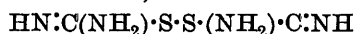


CCXXVIII.—*The Action of Nitrous Acid on Thiocarbamide and on Formamidine Disulphide. A New Structural Formula for Thiocarbamide.*

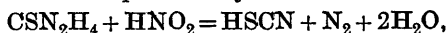
By EMIL ALPHONSE WERNER.

STORCH (*Monatsh.*, 1890, **11**, 452) has shown that when nitrous acid, in common with several other oxidising agents, is added to an acid solution of thiocarbamide, the feeble base



is produced, for which Fichter and Wenk (*Ber.*, 1912, **45**, 1373) have recently proposed the name formamidine disulphide. The present author (this vol., p. 2169) has pointed out that Storch's base is only formed by the action of oxidising agents on thiocarbamide when a strong acid ioniser is present. The base can be readily detected in solution, even when present in very small quantity, by (a) the immediate precipitation of sulphur on addition of ammonium hydroxide, and (b) the separation of the crystalline picrate (m. p. 153°) on addition of picric acid solution. When nitrous acid, or an alkali nitrite, was added to a solution of thiocarbamide containing sulphuric, nitric, or any other strong acid, an evanescent, red coloration was produced, whilst gas, consisting chiefly of nitric oxide, was rapidly evolved, and on applying the above tests the presence of formamidine disulphide was at once revealed. When the same experiment was made with a solution of thiocarbamide containing acetic acid, or any other equally feeble acid ioniser, such as nitrous acid itself, only a faint, yellow coloration was produced, gas was evolved which consisted chiefly of nitrogen, and on the application of the tests no formamidine disulphide could be detected; the addition of ferric chloride produced an intense blood-red colour due to thiocyanic acid formed as a result of the interaction; no such colour reaction was given with ferric chloride in the former experiment, until an excess of nitrous acid had been added; this is explained later.

Claus (*Annalen*, 1878, **179**, 129) examined the action of ethyl nitrite on an alcoholic solution of thiocarbamide, and considered the main change to consist in the reversion of the latter to ammonium thiocyanate; later A. E. Dixon (*Trans.*, 1892, **61**, 526), as a side-issue of an investigation on the constitution of certain complex derivatives of thiocarbamide, was led to repeat Claus' experiments, and showed that free thiocyanic acid is produced in the reaction, whilst not a trace of ammonia could be detected. The following equation has been given by Dixon as representing the chief result of the decomposition by nitrous acid:



and this has been confirmed in the main as the result of a quantitative study of the change.

It is obvious from the facts just recorded that the interaction of nitrous acid and thiocarbamide proceeds on two different lines according as a strong or a weak acid ioniser is present in the solution; the following results also show that the reaction, so far as the production of thiocyanic acid* is concerned, is divisible into two distinct stages when a strong acid is present, but is completed in a single stage in the presence of a weak acid.

When the theoretical amount of pure sodium nitrite was added gradually to a solution of thiocarbamide containing about 5 per cent. of nitric acid, the very sparingly soluble formamidine disulphide dinitrate, $\text{C}_2\text{S}_2\text{N}_4\text{H}_6 \cdot 2\text{HNO}_3$, was obtained, in accordance with the equation:



in amount equal to 92.39 per cent. of the theoretical, and by using a slight excess of the alkali nitrite the yield was increased to 93.75 per cent., which was the maximum obtainable.

In order to obtain a clear idea regarding the progress of the interaction under the different conditions mentioned, quantitative experiments were carried out in a Lunge's nitrometer, the full details of which are described in the experimental part.

A. *Examination of the 1st Stage.*—A known weight of thiocarbamide, together with the theoretical amount of pure sodium nitrite dissolved in a small quantity of water, was introduced into the nitrometer, and a sufficient amount of dilute sulphuric acid added. Gas was evolved with great rapidity, the liquid which at first assumed a red colour quickly changed to pale yellow, and the reaction was complete in a few minutes. The total volume of gas, which was in perfect agreement with the above equation, was found always to contain about 12 per cent. of nitrogen.

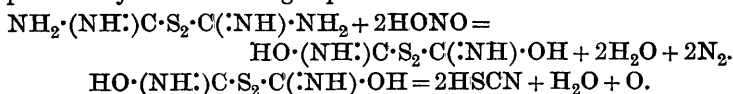
* Thiocyanic acid is slowly further oxidised by nitrous acid, with production of pure nitric oxide.

