LXXIV.—The Constitution of Carbamides. Part IV. The Mechanism of the Interaction of Urea and Nitrous Acid.

By EMIL ALPHONSE WERNER.

THE decomposition of urea by nitrous acid is generally considered to be properly expressed by the following simple equation:

 $CON_2H_4 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O_1$

and this reaction is frequently cited in text-books as additional evidence in support of the "carbamide" structure of urea.

Theoretically, this reaction should be available for the estimation of urea, as is commonly suggested in the literature; it is never used for this purpose, and it is doubtful whether it ever has been, since experiment has proved it to be quite valueless. On the other hand, it constitutes a well-known method for the estimation of nitrous acid, with a very fair degree of accuracy, on the supposition that the above equation is true. No doubt for this reason, and on account of the employment of other methods for the estimation of urea, this reaction has been considered all along as a normal change, scarcely deserving of any further investigation.

In continuation of the author's work on the constitution and properties of urea, its behaviour towards nitrous acid has been submitted to a careful quantitative study. The following are some of the more important facts which have been observed, and whilst they show what an erroneous conception has been generally entertained regarding the nature of this reaction, they fully justify the necessity for a proper investigation into the true mechanism of the change.

1. Urea and pure nitrous acid in aqueous solution did not interact. (Expts. IX, X.)

2. The presence of a strong acid (hydrochloric or nitric) quickly promoted a brisk interaction, even in dilute solutions, and the reaction was completed in a relatively short time.

3. The presence of a weak acid, such as acetic acid, did not promote an interaction, unless the concentration was abnormally high, and even then the velocity of the reaction was extremely slow.

4. The volume of nitrogen evolved was not a direct measure of the amount of urea decomposed, calculated on the basis -of the above equation; the quantity decomposed was much greater * than that indicated by the evolved nitrogen.

5. Only when urea was present in considerable excess was the volume of nitrogen evolved an approximately true estimate of the amount of nitrous acid decomposed.

6. The volume ratio of carbon dioxide to nitrogen (1:2) required by the equation has never been obtained; the proportion of carbon dioxide was always much higher; moreover, the composition of the gas was liable to much variation with small changes in concentration.

It is obvious that, so far as the usual explanation of this reaction is concerned, all these facts stand out as anomalies for which the ordinary equation offers no explanation.

Now, anomalies in such a reaction can have no reality; their apparent existence is the natural consequence of an erroneous conception of the change, and when the true constitution of urea is considered they appear as normal phenomena which reveal the true mechanism of the interaction.

Mechanism of the Interaction of Urea and Nitrous Acid.

In the course of a recent investigation on the properties of pure nitrous acid, Rây, Dey, and Ghosh (this vol., p. 414) noticed that a solution of the acid $(N/32\text{-HNO}_2)$ was practically without action on urea, "no matter how much urea was added." They found that the addition of sulphuric acid was necessary to promote and complete a reaction. This anomaly, they remark, "was without any apparent reason," a just comment when urea is believed to be carbamide. Pure nitrous acid in aqueous solution does not react with

* See remarks on page 870

urea until an amino-group is presented for attack, a condition brought about by the production of a salt of urea on the addition of a sufficiently strong acid, thus:

$$HN:C <_{O}^{NH_3} + HX = HN:C <_{OH}^{NH_2,HX}$$

The first stage of the reaction then takes place, in accordance with the equation *:

(a)
$$\operatorname{HN:C} \leq_{OH}^{NH_2,HX} + \operatorname{HNO}_2 = N_2 + \operatorname{HNCO} + 2H_2O + HX.$$

The cyanic acid is decomposed in two ways as fast as it is generated. It is hydrolysed, † thus:

(b)
$$HNCO + H_2O = NH_3 + CO_2$$
,

and directly attacked by nitrous acid, according to the equation :

(c) $HNCO + HNO_2 = CO_2 + N_2 + H_2O$ (see Expts. VII and VIII).

