 90).

Ionisation of the cyanate being assumed as the first step, O. and J. Masson have accounted for the formation of urea thus:

(A) 
$$\operatorname{CNO'} + 2\operatorname{H}_2O \longrightarrow \operatorname{NH}_4 + \operatorname{CO}_3''.$$
  
(B)  $\operatorname{CNO'} + \operatorname{NH}_4 = \operatorname{CON_9H}_4.$ 

A somewhat similar suggestion has been offered by Normand and Cumming (T., 1912, **101**, 1859) to explain the formation of urea when pure cyanic acid was hydrolysed in dilute solution, thus:

(C) 
$$2\mathbf{H}' + 2\mathbf{CNO'} + 2\mathbf{H}_2\mathbf{O} = \mathbf{CON}_2\mathbf{H}_4 + \mathbf{CO}_2$$
.

It was suggested, because the alkali cyanates show a neutral reaction, that cyanic acid must be a strong acid, and would, therefore, be highly ionised in dilute solution. From this suggestion the author ventures to differ. Alkali nitrites, for example, have a neutral reaction, yet nitrous acid is an extremely weak acid,  $K = 6 \times 10^{-4}$ , according to Rây and his co-workers (T., 1917, 111, 414). The properties of cyanic acid are distinctly those of a feeble acid, and the ease with which its ammonium salt is dissociated, whereby urea is formed, is a fact which bears directly on the immediate question.

It must be admitted that an ionic theory, such as is represented by equation (B), originally proposed by Walker, or by (C), fails to throw any light on the mechanism of the change, since no attempt has been made to show in what way urea is formed from the interaction of the respective ions NH<sub>4</sub> and CNO'. With the deceptive 'carbamide' structure in view, it has evidently been considered useless to attempt to pursue the mysterious changes by which the ions effect such a result. Now an ionic theory is not in agreement with the facts; Walker found, contrary to expectation, that the velocity of the transformation of ammonium cyanate into urea was greater in the presence of alcohol than in the presence of water, and since there must be fewer ions present in the former condition, it has been assumed that the velocity of the interaction (B)must be greater in the presence of alcohol. It must be conceded that this is but a speculation, to meet a fact, rather than an ex-Since alcohol will promote dissociation of ammonium planation. cyanate, whilst diminishing ionisation, the increased velocity of the transformation under such conditions appears as a normal phenomenon in perfect agreement with the author's theory of the change (loc. cit.).

The formation of urea from metallic cyanates is explained in a simple manner, on the basis of hydrolytic dissociation \* as the first step in the change, thus:

$$KOCN + H_2O \rightleftharpoons KOH + (HOCN \rightleftharpoons HN:CO)$$
  
 $HOCN + H_2O = NH_8 + CO_2 = KHCO_3$   
 $NH_2$ 

HN:CO + NH<sub>3</sub> = HN:C $<_{0}^{NH_{3}}$ , and HOCN + NH<sub>3</sub> = NH<sub>4</sub>·OCN.

The following results illustrate how slowly potassium cyanate was hydrolysed in solution at the ordinary temperature.

\* Pure potassium cyanate shows a slight alkalinity towards phenolphthalein after immediate dissolution in water.

### TABLE VII.

## . Potassium Cyanate, N/2. Mean $t^{\circ}=16^{\circ}$ .

|           | Time. |      |       | KOCN hydrolysed. | Time.   | KOCN hydrolysed. |  |  |
|-----------|-------|------|-------|------------------|---------|------------------|--|--|
| 7         | days  |      | • • • | 11.4 per cent.   | 42 days | 81.8 per cent.   |  |  |
| 13        | ,,    |      |       | 22.4 ,,          | 49 ,,   | 87.8 ,,          |  |  |
| <b>21</b> | ,,    | •••• | •••   | 43.2 ,,          | 56 ,,   | 91·6 ,,          |  |  |
| <b>28</b> | ,,    |      | •••   | 56-8 ,,          | 63 ,,   | 94.5 ,,          |  |  |
| 35        | ,,    | •••  |       | 69.7 ,,          | 70 ,,   | 98·7 ,,          |  |  |

The amount of urea found in solution at the end of ten weeks was 0.94 gram; from 8.1 grams of potassium cyanate, equation (d) would require 1.5 grams of urea. The conditions were less favourable for the formation of urea than when hydrolysis was effected at 80°, at which temperature ammonium cyanate would not be formed.