This is due to interaction of nitrous acid and formamidine disulphide, which accompanies the primary change, and explains at once the slight deficiency in the yield of the base, noticed in the previous experiment.

B. Examination of the 2nd Stage.—Experiment A was repeated, and after the evolved gas had been expelled from the nitrometer, a second theoretical amount of the alkali nitrite dissolved in a small quantity of water was introduced. A small quantity of gas was rapidly evolved; this was followed by a short interval of quiescence, after which gas was set free with increasing rapidity, whilst the liquid became deep red in colour. The reaction was completed in a few minutes. The total volume of gas was almost identical with that evolved in the first stage; it contained nearly 16 per cent. of nitric oxide; the remainder was nitrogen, and the residual liquid was rich in thiocyanic acid.

It is obvious from the results of experiment A that the liquid at the end of the first stage must contain a small quantity of unchanged thiocarbamide, to which is due the sudden evolution of a small amount of gas, preceding the quiescent phase when stage two properly speaking really starts, and which also accounts for portion of the nitric oxide found.

The decomposition in the second stage may be provisionally explained by the following equations:



No oxygen could be detected in the gaseous product, as it was used up in oxidising some of the thiocyanic acid, the amount of which in the residual liquid was found to be only 83·56 per cent. of that required by the above equation. The oxidation of thiocyanic acid takes place as follows: $\text{HSCN} + 3\text{O} = \text{SO}_3 + \text{HCN}$; one atomic proportion of oxygen would therefore be capable of oxidising one-sixth of the total quantity of thiocyanic acid produced, that is, 16·66 per cent., the difference between the theoretical and the amount actually found, namely, $100 - 83·56 = 16·44$, is in close agreement with this result.

When nitrous acid and thiocarbamide or formamidine disulphide were allowed to interact in the presence of dilute acetic or nitric acid, a small quantity of sulphuric acid was always found in the final product; in one experiment carried out in presence of dilute nitric acid, the sulphuric acid formed was estimated, and was found to correspond with the deficiency in the thiocyanic acid (see Expt. III).

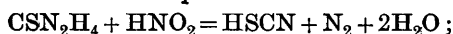
C. Examination of the Interaction in a Single Operation in

Presence of Dilute Sulphuric Acid.—A solution containing two molecular proportions of alkali nitrite and one of thiocarbamide was directly treated with dilute sulphuric acid in the nitrometer. The evolution of gas was very rapid at the start, and whilst no quiescent stage could be detected, there was very perceptible diminution in the violence of the reaction when about half the final volume of gas had been evolved. The proportion of nitric oxide amounted to 58·5 per cent.; the remainder was nitrogen; the equation:



requires equal volumes of the two gases. Since in all these interactions the departure from the theoretical, as regards the composition of the gas evolved, is always NO for N₂, or vice versa, the final volume of gas has been found in each case to agree very closely with that required by the equation.

D. Examination of Interaction in Presence of Acetic Acid, one stage only.—Equal molecular proportions of thiocarbamide and sodium nitrite, dissolved in a small quantity of water, were treated with sufficient dilute acetic acid in the nitrometer. A slight brownish-red colour is at first developed, which quickly changed to pale yellow, gas was freely evolved, and the reaction was completed after a few minutes. The total volume of gas set free was in perfect agreement with the equation:



it was found, however, to contain 8·6 per cent. of its volume of nitric oxide, whilst the amount of thiocyanic acid present in the residual solution was 85·3 per cent. of that required by the equation. No formamidine disulphide could be detected as a product of the change; the nitric oxide must therefore have been produced as a by-product of the oxidation of a portion of the thiocyanic acid, and as some sulphuric acid was found in the solution this is confirmed.

When the interactions just described are carried out in very dilute solutions, the composition of the evolved gas is not altered, proving that the secondary reactions are not influenced by dilution.

The main results obtained may be briefly summarised as follows, leaving aside the secondary changes:

(i) When nitrous acid and thiocarbamide interact in aqueous solution in the presence of a weak acid, thiocyanic acid is directly produced with evolution of nitrogen, and the change takes place between equal molecular proportions of the two compounds.

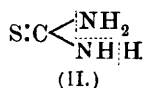
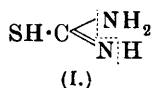
(ii) When nitrous acid and thiocarbamide interact in aqueous solution in the presence of a strong acid, formamidine disulphide

is produced with evolution of nitric oxide, and is then decomposed with formation of thiocyanic acid, and evolution of nitrogen. Two molecular proportions of nitrous acid to one of thiocarbamide are required to complete the change.