Both these decompositions proceed simultaneously with the primary reaction (a), but the relative proportions in which they take place can be varied at will, within certain limits, by adopting suitable conditions which will be presently shown.

The production of cyanic acid has been easily demonstrated by its isolation in the form of the silver salt; thus when urea was attacked by nitrous acid in the presence of silver nitrate and a small excess of nitric acid, a yield of pure silver cyanate was obtained equal to 42 per cent. of the theoretical, calculated on the equation:

(d) $HN:C <_{OH}^{NH_2,HNO_3} + HNO_2 + AgNO_3 =$

 $N_2 + AgOCN + 2HNO_8 + 2H_2O_1$

Considering the favourable conditions for hydrolysis, and the very sensible solubility of silver cyanate in dilute nitric acid, such a result was even more successful than could reasonably have been expected.

It will be seen now that when urea (in the form of a salt) and nitrous acid interact, a certain proportion of nitrogen from the urea is always fixed as an ammonium salt, and herein lies the fallacy of the reaction, so far as the estimation of urea is concerned.

The variations observed in the ratios of carbon dioxide to nitrogen are thus easily explained, since the volume of nitrogen evolved is lowered in proportion to the amount of cyanic acid hydrolysed. The latter change can be only partly suppressed, even under the

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^{*} No doubt this decomposition originates through the medium of diazotisation.

[†] Cyanic acid in water alone is hydrolysed to urea, $2\text{HNCO}+\text{H}_2\text{O}=\text{CON}_2\text{H}_4+\text{CO}_2$ (Normand and Cumming, T., 1912, 101, 1859); in the presence of mine ral acid, of course, the change is as above.

most favourable conditions (that is, high concentration and nitrous acid in excess), with the result that the ratio of carbon dioxide to nitrogen evolved is never that which has been erroneously assumed.

Now, according to the above explanation, the interaction of urea and nitrous acid is theoretically clearly divisible into two stages, during the first of which one molecule of urea is completely decomposed by one molecule of nitrous acid, instead of by two molecules, as has been commonly, but falsely, supposed.

This has been easily proved experimentally, by adopting the exact conditions which the theory rigorously demands, namely, (1) the presence of urea in excess at the outset, (2) a low concentration of nitrous acid, (3) the presence of mineral acid in excess of that required to neutralise ammonia generated from the hydrolysis of cyanic acid, and so to maintain the proper configuration of the urea molecule. Under these conditions the decomposition of cyanic acid by nitrous acid can be almost completely suppressed in favour of its decomposition by hydrolysis.

A knowledge of the amount of cyanic acid hydrolysed, compared with the volume of nitrogen evolved, is an all-important factor, by means of which a very clear insight into the mechanism of the reaction has been obtained.

The following results illustrate the degree of success which has been realised in experimentally proving the problem which is indicated by the theory of the change now put forward.

		Тав	LE I.			
Molecular r atios	I. $CON_2H_4 + HNO_2$. 1:1 92.5 per cent.		$\begin{matrix} \text{II.} \\ \text{CON}_2\text{H}_4 + \text{HNO}_2. \\ 1 \cdot 5 : 1 \end{matrix}$ 95.73 per cent.		111.CON2H4+HNO2,2:199.34 per cent.	
Nitrogen evolved, calculated on the theoretical						
HNCO hydrolysed	87.0	,,	96.0	,,	99.5	,,
HNCO decom- posed by HNO ₂	13 ·0	,,	4 ·0	,,	0.2	,,
Proportion of urea actually de- composed by one molecule of HNO ₂	79.5	,,	91.73	"	98·84	,,
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$CO_2 = 43 \cdot 1$ $N_2 = 53 \cdot 6$ $NO = 3 \cdot 2$	>> >> >>	$CO_2 = 43.2$ $N_2 = 54.5$ NO = 2.2	>> >> >>	$CO_2 = 44 \cdot 2$ $N_2 = 54 \cdot 3$ $NO = 1 \cdot 3$,, ,,
Ratio CO ₂ to N	1:1.24		1:1.26		1:1.22	

