

II.—*Comparison of the Actions of Hypochlorites and Hypobromites on some Nitrogen-Compounds.*

By H. J. H. FENTON, B.A., University Laboratory, Cambridge.

IN a former paper (*Chem. Soc. Jour.*, July, 1878) I showed that urea, when acted upon by a hypochlorite in presence of a caustic alkali, gives off only one-half of its nitrogen in the cold, the other half remaining probably as a cyanate, whereas a hypobromite, as is well known, causes all the nitrogen to be evolved.

I thought, therefore, that it would be of interest to compare the actions of these two reagents on some bodies more or less analogous to urea in constitution.

The first substance I selected for experiment was *carbamate of ammonium*, the interesting results of Kolbe and Basaroff (*Chem. Soc. Jour.* [2], 6, 194) having shown the close relation of this body to urea. The sample used was prepared by union of the dry gases. Weighed quantities of it having been enclosed in thin stoppered tubes, were introduced into flasks containing the hypochlorite or hypobromite solution, and excess of caustic alkali. The flasks having been connected with delivery-tubes, the thin vessels containing the ammonium carbamate were broken by shaking, and the resulting gas measured, in the same manner as in my experiments on urea.

When either hypochlorite or hypobromite of soda is used, a rapid

evolution of nitrogen ensues, but, as in the case of urea, only half the nitrogen is given off with the hypochlorite, and the whole with hypobromite.

Thus, with hypochlorite of soda—

- (1.) ·1063 gram ammonium carbamate gave 15·5 c.c. N., and  
 (2.) ·1293       "       "       "       19·49 c.c.

theory requiring (for the whole of the nitrogen) 30·52 c.c. and 37·1 c.c. respectively.

With hypobromite of soda

- 0610 gram gave ..... 17·29 c.c. N  
 Theory requiring ..... 17·50   ,,

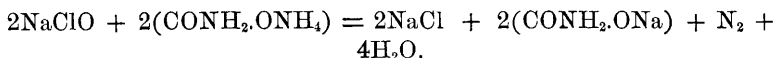
The residue from the action of hypochlorite of soda, as is the case with urea, shows no ammonia reaction with Nessler's solution, and gives off no more gas, even with a large excess of hypochlorite (except on long standing, when a slow decomposition appears to take place); but if, after reducing the excess of hypochlorite with  $\text{SO}_2$ , the solution be acidified with hydrochloric acid, abundant ammonia reactions are obtained.

The residue from the action of a hypochlorite on urea, however, was shown to be unaffected by the addition of a hypobromite, whereas, if this carbamate residue be so treated, a rapid evolution of the remaining half of the nitrogen takes place.

Thus, the residue from experiment (1) above, treated with hypobromite of soda, gave 14·7 c.c. N., and that from (2) gave 18·21 c.c.

It is evident, therefore, that the remaining half of the nitrogen in the carbamate residue does not exist as a cyanate. Moreover, if to this residue a slight excess of ammonia be added, and then a slight excess of calcium chloride, and the solution be filtered, the clear filtrate gives on boiling an abundant precipitate of calcium carbonate.

I conclude, therefore, that the nitrogen remains in this residue, in the form of carbamate of soda. Thus :—



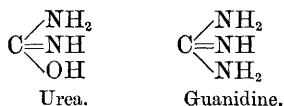
A solution possessed of exactly similar properties as this residue is obtained by dissolving carbamate of ammonium, or the commercial carbonate, in strong caustic soda, and allowing the mixture to stand over sulphuric acid for a day or two.

It appears, therefore, that carbamate of soda can exist, and is tolerably stable in presence of caustic soda.

The action of hypobromite of soda thus affords a ready method of distinguishing a carbamate from a cyanate.

## 14 FENTON ON THE ACTIONS OF HYPOCHLORITES AND

The next substance which engaged my attention was *guanidine*, Wanklyn and Gamgee and others having suggested its relation to urea, both possibly being derivatives of marsh-gas (*Journ. Chem. Soc.* [2], 6, 31).



Crystals of guanidine carbonate and nitrate were used, and the experiments conducted in the same way as before.

·1925 gram of guanidine carbonate gave 43·7 c.c. N with sodic hypochlorite. Theory = 71·8 c.c.; and

·2523 gram gave 64·16 c.c. N with hypobromite. Theory = 94·1 c.c.

Again, ·1664 gram of guanidine nitrate gave 32·18 c.c. N with hypochlorite. Theory = 45·7; and

·1136 gram gave 20·24 c.c. with hypobromite. Theory = 31·25.