(iii) The respective interactions are independent of the concentration.

(iv) Nitrites may be rapidly and accurately estimated by means of thiocarbamide.

The reactions and properties of formamidine disulphide are in agreement with the constitutional formula originally proposed by Storch (*loc. cit.*), namely, $\text{NH}_2 \cdot (\text{NH}) \cdot \text{C} \cdot \text{S}_2 \cdot \text{C} \cdot (\text{NH}) \cdot \text{NH}_2$, and its production from thiocarbamide has been generally accepted as strong evidence in support of the unsymmetrical formula $\text{NH}_2 \cdot \text{C} \cdot (\text{NH}) \cdot \text{SH}$ for the latter. Storch was led to conclude from his work that thiocarbamide in acid solution, at all events, has this constitution. It is evident from the results recorded in the present paper, and also in that on "The Interaction of Iodine and Thiocarbamide" (this vol., p. 2166), that this view of the constitution of the substance is not alone sufficient to explain the different facts observed. There can certainly be little, if any, objection to the proposition that the production of thiocyanic acid is in better agreement with the unsymmetrical than with the symmetrical formula of thiocarbamide, namely,



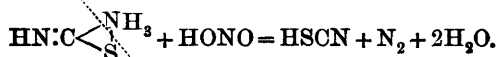
even if the change of $\text{H} \cdot \text{NCS}$ into $\text{H} \cdot \text{SCN}$ as derived from formula (II) is admitted. To support the unsymmetrical formula it might also be argued that since formamidine disulphide is only stable in presence of a strong acid, it may be produced as an intermediate product when nitrous acid reacts with thiocarbamide in the presence of a weak acid, but having under such conditions only an ephemeral existence it is immediately decomposed into thiocyanic acid with evolution of nitrogen. This, however, is contrary to the observed facts, for a much larger proportion of nitric oxide would be produced if this took place.

If the unsymmetrical formula, therefore, is accepted, and it is the more likely, it is evident that the presence of a strong acid, in bringing about a condition favourable to the production of formamidine disulphide, must induce an alteration in the structure of the thiocarbamide molecule which is not produced by the presence of a weak acid, and is different from that pre-existent in the ordinary neutral solution of the substance.

The following theory of the constitution of thiocarbamide does

not appear to have been hitherto suggested, and seems to have a serious claim to consideration, since it offers an important clue to the explanation of the particular phenomena under discussion.

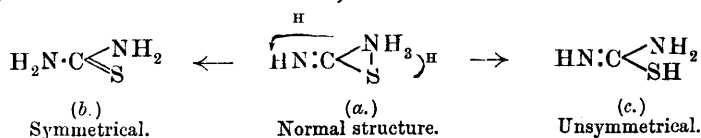
In the structural formula $\text{HN}:\text{C} \begin{smallmatrix} \text{NH}_2 \\ \text{SH} \end{smallmatrix}$ a mutual attraction must exist between the respective positive and negative NH_2^- and SH -groups, resulting in the assumption of a configuration represented by the formula $\text{HN}:\text{C} \begin{smallmatrix} \text{NH}_3 \\ \text{S} \end{smallmatrix}$, bearing in mind that thiocarbamide is only capable of forming salts with the stronger acids, resembling in this respect the amino-acids and compounds of like constitution. A configuration such as this would not be disturbed by the presence of a feeble acid in solution, and hence would directly yield thiocyanic acid and nitrogen when attacked by nitrous acid, thus:



The addition of a strong acid, on the other hand, would at once destroy the "ammonia constitution," and by producing a salt of the structure $\text{NH}:\text{C} \begin{smallmatrix} \text{NH}_2, \text{HX} \\ \text{SH} \end{smallmatrix}$ would effect the necessary alteration in the constitution of the thiocarbamide required for the production of formamidine disulphide. The mechanism of the interaction of iodine and thiocarbamide can also be satisfactorily explained by the aid of this new formula (see p. 2175).

The structure of thiocarbamide which is now proposed, whilst it explains the phenomena under notice in a simple manner, has several other claims to consideration which must be left over for discussion in a future communication; attention, however, may be drawn to the following points, which have a direct bearing on the present investigation.

If this constitutional formula represents the structure of thiocarbamide under normal conditions, that is, in a neutral solution or even in the presence of a weak acid, it explains how the compound can give rise to products derived either from the symmetrical or unsymmetrical structure already recognised, according as the conditions are altered, thus:



If (a) represents the normal structure, the migration of a hydrogen atom in either of the directions shown will at once give rise to structure (c) or (b) as the case may be, whilst the change

from (a) to (c) is apparently determined by a strong acid or other reagent having a similar influence; the change from (a) to (b) (if such does occur) must require some other condition.