It will be seen, on viewing the results of the above experiments (the full details of which are given under Expts. V., VII., and VIII.), that the amount of urea decomposed by one molecular proportion of nitrous acid, according to the equation

$$HN:C <_{OH}^{NH_2,HX} + HNO_2 = N_2 + HNCO + 2H_2O + HX$$

was less than that indicated by the volume of nitrogen evolved. The difference was most marked when the exact proportions (equal molecules) of urea and nitrous acid required by the equation were used, since the conditions were less favourable for a quantitative realisation of the second change, namely,

 $HNCO + H_2O + HX = NH_4X + CO_{22}$

than when a considerable excess of urea was present. In the latter case, the desired object was almost fully attained (III), and the true nature of the primary stage of the reaction thereby established.

As regards the composition of the evolved gases, the ratio of carbon dioxide to nitrogen was in each case approximately $1:1\cdot20$; this, of course, was not the true value, since a very sensible amount of carbon dioxide was held in solution in the residual liquid; when corrected, in the case of result III, for example, the true ratio was $CO_2=1$, $N=1\cdot02$, or 1:1 as required by the combination of the two equations.

It may be well to direct attention here to the constant presence of a small amount of nitric oxide in the evolved gas; whilst this was no doubt due to the decomposition of a corresponding proportion of nitrous acid, thus, $3\text{HNO}_2 = \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$, it was not found possible to eliminate it completely, even when urea was in excess and the concentration of nitrous acid, at the outset of the reaction, was as low as N/20. Under such conditions as are commonly adopted, in the estimation of nitrous acid by the aid of urea, the proportions of nitric oxide may easily amount to between 6 and 8 per cent. of the evolved gases, according to the particular concentration of the solution used. This fact appears to have been generally overlooked.

It is obvious when the ratios $HNO_2:N$ and $3HNO_2:2NO$ are compared that the presence of nitric oxide must lead to a result in excess of the true value; for example, in the case of result III, table I, if the nitric oxide found was included as nitrogen, the yield of the latter would appear as 101.8 per cent. of the theoretical.

Rây and his co-workers (*loc. cit.*), using a solution of nitrous acid of concentration N/32, obtained a result which they found was in excess of the true value in nearly the same proportion as above, and no doubt for the same reason. This decomposition of

nitrous acid readily explains why a solution of comparatively high concentration, say $HNO_2 = N/6$, can slowly attack urea; the generation of nitric acid gradually brings about the required condition.

The results under table I were obtained by adding the theoretical proportion of nitrous acid slowly and at intervals to the acid solution of urea. A very low concentration of nitrous acid was thus ensured throughout the progress of the reaction.

When the molecular proportion of nitrous acid was added all at once, the concentration at the outset being $\text{HNO}_2 = N/6$, the results, as was to be expected, were very different, as shown below (Expts. IV. and V.).

TABLE II.

Molecular ratios Nitrogen evolved	$\begin{matrix} {\rm I.} \\ {\rm CON_2H_4+} \\ 1:1 \\ 91{\cdot}46 {\rm \ pe} \end{matrix}$	HNO ₂ . r cent.	$\begin{matrix} \text{II.} \\ \text{CON}_2\text{H}_4 + \\ 1 \cdot 5 : \\ 94 \cdot 40 \text{ pe} \end{matrix}$	HNO2 l r cent.	$\begin{array}{c} \text{III.} \\ \text{CON}_2\text{H}_4 + \\ 2:1 \\ 96.48 \text{ pe} \end{array}$	HNO_2 r cent.
HNCO hydro- lysed HNCO decom- posed by HNO ₂	71.5 28.5	,, ,,	$74 \cdot 5$ 25 · 5	,, ,,	76·0 24·0	,, ,,
Urea actually de- composed by HNO ₂	62·96	,,	68:90	,,	72·48	,,
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{c} {\rm CO_2} = 36 \cdot 5 \\ {\rm N_2} = 59 \cdot 2 \\ {\rm NO} = 4 \cdot 2 \end{array}$	>> >> >>	$CO_2 = 37.8$ $N_2 = 59.08$ NO = 3.06	,, ,, ,,	$\begin{array}{c} {\rm CO_2} = 43 \cdot 6 \\ {\rm N_2} = 54 \cdot 1 \\ {\rm NO} = 2 \cdot 2 \end{array}$,, ,,

