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XXXVI.—Action of Hypochlorites on Urea.

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E. W. DAVY, in 1854, proposed a method of estimating urea, by measuring the volume of nitrogen evolved from it when acted upon by a hypochlorite. His numbers show that he obtained nearly the whole of the nitrogen in this way. The results of subsequent authors are

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similar, but do not appear to be always constant. Handfield Jones, for instance, remarks that "every solution of chloride of soda does not answer equally well."

A pupil of mine (Mr. Street) in this laboratory, wishing to estimate urea, happened to use this method, but added an excess of caustic alkali, to ensure, as he thought, the retention of the carbon dioxide formed in the reaction. On calculating his result, we found that only about half the theoretical volume of nitrogen had been obtained.

I have since found that it is invariably the case, that when urea is acted upon by a hypochlorite in the cold, in presence of a caustic alkali, only half the nitrogen is evolved. Thus—

		Urea.	Theory.
·13841	gram gave	 25.31 c.c. N (corr.	) - 51.6
,,	,,	 25.49	
,,	,,	 25.59	
·06571	gram gave	 11.9 c.c. N	- 24.5
,,	.,,	 <b>1</b> 1·9	
,,	39	 12.3	
,,	39	 11.7	
.,		 12.2	
·3291	gram gave	 60 <sup>.</sup> 76 c.c.	-122.7

The mean of 18 experiments gave 18.22 per cent. of nitrogen, theory requiring 37.3.

Several samples of hypochlorites were tried, prepared in various ways; also urea from different sources, and all gave the same result.

Afterwards I tried the effect of using an alkaline carbonate in place of caustic alkali, and in this case nearly the whole of the nitrogen was evolved.

Thus with the same sample of hypochlorite,  $\cdot 10303$  gram urea gave  $35\cdot3$  c.c. N., when only sodium carbonate was present, but  $19\cdot02$  in the presence of caustic soda. (Theory =  $38\cdot4$ .) This difference probably accounts for the inconsistent results obtained by many authors.

My object was then to find out what becomes of the remaining half of the nitrogen, when caustic alkali is present. It is evident that it cannot remain as urea, for on adding a large excess of either a hypobromite or hypochlorite to the residue, no further evolution of gas takes place. For the same reason it cannot remain as an ammonia salt, hypochlorites and hypobromites evolving approximately the whole of the nitrogen from these. Moreover, the residue gives no reaction with Nessler's solution; but if, after reducing the excess of hypochlorite with sulphurous acid, the solution be acidified with dilute hydrochloric acid, and again rendered alkaline, an abundant reaction is obtained with Nessler's test, and the liquid, if treated with a hypochlorite or hypobromite, gives the remaining half of the nitrogen.

Thus 10999 gram urea gave 19.89 c.c. and 19.7 c.c. respectively, in two experiments with hypochlorite. After reducing, acidifying, evaporating to a small bulk, and rendering alkaline with NaHO, the first gave 19.41 c.c. N, with NaClO, and the second 19.29 c.c. with NaBrO. From these results I concluded that the second half of the nitrogen remains as a cyanate, the reaction of a hypochlorite on urea in presence of caustic alkali, being—

## $2N_2H_4CO + 3NaClO + 2NaHO = 2NaCNO + N_2 + 3NaCl + 5H_2O.$

In order further to confirm the presence of cyanate in the residue, I reduced with sulphurous acid, as before, carefully neutralised with dilute nitric acid, and added excess of silver nitrate. The precipitate so obtained was digested with dilute hydrochloric acid, and this acid solution gave abundant evidence of ammonia with all tests, whereas only traces could be found in the silver nitrate filtrate when treated in the same way.

Cupric nitrate likewise gave a greenish precipitate in the neutral solution after reduction with ferrous sulphate and filtering. It will be seen in the above equation, that no carbon dioxide is formed in this reaction. This was confirmed by acting on urea with a clear solution of calcium hypochlorite, containing excess of lime-water. Half the nitrogen was evolved as usual, and no precipitation took place. If, however, a nearly neutral solution of calcium hypochlorite be used, the solution at first remains clear; but on standing for some time, a further evolution of nitrogen and gradual separation of calcic carbonate take place.

A solution of pure potassium cyanate evolved no trace of gas with either hypochlorite or hypobromite, in presence of a caustic alkali.

This reaction may, perhaps, help to throw light on the constitution of urea; and also, it affords an easy method of detecting and approximately estimating urea in presence of ammonia salts.

For detection, it is only necessary to treat with a hypochlorite and caustic alkali, until all action had ceased, and then test for cyanate as above. For quantitative estimation, the solution is divided into two equal parts, one treated with hypochlorite and caustic alkali, and the other with hypobromite, and the evolved nitrogen measured.

There appears to be a mean loss of about  $2\frac{1}{2}$  per cent. of the evolved nitrogen in all hypochlorite reactions, whether from urea or ammonia salts, and of about 8 per cent. in hypobromite reactions, in ordinary forms of apparatus. (The greater loss with hypobromite is probably due to its far more rapid action, and consequently greater chance of spirting, Sleich having shown that by passing the evolved gas

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through more hypobromite, the loss is reduced to 1 per cent.) Thus  $\cdot 10728$  gram urea evolved 21.95 c.c. N as a mean of six experiments with NaBrO. (Theory = 24.009.)

- ·11957 gram NH<sub>4</sub>Cl gave 23·14 c.c. N with NaBrO. (Theory = 25.01.)
- '060 gram  $NH_4Cl$  gave 12.16 c.c. N with NaClO (in presence of caustic soda). (Theory = 12.54) = each as a mean of two experiments.

Thus, if A and B are the volumes of nitrogen (in cubic centimeters) obtained with hypobromite and hypochlorite respectively, and x the weight of urea (in grams)—

$$\left(\frac{\mathbf{A} \times 100}{92}\right) - \left(\frac{\mathbf{B} \times 100}{97.5}\right) = \frac{\mathbf{a} \times 373}{2}$$

In order to verify this equation, two mixtures were taken, each containing  $\cdot 05202$  gram urea, and  $\cdot 02433$  gram NH<sub>4</sub>Cl. The first treated with NaBrO gave 22.77 c.c. N, and the second with NaClO gave 15.05 c.c. N.

By the above formula this gives x = .0499.

I tried several forms of apparatus for these experiments, but wishing to perform many operations at the same time, I found the following the most simple and convenient. A small flask is fitted with an indiarubber stopper and delivery tube; the latter just dips under the surface of water in a shallow dish, and when the stopper is adjusted, is quite full of air. The solution to be examined is introduced, and the acting liquid placed in a separate tube inside the flask, as usual. This latter precaution is generally unnecessary in hypochlorite reactions, especially with urea, as the action does not begin for some time.

A graduated gas-tube is now placed over the orifice of the delivery tube, and the action commenced. The flask is shaken from time to time, due precautions being taken to keep the temperature constant from beginning to end of the operation. When the evolution has entirely ceased the delivery tube is still just full of gas, so that the volume collected is a true measure of that evolved. The delivery tube is then transferred to a tall vessel of water, and the volume read off with the usual precautions.

I intend shortly to investigate the action of hypochlorites on other nitrogenous bodies.