This formula also shows a much closer structural relationship between thiocarbamide and ammonium thiocyanate, and while it suggests that the transformation of the latter into the isomeric compound is brought about by the migration of a single atom of hydrogen, instead of two, as required by the other formulæ, it also gives a hint of the possible mechanism of the isomeric transformation being as follows: ammonium thiocyanate on heating dissociates partly into ammonia and thiocyanic acid, the latter changes to isothiocyanic acid, which then re-unites with ammonia to produce thiocarbamide, from which it follows that the amount of the latter formed is in a great measure dependent on the extent of the dissociation of ammonium thiocyanate at the temperature of 170—180°, beyond which the thiocarbamide commences to decompose.

EXPERIMENTAL.

Action of Nitrous Acid on Thiocarbamide in Presence of Nitric Acid.

Expt. I.—0.76 Gram of pure thiocarbamide was dissolved in 40 c.c. of water, 2 c.c. of nitric acid (D 1.42) were added, and 0.69 gram of sodium nitrite* dissolved in 20 c.c. of water was added gradually with constant stirring while the liquid was cooled to about 0°. Formamidine disulphide dinitrate, $C_2S_2N_4H_6 \cdot 2HNO_3$, was precipitated as a white, microcrystalline powder, which was collected, washed with absolute alcohol and then with ether, and dried in the air. The theoretical yield of the dinitrate, formed from the above weight of thiocarbamide in accordance with the equation:



should be 1.38 grams, whilst the weight obtained was 1.275 grams or 92.39 per cent. of the theoretical.

Expt. II.—In this case the operation was carried out as before, but the alkali nitrite was added in slight excess, that is, until a drop of the solution just ceased to decolorise a drop of dilute iodine solution, which proved the absence of any unchanged thiocarbamide.

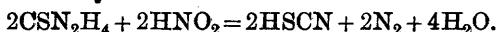
Weight of dinitrate obtained = 1.29 grams = 93.75 per cent. of the theoretical.

* The specimen of sodium nitrite used in all the experiments contained 95.4 per cent. of $NaNO_2$, and a proportionate weight corresponding with the theoretical required was used in each case.

Expt. III.—1.52 Grams of thiocarbamide were dissolved in 150 c.c. of water containing 3 c.c. of nitric acid, and a 6 per cent. solution of sodium nitrite was gradually added with constant stirring until a drop of the solution ceased to give a precipitation of sulphur on addition of ammonium hydroxide solution, proving that all the formamidine disulphide was decomposed. At first there was evolution of brown fumes (due to the nitric oxide set free), but when slightly more than half the required amount of nitrite had been added, the brown fumes ceased, whilst gas (nitrogen) continued to be evolved to the end. The residual solution was made up to 300 c.c. by addition of distilled water:

41.5 c.c. were required for complete precipitation of 25 c.c. of $N/10\text{-AgNO}_3$. $\text{HSCN} = 0.1475$. Hence, total $\text{HSCN} = 1.066$ or 90.3 per cent. of the theoretical.

Theory requires 1.18 grams for the complete conversion of thiocarbamide into thiocyanic acid in accordance with the equation:



Formamidine disulphide was produced, and then decomposed by further addition of nitrous acid:

100 c.c. of the solution gave 0.1538 BaSO_4 . Total = 0.4614. Hence $\text{HSCN} = 0.116$.

$1.066 + 0.116 = 1.182$ HSCN . Theory requires 1.18.

Expt. IV.—The last experiment was repeated, with the difference that the theoretical amount of sodium nitrite, namely, 2.76 grams, was added, and the solution diluted to 300 c.c.:

47.85 c.c. were required for complete precipitation of 25 c.c. of $N/10\text{-AgNO}_3$. Total, $\text{HSCN} = 0.0986$, or 83.56 per cent. of the theoretical (1.18).

The solution was found to contain a small quantity of unchanged thiocarbamide. The sulphuric acid formed was not estimated.

Action of Nitrous Acid on Thiocarbamide in the Presence of Acetic Acid.