Whilst the volume of nitrogen evolved was only slightly below that previously observed, the amount of urea decomposed was, in each case, much less than before. This was the natural result of the much greater facility offered for the decomposition of cyanic acid by nitrous acid at the higher concentration. The latter was also responsible for the slight increase in the proportions of nitric oxide. The constancy * to be observed in the proportions of carbon dioxide and nitrogen in the evolved gases, as shown in both tables, in spite of the fairly wide differences in the proportions of urea decomposed, is easily explained when the ratios of cyanic hydrolysed to cyanic decomposed by nitrous acid are considered.

As regards the very slow reaction which was noticed to take place between urea and nitrous acid in the presence of acetic acid (when $HNO_2 = N/4$), this was entirely due to the gradual decom-

^{*} Within the limits of experimental error, the rate of mixing, for instance, which affects the velocity of the reaction, has a decided influence on the above ratios.

position of the former acid. Urea acetate has been described by Matignon (*Compt. rend.*, 1891, **112**, 1369) as a compound which was completely dissociated in aqueous solution, hence acetic acid could not establish the essential condition required to promote the desired interaction (Expts. IX. and X.).

Decomposition of Urea in the Presence of Two Molecular Proportions of Nitrous Acid.

The results recorded in table I have conclusively proved that urea can be completely decomposed by one molecular proportion of nitrous acid; that this is not accomplished under the conditions which are commonly employed is solely due to the disturbing effect of the secondary reaction (c).

Now, according to the usual interpretation of the change, two molecular proportions of nitrous acid should be required to decompose one of urea.

The effect after treating urea directly with nitrous acid in these proportions, and at different concentrations, in the presence of hydrochloric acid to promote the change are given below (for details see Expts. I., II., and III.).

TABLE III.

	Nitrogen evolved. Per cent.	Composition of evolved gases. Per cent.
$\left. \begin{array}{c} \mathrm{HNO}_2 \ N/3 \\ \mathrm{I.} \ \ \mathrm{Urea} \ N/6 \\ (2 \ \mathrm{c.c.} \ N \mathrm{-HCl}) \end{array} \right\}$	72.02	$CO_2 = 35.0, N_2 = 55.4, NO = 9.5$
$\left. \begin{array}{c} \mathrm{HNO}_2 \ N/6 \\ \mathrm{II.} \ \mathrm{Urea} \ N/12 \\ (2 \ \mathrm{c.c.} \ N \cdot \mathrm{HCl}) \end{array} \right\}$	71.99	$CO_2 = 32.1$, $N_2 = 58.2$, $NO = 9.6$
$\left.\begin{array}{c} \operatorname{HNO}_2 N/8\\ \operatorname{III.} \operatorname{Urea} N/16\\ (2 \text{ c.c. } N \cdot \operatorname{HCl} \end{array}\right\}$	69.19	$CO_2 = 32.6$, $N_2 = 57.3$, $NO = 10.0$
$\left. \begin{array}{c} \mathrm{HNO}_2 \ N/10 \\ \mathrm{IV.} \ \mathrm{Urea} \ N/20 \\ \mathrm{(3 \ c.c. \ N-HCl)} \end{array} \right\}$	72.07	$CO_2 = 31.1$, $N_2 = 58.1$, $NO = 10.4$

In each case it was readily proved that all the urea had been decomposed, whilst an excess of nitrous acid remained, yet in round numbers only about 70 per cent. of the theoretical proportion of nitrogen was evolved. The remainder of the nitrogen was, of course, present as ammonium chloride * in the residual solution

^{*} It is interesting to note that Claus (*Ber.*, 1872, **4**, 140) long ago noticed the formation of ammonia when nitrous acid reacts with urea; thus, he gave the following equation for the reaction in the cold; $2\text{CON}_2\text{H}_4 + \text{N}_2\text{O}_3 =$

It will be noticed also that, even without allowing for carbon dioxide held in solution, the ratio of carbon dioxide to nitrogen was still well below that of 1:2 as required.