When potassium cyanate was hydrolysed at  $100^{\circ}$  under reflux, urea was formed to the extent of 18.44 per cent. of the theoretical, equation (d). No urea was found when potassium cyanate (N/5)was hydrolysed at 100° in presence of sodium hydroxide (N/2.5)(Expts. I, II, and III). It may therefore be safely concluded that no urea would be regenerated during the progress of its decomposition in the presence of sodium hydroxide in an open vessel; on the other hand, a condition favourable to its regeneration, to some extent, would be brought about in a sealed tube, more particularly in the later stages of the reaction. This fact must also be taken into account in considering the results obtained by Fawsitt (*loc. cit.*) for the velocity of the decomposition of urea in the presence of alkalis.

### EXPERIMENTAL.

As regards the results given under table I, it is only necessary to point out that the titrations of residual acidity after each experiment were made with methyl-orange as indicator. The urea used (0.6 gram in each case) was twice recrystallised from alcohol. All the experiments were made with the same flask and reflux condenser, and a quiet, continuous ebullition was maintained throughout. Each experiment was duplicated.

The following method was adopted in obtaining the results of the decomposition of urea in the presence of sodium hydroxide.

Expts. tables II-V.—0.6 Gram of urea, 10 c.c. of N-sodium hydroxide, and 40 c.c. of water (concentration N/5) were heated to the boiling point in a distillation flask (150 c.c.) of resistance glass, carrying a stoppered delivery tube, through which a continuous supply of recently boiled distilled water was maintained, so that the volume of liquid was kept, as nearly as possible, constant

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throughout the process of distillation. The ammonia evolved was absorbed in an excess of normal acid contained in a suitable receiver attached to a vertical condenser connected with the distillation flask. At the end of an experiment the residual solution was rapidly cooled under the tap; the cyanate radicle was estimated (1) by precipitation with silver nitrate in the neutral solution, after the 'carbonate' had been removed by barium nitrate and barium hydroxide; the excess of silver nitrate was titrated by Volhard's method; (2) by addition of the solution to an excess of hydrochloric acid, which was afterwards titrated, using methyl-orange as indicator. A lower result was almost invariably obtained by this method; this was due to slight loss of cyanic acid, the odour of which was very noticeable when the liquid was added to excess of normal acid; the solution was allowed to remain, until the odour had disappeared, to ensure complete hydrolysis of cyanic acid before titration. The following examples will suffice to show how the values for the two phases were calculated:

> 0.6 gram  $\text{CON}_2\text{H}_4 \longrightarrow 2\text{NH}_3 = 20$  c.c. N-HCl, NaOCN=100 c.c. N/10-AgNO<sub>3</sub>.

Table III. One Hour.—Ammonia evolved = 2.95 c.c. N-HCl.

Sodium cyanate present in residual solution = 21.25 c.c. N/10-AgNO<sub>3</sub>. Hence, phase I = 21.25 per cent.; if hydrolysed, this would be obviously equivalent to ammonia = 2.125 c.c. N-HCl. Hence, omitting the third decimal number,  $(2.95 + 2.12) \times 5 = 25.35$  per cent. of urea decomposed, and 25.35 - 21.25 = 4.10 per cent. phase II.

Table IV. Four Hours.—Ammonia evolved=9.4 c.c. N-HCl.

Sodium cyanate present= $36\cdot1$  c.c. N/10-AgNO<sub>3</sub>= $36\cdot1$  per cent. phase I; hence,  $(9\cdot4+3\cdot61)\times5=65\cdot05$  per cent. of urea decomposed; therefore, phase II,  $65\cdot05-36\cdot1=28\cdot95$  per cent.