Expt. V.—1.52 Grams of thiocarbamide were dissolved in 150 c.c. of water containing 5 c.c. of acetic acid, and 1.38 grams of sodium nitrite (molecular proportions) dissolved in 25 c.c. of water were added gradually as before. Gas was evolved, with slight accompaniment of brown fumes; the solution when tested immediately after the first addition of alkali nitrite gave a deep red colour with ferric chloride, but no precipitate of sulphur was produced on addition of ammonium hydroxide. The solution was diluted to 300 c.c.:

47.9 c.c. were required for precipitation of 25 c.c. of $N/10\text{-AgNO}_3$.
Total HSCN = 83.47 per cent. of theoretical.

The solution contained a small quantity of unchanged thiocarbamide. Sulphuric acid was formed, but was not estimated.

The last two experiments prove that when the theoretical amount of nitrous acid is added all the thiocarbamide is not decomposed, on account of the secondary reaction, namely, oxidation of thiocyanic acid, which accompanies the primary change.

Determination of the Volume and Composition of the Evolved Gases.

Expt. VI.—0.076 Gram of thiocarbamide and 0.069 gram of sodium nitrite dissolved in 2 c.c. of water were introduced into the nitrometer over mercury, and 1 c.c. of dilute sulphuric acid (1:7) was added. Gas was evolved with great rapidity, and the reaction was completed in a few moments. Heat was developed, and after twenty minutes the volume of gas was 24.3 c.c. at 18.5° and 764 mm., or 22.36 c.c. at 0° and 760 mm.

The equation:



requires 22.4 c.c. at 0° and 760 mm.

Ten c.c. of a freshly prepared saturated solution of ferrous sulphate were now introduced into the nitrometer.

Volume of residual gas = 3.1 c.c. The composition was therefore $\text{NO} = 21.2 = 87.24$ per cent., $\text{N} = 3.1 = 12.76$ per cent.

The residual gas was quite free from carbon dioxide, and had the properties of nitrogen. The presence of this gas is the result of the secondary reaction between nitrous acid and formamidine disulphide.

Expt. VII.—The last experiment was repeated, and the evolved gas having been expelled from the nitrometer, 0.069 gram of sodium nitrite dissolved in 1 c.c. of water was introduced. A small quantity of gas was immediately evolved, and after a few moments the evolution of gas continued with increasing rapidity, and the reaction was completed in a few minutes.

Volume = 23.8 c.c. at 18.5° and 764 mm., or 21.86 c.c. at 0° and 760 mm. After treatment with FeSO_4 , volume = 20 c.c. The composition was therefore $\text{NO} = 3.8 = 15.97$ per cent., $\text{N} = 20.0 = 84.03$ per cent.

The nitric oxide is partly due to the presence of thiocarbamide which had escaped conversion into formamidine disulphide as a result of the secondary reaction which occurs in the first stage.

The interaction of nitrous acid and formamidine disulphide cannot be explained without admitting the production of oxygen, thus:



This gas could not be present with nitric oxide, and the results show that the oxygen must oxidise some of the thiocyanic acid produced with evolution of nitric oxide, since the latter was in slight excess of the theoretical, whilst the nitrogen was correspondingly too low (see also Expt. XI.), thus:

1st stage	NO = 87·24	N = 12·76
2nd „	NO = 15·97	N = 84·03
		<hr/> 103·21	<hr/> 96·79

Expt. VIII.—0·076 Gram of thiocarbamide and 0·138 gram of sodium nitrite (that is, two molecular proportions of nitrous acid to one of thiocarbamide) were dissolved in 2 c.c. of water, and 1 c.c. of dilute sulphuric acid was added.

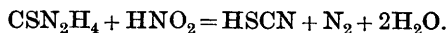
Volume of gas obtained = 49·4 c.c. at 19° and 757 mm., or 45·01 c.c. at 0° and 760 mm. After treatment with FeSO_4 , volume = 21·5 c.c. The composition was therefore $\text{NO} = 27·9 = 56·47$ per cent., $\text{N} = 21·5 = 43·53$ per cent.

Thus, when the interaction was carried out in a single operation, the proportion of nitric oxide evolved was slightly greater than when the decomposition was completed in two stages. The residual solution contained some formamidine disulphide; the higher proportion of nitric oxide was due to the complete conversion of the thiocarbamide into the base in accordance with the first stage reaction.

Expt. IX.—0·076 Gram of thiocarbamide and 0·069 gram of sodium nitrite (molecular proportion) were dissolved in 2 c.c. of water and 1 c.c. of acetic acid added.

Gas obtained = 24·4 c.c. at 20° and 764 mm., or 22·33 c.c. at 0° and 760 mm.