An equally marked divergence from the theoretical results was obtained by carrying out the reaction in two separate stages. It will be obvious that, according to the usual, but false, explanation of the change, such a procedure should give similar results for each stage. This was not so. Whilst the first stage was represented by the values given under I, table II, the volume of nitrogen evolved in the second stage was equal to only $26\cdot38$ per cent. of the original amount of urea present, hence $62\cdot96 + 26\cdot38 = 89\cdot34$ per cent.; nitrogen from the remainder of the urea (10.66 per cent.) was fixed as ammonium chloride in the second stage (see Expt. IV.).

The composition of the evolved gases, namely, $CO_2 = 22.4$ per cent., $N_2 = 50.7$ per cent., NO = 26.8 per cent., was very different from that of the gases set free in the first stage.

A rather remarkable paradox makes its appearance when the results are compared on the basis of the false and of the true equations; thus, according to the usual interpretation of the reaction, the amount of urea decomposed was roughly 30 per cent. greater (table III) than indicated by the volume of nitrogen set free, whereas in reality the amount of urea decomposed was much less than required by the volume of nitrogen evolved. The paradox, of course, is but a phantom; its existence is just as unreal as the usual explanation of the change is incorrect.

A contemplation of the results just recorded, and so easily demonstrated, makes it almost impossible to believe that the behaviour of urea towards nitrous acid has ever been seriously studied with the object of obtaining evidence to support the supposed "carbamide" formula.*

Whilst the present study of the reaction has supplied further proof of the cyclic formula, it has also brought to light yet another

 $(NH_4)_2CO_3 + 2N_2 + CO_2$. It was assumed, however, that usea was hydrolysed to ammonium carbonate during the process, apparently independent of the reaction with nitrous acid, since the proportion of carbon dioxide to nitrogen evolved is shown to be the same as in the usual equation; probably for this reason, the observation is never mentioned in the text-books.

* Emmerling (A., 1886, 50, 747; the original paper in *Landw. Versuchs-Stat.*, 1886, 440, was not available) studied the decomposition of urea by nitrous acid in the presence of nitric acid and acetic acid respectively, both in cold and in hot solutions. The volume of nitrogen evolved was found never to be equal to the theoretical, but no apparent attempt was made to offer any explanation of the results.

of the many fallacies which abound throughout the chemistry of urea.

The origin of these is not far to seek.

Instead of a careful study of the properties and reactions of urea being made the groundwork for solving the problem of its constitution, an almost infallible belief in the truth of the carbamide formula has all along been the predominant factor in determining what these properties and reactions should be.

Secondary changes, seemingly unimportant by-products, apparent abnormalities in certain reactions, and so forth, have been pushed aside as of little consequence so long as the end result could be made to fit in with the "carbamide" structure.

EXPERIMENTAL.

With one exception, all the experiments were made with the aid of a Lunge nitrometer. The specimen of sodium nitrite used for the generation of nitrous acid contained 97.18 per cent. of NaNO₂; * a proportionate weight (71:69) corresponding with the theoretical required was used in each case.

Action of Nitrous Acid on Urea in Molecular Proportions of Two to One.

Expt. I.—0.03 Gram of pure urea and 0.071 gram of sodium nitrite dissolved in 1 c.c. of water were introduced into the nitrometer over mercury, and 2 c.c. of *N*-hydrochloric acid directly added.

Concentration at outset, $HNO_2 = N/3$, $CON_2H_4 = N/6$. The reaction was apparently completed within thirty minutes, whilst more than four-fifths of the gas had been evolved after five minutes. In this and all other experiments not less than one hour was allowed to elapse before the gas was measured and analysed.