It appears, therefore, that the yield of nitrogen is approximately the same with either reagent, and that this is equivalent to almost exactly two-thirds of the total nitrogen, one-third remaining behind in either case, probably as a cyanate: for the residues from these reactions behave just like that from the action of hypochlorites on urea, giving no ammonia reactions until acidified.

The evolution of nitrogen is almost equally rapid with either reagent in this case.

*Biuret* was next tried in a similar way.

	Theory.
·1935 gram with hypochlorite gave 21·38 c.c. N = 63·06	
·1322        „        hypobromite        „    27·43 c.c. N = 43·09	

These numbers correspond with an evolution of almost exactly one-third of the total nitrogen with a hypochlorite, and of two-thirds with a hypobromite.

The residues from these reactions appear to behave like that from urea, the hypochlorite residue being unaffected by the addition of a hypobromite, and giving no ammonia reaction until acidified.

In the case of hypochlorite, the evolution of nitrogen is here slow, whereas with hypobromite it is immediate, as is the case with urea.

The quantities of nitrogen evolved by these two reagents from those bodies which I have as yet investigated, are therefore as follows:—

	Urea.	Ammonium carbamate.	Guanidine.	Biuret.	Ammonia salts.	Cyanates.
NaClO...	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{3}$	all	none
NaBrO...	all	all	$\frac{2}{3}$	$\frac{2}{3}$	all	none

The nitrogen in these bodies evidently exists in three distinct conditions as regards the action of these two reagents. 1st, that which is evolved by either hypochlorite or hypobromite; 2nd, that which is evolved by hypobromite only; 3rd, that which is evolved by neither reagent.

When hypochlorite of soda acts upon *urea* or *biuret*, the nitrogen originally existing in the second condition is transformed into the third condition.

It may be noticed that in these two reactions the evolution is slow, whereas in the others, the effect produced is almost instantaneous.

It is not easy to reconcile these facts with the formulæ usually adopted for the above compounds.

The formula for urea, however, proposed by Wanklyn and Gamgee

$\text{C} \begin{array}{l} \text{OH} \\ \diagup \\ \text{NH} \\ \diagdown \\ \text{NH}_2 \end{array}$ , or that suggested by Heintz (*Ann. Chem. Pharm.*, **150**, 73) and

others,  $\text{C} \begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{=N} - \text{N} \\ | \quad | \\ \text{O} \quad \text{H} \quad \text{H} \end{array}$ , will readily explain the actions of the two reagents on this body.

We might, for instance, assume that the *first* condition of nitrogen mentioned above is that in which it is united to carbon by one of its "affinities;" the *second* by two; and the *third* by three.

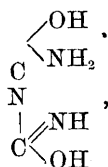
Now taking Wanklyn's formula, it is evident that a hypochlorite would remove the  $\text{NH}_2$  group, leaving  $\text{C} \begin{array}{l} \text{OH} \\ \diagup \\ \text{NH} \\ | \\ \text{NH} \end{array}$ , and this being incapable of existence, would lose H and become  $\text{C} \begin{array}{l} \text{OH} \\ \diagup \\ \text{N} \\ \diagdown \\ \text{N} \end{array}$ , or normal cyanic

acid. The nitrogen being now in the third condition, is no longer capable of being attacked by a hypobromite or hypochlorite.

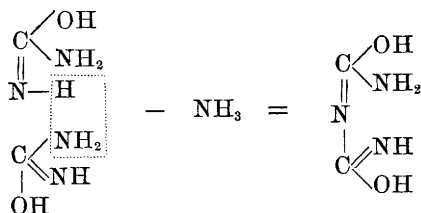
Ammonium carbamate may be  $\text{C} \begin{array}{l} \text{OH} \\ \diagup \\ \text{NH} \\ \diagdown \\ \text{ONH}_4 \end{array}$ , and this, when acted upon by a hypochlorite, loses  $\text{NH}_3$ , and (in presence of caustic soda)  $\text{C} \begin{array}{l} \text{OH} \\ \diagup \\ \text{NH} \\ \diagdown \\ \text{ONa} \end{array}$  remains. The nitrogen in this body being in the second condition, is attacked only by hypobromite.

In *biuret* we have three atoms of nitrogen, each in a different condition.

Its constitution may therefore be—



being formed from urea thus :—



In *guanidine* there are two atoms of nitrogen in the first condition, both being evolved by a hypochlorite or hypobromite, and one in the third condition being unattacked by either.

Its constitution, on the above supposition, must therefore be represented in some such way as—