Theory requires 22·4 c.c. at 0° and 760 mm. in accordance with the equation:



After treatment with FeSO_4 , volume = 22·3 c.c. at 20° and 764 mm. The composition was therefore $\text{NO} = 2·1 = 8·61$ per cent., $\text{N} = 22·3 = 91·39$ per cent.

The nitric oxide was present as a result of the oxidation of portion of the thiocyanic acid formed, and some unchanged thiocarbamide was found in the residual solution obtained in a repetition of this experiment.

The following experiment proves that the proportion of nitric

oxide is not materially altered by dilution; the secondary reaction evidently proceeds just the same.

Expt. X.—0.076 Gram of thiocarbamide and 0.069 gram of sodium nitrite were dissolved in 16 c.c. of water* (a 0.5 per cent. solution of the two substances), and 1 c.c. of acetic acid was added.

Gas was very slowly evolved, as compared with the other experiments, fifty minutes being required to complete the interaction.

Gas obtained = 22.9 c.c. at 18° and 764 mm., or 21.16 c.c. at 0° and 760 mm. After treatment with FeSO_4 , volume = 20.9 c.c. The composition was therefore $\text{NO} = 2.0 = 8.73$ per cent., $\text{N} = 20.9 = 91.27$ per cent., which is in close agreement with the last experiment; the smaller volume of gas evolved is due to the solvent action of the comparatively large quantity of water which was present.

Expt. XI. Direct Decomposition of Formamidine Dinitrate by Alkali Nitrite.—0.276 Gram of formamidine dinitrate was mixed with 1 c.c. of water in the cup of the nitrometer, and drawn into the tube; an additional c.c. of water was used to wash in the last traces of the salt; 0.138 gram of sodium nitrite dissolved in 2 c.c. of water was then introduced. Gas was immediately evolved, and the reaction was completed in a few minutes.

Gas obtained = 46.4 c.c. at 19° and 756 mm., or 42.22 c.c. at 0° and 760 mm. After treatment with FeSO_4 , volume = 40. The composition was therefore $\text{NO} = 6.4 = 13.79$ per cent., $\text{N} = 40.0 = 86.21$ per cent.

The nitric oxide in this case was entirely a by-product of the oxidation of portion of the thiocyanic acid.

The Estimation of Nitrites by means of the Interaction with Thiocarbamide.

The results obtained in all the foregoing experiments have shown that the decomposition of thiocarbamide is incomplete when the theoretical amount of nitrous acid is used, on account of the secondary reaction which takes place. On the other hand, when molecular proportions of the two substances interact either in the presence of dilute sulphuric or acetic acid, the total volume of gas evolved is in perfect agreement with the respective equations which represent the change in each case.

For example, in *Expt. VI*, in presence of dilute sulphuric acid, the corrected volume of gas obtained was 22.36 c.c., and in *Expt. IX.*, in presence of acetic acid, the corrected volume of gas obtained was 22.33 c.c.

Theory requires in each case 22.4 c.c. at 0° and 760 mm. The actual composition of the gas evolved is of no importance so far as

* The water was previously boiled and quickly cooled.

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the estimation of the nitrite is concerned, since nitric oxide takes the place of nitrogen, or vice versa, as the case may be. In order to test the method, a sample of sodium nitrite was carefully estimated by the well-known method, using ordinary carbamide, and after absorption of the carbon dioxide by means of sodium hydroxide, the following results were obtained:

0.069 gave 23.5 c.c. N_2 (moist) at 18° and 752 mm., or 21.37 c.c. N_2 (dry) at 0° and 760 mm.

Theory requires 22.4 c.c. $NaNO_2 = 95.4$ per cent.

Expt. A.—0.069 gram of sodium nitrite and 0.1 gram of thio-carbamide were dissolved in 2 c.c. of water, and having been introduced into the nitrometer, 1 c.c. of dilute sulphuric acid (1:7) was added.

Gas evolved = 23.7 c.c. at 18° and 752 mm., or 21.55 c.c. (dry) at 0° and 760 mm.

Expt. B.—An exact repetition of *A*, 1 c.c. of acetic acid being used instead of sulphuric acid.

Gas evolved = 23.7 c.c. at 18° and 752 mm., or 21.55 c.c. (dry) at 0° and 760 mm.

$$NaNO_2 = \frac{21.55}{22.44} = 96.21 \text{ per cent.}$$

The result, which is 0.81 per cent. higher than that obtained by using ordinary carbamide, is very probably the more correct, as the gas has merely to be read off directly, and no subsequent manipulation is required. Further experiments are in progress to test the method against other processes.

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