Gas evolved = 31.4 c.c. at 18° and 766.5 mm. $CO_2 = 11$ c.c., NO = 3 c.c., $N_2 = 17.4$ c.c.

Volume of nitrogen at N.T.P. $=16\cdot134$ c.c., $=72\cdot02$ per cent. of the theoretical. (Theory $=22\cdot4$ c.c. at N.T.P.)

Expt. II.—As above, but $HNO_2 = N/6$, $CON_2H_4 = N/12$.

Gas evolved = 29.7 c.c. at 16° and 763.5 mm. $CO_2 = 9.55$ c.c., NO = 2.85 c.c., $N_2 = 17.3$ c.c.

* Estimated by the thiourea method (T., 1912, 101, 2190, and Coade and Werner, T., 1913, 103, 1221).

Volume of nitrogen at N.T.P. = 16.126 c.c., = 71.99 per cent. of the theoretical.

Expt. III.—The last experiment was repeated to prove the cause for the deficiency of the evolved nitrogen.

After the evolution of gas had ceased, the residual liquid was well washed out of the nitrometer. It required for neutralisation, using methyl-orange as indicator, 6.1 c.c. of N/10-sodium hydroxide. Since 1 c.c. of N-hydrochloric acid was directly neutralised in liberating nitrous acid, there should have remained, according to the usual equation, free acid equivalent to 10 c.c. of N/10sodium hydroxide. Hence $10-6\cdot 1=3\cdot 9$ c.c. of N/10-hydrochloric acid were neutralised by ammonia from the hydrolysis of cyanic acid. Now, according to equations (a) and (b) (p. 865), the maximum amount of acid that could be thereby neutralised would be 5 c.c. of N/10-hydrochloric acid, therefore 78 per cent. of the theoretical proportion of cyanic acid was hydrolysed, or so much of its nitrogen was fixed as ammonium chloride. The remainder of its nitrogen, namely, 22 per cent., was set free (equation c), together with that from urea, in accordance with equation (a).

Since all the urea was decomposed with the liberation of half of its nitrogen, we have 50 + 22 = 72 per cent. of the total nitrogen set free, which was in complete agreement with the result obtained from Expt. II.

As the results with urea and nitrous acid (1:2) at lower concentrations (table III) were obtained in a manner similar to the above, further details are unnecessary.

Action of Nitrous Acid on Urea (2:1) in Two Stages.

Expt. IV. First Stage.—0.06 Gram of urea and 0.071 gram of sodium nitrite were dissolved in 4 c.c. of water, and 2 c.c. of N-hydrochloric acid directly added.

Concentration, $\text{CON}_2\text{H}_4 = N/6$, $\text{HNO}_2 = N/6$.

Gas evolved = 37.5 c.c. at 18° and 763 mm. $CO_2 = 13.7$ c.c., NO = 1.6 c.c., $N_2 = 22.2$ c.c.

Volume of nitrogen at N.T.P. = 20.49 c.c., = 91.46 per cent. of the theoretical.

Second Stage.—The gas having been expelled from the nitrometer (from a repeated experiment), 0.071 gram of sodium nitrite dissolved in 1 c.c. of water was added, and then 1 c.c. of N-hydrochloric acid. The evolution of gas was very much slower than in the first stage, and five hours were allowed for the completion of the reaction.

Gas evolved = 25.3 c.c. at 18° and 769.3 mm. $CO_2 = 10.25$ c.c., NO = 2.35 c.c., $N_2 = 12.7$ c.c.

Volume of nitrogen at N.T.P. = 11.82 c.c. = 52.76 per cent. of the theoretical.

An analysis of the residual solution after the first stage showed that 7.15 c.c. of N/10-hydrochloric acid had been neutralised, equivalent to 71.5 per cent. of cyanic acid hydrolysed, therefore 28.5 per cent. of the evolved nitrogen was the result of the reaction between nitrous acid and cyanic acid (equation c); hence 91.46 - 28.5 = 62.96 per cent. of the urea present was decomposed in this stage.