A second experiment, in which the residual sodium cyanate was hydrolysed [method (2)], gave ammonia=3.55 c.c. N-HCl=35.5 per cent. phase I; ammonia evolved=9.45 c.c. N-HCl. Hence, 65.0 per cent. of urea decomposed, and phase II=29.5 per cent.

Whilst no great accuracy is claimed for the values representing each phase, on account of the difficulty experienced in maintaining the volume of solution constant, the order of the results, so far as the amount of urea decomposed was concerned, can be certainly trusted within 2 or 3 per cent., and since this was one of the chief facts which it was sought to prove, no further useful information was likely to be obtained by extending the time of heating beyond three or four hours.

The following is an example of an experiment with barium hydroxide.

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Table VI. Four Hours.—Ammonia evolved = 6.5 c.c. N-HCl. Barium carbonate precipitated, neutralised 4.5 c.c. N-HCl. Hence (from 0.6 gram of urea) amount of urea decomposed = 32.5 per cent. from ammonia estimation and = 22.5 per cent. from amount of barium carbonate precipitated, calculated on basis of usual equation.

Barium cyanate in residual solution = 29.9 c.c. N/10-AgNO<sub>3</sub>. Hence phase I=29.9 per cent., and  $(6.5+2.99) \times 5 = 47.45$  per cent. of urea decomposed, therefore phase II=17.55 per cent.

## Estimation of Urea Formed During Hydrolysis of Potassium Cyanate.

Expt. I.—2.025 Grams of potassium cyanate dissolved in 50 c.c. of water (N/2) were boiled under reflux for three hours (crystals of ammonium carbonate gradually formed on the sides of the reflux tube), at the end of which time only 1.3 per cent. of the salt remained unchanged. The residue, after the solution was evaporated to dryness at 100°, was extracted with hot alcohol, and the residue from the latter solution, after removal of all ammonium salt, gave, when decomposed with an excess of alkaline solution of sodium hypobromite in the nitrometer, 28.45 c.c. N<sub>2</sub> at 24° and 764 mm.=25.5 c.c. N<sub>2</sub> at N.T.P., equal to 0.06825 gram of urea = 18.44 per cent., calculated on equation (b). The presence of urea was qualitatively proved by its behaviour towards urease, and precipitation as urea nitrate.

*Expt. II.*—8.1 Grams of potassium cyanate dissolved in 200 c.c. of water (N/2) were allowed to remain for ten weeks at the laboratory temperature; 25 c.c. of the solution, after removal of ammonium carbonate, gave 44.09 c.c. N<sub>2</sub> at N.T.P., equal to 62.99 per cent. of urea formed, on basis of equation (b).

*Expt. III.*—0.81 Gram of potassium, 20 c.c. of *N*-sodium hydroxide, and 30 c.c. of water were boiled for three hours in a distillation flask, whilst the concentration was maintained nearly constant. The residual solution gave no nitrogen when tested as above with alkaline sodium hypobromite.

#### Summary.

(1) The decomposition of urea when heated in aqueous solution in the presence of acids or of alkalis is primarily dependent on its dissociation into ammonia and cyanic acid.

(2) The so-called 'hydrolysis of urea' under such conditions is no more than the hydrolysis of cyanic acid or of an alkali cyanate, as the case may be, and hence is not a change which gives any support to a 'carbamide' structure, as so commonly suggested.

(3) Under comparable conditions, the velocity of the decomposition of urea is greater in the presence of sodium hydroxide than in the presence of hydrochloric acid, because the proportion of free urea in solution is greater in the former case.

(4) Whilst an ionic theory fails to throw any light either on the conversion of ammonium cyanate into urea or on the formation of urea during the hydrolysis of cyanic acid or of metallic cyanates, it is not in agreement with the facts.

(5) The effect of alcohol in accelerating the transformation of ammonium cyanate into urea and in retarding the decomposition of urea in solution is easily explained by the dissociation theory, with which it is in perfect agreement.

(6) A sterilised solution of urea does not suffer any 'hydrolysis' or reversion to ammonium cyanate at the ordinary temperature. The latter phenomenon can only arise from the dissociation of urea as a preliminary to the change.

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