Therefore only 37.04 per cent. of urea remained to be attacked by nitrous acid in the second stage, and since 52.76 per cent. of nitrogen was evolved, it follows that 52.76 - 37.04 = 15.72 per cent. of the nitrogen set free in this stage was due to the above reaction (equation c).

A comparison of the results from the two stages is not without interest.

	First stage.	Second stage.
	$\operatorname{Per}\operatorname{cent}$.	Per cent.
Urea decomposed	= 62.96	37.04
HNCO hydrolysed	= 71.50	57.60
HNCO decomposed by HNO_2 .	= 28.50	42 · 4 0
		40 F
~	$CO_2 = 36.5$	40.5
Composition of evolved gas	$\{ N_2 = 59 \cdot 2 \}$	50.1
	$(NO = 4 \cdot 2)$	9.3
Ratio $CO_2 : N_2$	1:1.62	1:1·23

Since nitrous acid was in considerable excess in the second stage (which should not be the case, according to the usual equation), the proportion of cyanic acid attacked by it to cyanic acid hydrolysed was much greater than in the first stage.

Decomposition of Urea by One Molecular Proportion of Nitrous Acid.

In order to illustrate how the results given under table I were obtained, it will be sufficient to state the details of the most successful experiment.

Expt. V.-0.12 Gram of urea was dissolved in 3 c.c. of N-hydrochloric acid, and the solution introduced into the nitrometer; 0.071 gram of sodium nitrite dissolved in 2 c.c. of water was placed in the cup (previously rinsed) of the nitrometer, and added gradually in four separate portions to the urea solution. The reaction, which was hastened by shaking to ensure rapid mixing, was allowed to complete itself before each addition of the sodium nitrite.

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Gas evolved (after one hour)=44.2 c.c. at 18° and 766.4 mm.; $CO_2=19.6$ c.c.; NO=0.6 c.c.; $N_2=24.0$ c.c.

Volume of nitrogen at N.T.P. = 22.252 c.c. = 99.34 per cent. of the theoretical.

The residual solution from a similar experiment required 10.05 c.c. of N/10-sodium hydroxide for neutralisation.

Hence 20 (2 c.c. of *N*-hydrochloric acid originally free) -10.05 = 9.95 c.c. of *N*/10-hydrochloric acid were neutralised as the result of cyanic acid hydrolysis, which was therefore almost complete. Therefore the amount of urea actually decomposed was 99.34 - 0.5 = 98.84 per cent. of the theoretical, only 0.5 per cent. of the evolved nitrogen being derived from cyanic acid.

Therefore one molecule of urea was decomposed by one molecule of nitrous acid.

Isolation of Cyanic Acid, as the Silver Salt, from the Interaction of Urea and Nitrous Acid.

Expt. VI.—0.6 Gram of urea and 0.71 gram of sodium nitrite were dissolved in 40 c.c. of ice-cold water and to the solution 1.7 grams of silver nitrate previously dissolved in 5 c.c. of water and 5 c.c. of N-nitric acid were added. As the pale cream-coloured precipitate of silver nitrite, which was immediately formed, gradually disappeared, it was replaced by a snow-white precipitate of silver cyanate.

During the progress of the reaction, further 5 c.c. of N-nitric acid were added. After an hour the precipitate was collected, washed, and dried: It gave none of the reactions for nitrous acid, and contained Ag=71.84 per cent. (AgOCN requires Ag=72 per cent.); on adding a few drops of sulphuric acid to the dry salt the characteristic pungent odour of cyanic acid was evolved.

The weight of silver cyanate obtained was 0.63 gram, which was equal to 42 per cent. of the theoretical for equation (d).

The Interaction of Cyanic Acid and Nitrous Acid.

As this change does not appear to have been hitherto examined, the following experiments were made in order to prove the validity of equation (c) already given.

Expt. VII.—0.081 Gram of pure potassium cyanate and 0.071 gram of sodium nitrite were dissolved in 2 c.c. of water and introduced into the nitrometer; 3 c.c. of *N*-hydrochloric acid were added, that is, 1 c.c. of acid in excess, to counteract the neutralising effects of hydrolysis.

Concentration at outset, HNO_2 and HNCO = N/5.

The evolution of gas was very rapid, and the reaction was practically completed within five minutes.

Gas evolved after one hour = 34.3 c.c. at 16° and 757.8 mm.; $CO_{\circ} = 19.1$ c.c.; NO = 3.6 c.c.; $N_{2} = 11.6$ c.c.

Volume of nitrogen at N.T.P. = 10.72 c.c. = 47.8 per cent. of the theoretical. Therefore 52.2 per cent. of cyanic acid had been hydrolysed.

Expt. VIII.—The above experiment was repeated. The residual solution required for neutralisation 8.5 c.c. of N/10-sodium hydroxide, instead of 4.78 c.c. as required by the gasometric analysis. The apparent discrepancy was easily explained when the above results were considered. The volume of nitric oxide evolved (3.33 c.c. at N.T.P.) represents a decomposition of 22.3 per cent. of nitrous acid, with the generation of nitric acid equivalent to 0.74 c.c. of N/10-sodium hydroxide, whilst the proportion of cyanic hydrolysed showed that free nitrous acid remained equivalent to 3 c.c. of N/10-sodium hydroxide. Hence $4.78 \pm 0.74 \pm 3.0 = 8.52$ c.c. of N/10-sodium hydroxide were required, which is in complete agreement with the value actually found. The presence of unchanged nitrous acid in the residual liquid was easily proved.

Therefore the reaction between cyanic acid and nitrous acid takes place theoretically between equal molecular proportions, but at a concentration of N/5 the velocity of hydrolysis of cyanic acid is slightly higher than that of the primary change.

The Behaviour of Urea towards Pure Nitrous Acid alone or in the Presence of Acetic Acid.

Expt. IX.—0.03 Gram of urea and 0.071 gram of sodium nitrite were dissolved in 2 c.c. of water and 2 c.c. of *N*-acetic acid were added. Concentration of $\text{HNO}_2 = N/4$.

There was no preceptible evolution of gas until after a considerable time; thus, after twenty-four hours 7.4 c.c. had been evolved and at the end of ninety-six hours, when the experiment was stopped, the volume of the evolved gas was=12.6 c.c. at 13° and 758 mm. The volume of nitrogen at N.T.P. was=6.56 c.c., and the original gas contained 9.5 per cent. of nitric oxide.

The slow action was primarily brought about as a result of the gradual decomposition of nitrous acid, whereby urea nitrate was slowly generated. Rây and his co-workers (*loc. cit.*) have shown that even at 0° the most concentrated solution of nitrous acid, stable for only a short time, was approximately N/5.5.

Expt. X.—The same proportions of urea and sodium nitrite as before were dissolved in 29 c.c. of water, and 1 c.c. of *N*-acetic acid was added. Concentration of $HNO_2 = N/30$.

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After remaining for three days in the nitrometer, the volume of gas evolved was 0.8 c.c. Yet when 2 c.c. of *N*-hydrochloric acid were added, a fairly brisk reaction was quickly promoted, and even at this low concentration was almost completed at the end of half an hour.

Summary.

(1) Urea is not attacked by pure nitrous acid alone, or even when a second very weak acid is present.

(2) When a salt of urea is produced, by the presence of a sufficiently strong acid, it is immediately attacked by nitrous acid, because an amino-group is thereby presented for such attack.

(3) One molecule of urea (as a salt) requires but one molecule of nitrous acid for its decomposition into nitrogen, cyanic acid, and water, since only one amino-group is present.

(4) Cyanic acid and nitrous acid react in equal molecular proportions, with the production of nitrogen, carbon dioxide, and water.

(5) The usual interpretation of the reaction between urea and nitrous acid, which has been hitherto accepted, is incorrect; first, because it is in contradiction to the experimental facts, and, secondly, because it is based on an erroneous conception of the constitution of urea.

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