LVI. *The Action of Alkaline Hypobromite on Ammonium Salts, Urea, and Oxamide. Part I.*

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ABOUT two years ago I was called upon to determine the amount of urea in solutions containing other nitrogenous bodies. The hypobromite method being inapplicable in consequence of the solution of nitrogen from nitrogenous bodies other than urea which were present, I was led to study the action of alkaline hypobromite on several well-defined compounds containing nitrogen. Some of the results obtained I now beg to lay before the Society.

Action of Alkaline Hypobromite on Ammonium Salts.

When these bodies in aqueous solution are subjected to the action of the hypobromite, the mixture effervesces briskly, evolving gaseous nitrogen. Knop and Wolf (*Chem. Centralblatt*, 1860, 257) have studied this reaction. In their experiments they obtained the whole of the nitrogen in the gaseous form. They recommend the process, and describe an apparatus for the quantitative estimation of ammonium salts. Abnormal results were obtained with ammonium oxalate.

Dietrich (*Zeit. Anal. Chem.*, v, 40) states that there is a constant loss of 2.50 per cent. of nitrogen in the reaction, and he considers that this proportion of the nitrogen remains dissolved in the solution. Wagner (*ibid.*, xiii, 383) confirms Dietrich as to the percentage of loss of nitrogen. Knop (*ibid.*, ix, 226) states that there is no loss if the solution is not very weak and the nitrogen is not allowed to escape from contact with the hypobromite until the reaction is completed; if this precaution be omitted, the nitrogen will contain undecomposed ammonia, and the results will be too low.

From the ready way in which the nitrogen can be evolved, I was led to hope that Knop's process would be a good and expeditious one. With excessively strong soda-solution freshly charged with bromine, the amount of gas obtained is equal to the theoretical amount of nitrogen in the quantity of ammonium salt operated on. The mean of two experiments on 5 c.c. of a 2 per cent. solution of ammonium sulphate gave 99.7 per cent. of the total nitrogen. Such viscid solutions are objectionable on account of their tendency to envelop air on agitation which is liberated on dilution during an experiment.

The mean of four experiments with the same ammonium sulphate

solution and a slightly weaker alkaline hypobromite solution, gave 95.5 per cent. of the total nitrogen.

With an alkaline hypobromite solution of the strength recommended by Knop, the mean of four experiments gave 93.3 per cent. of the total nitrogen of the ammonium salt.

With hypobromite of Knop's strength and an apparatus for collecting the gas over the hypobromite without dilution, the mean of three experiments gave 92.8 per cent. of the total nitrogen. In these cases no increase in the volume of the gas was obtained by allowing it to remain in contact with excess of the alkaline hypobromite.

A large number of experiments have been made in this direction which lead me to conclude that, with Knop's strength of alkaline hypobromite and the ordinary forms of apparatus, there is a deficiency of about 7 per cent. of the total nitrogen of the ammonium salt.

When the solution of Knop's strength is diluted with an equal volume, or even two volumes, of water, I find that the amount of nitrogen suppressed is practically the same as when the undiluted solution is employed.

The Action of Alkaline Hypobromite on Urea.

This action has been studied by Knop, Russell and West, Dupré, and several other chemists.

When the mean solution is treated with the hypobromite, nitrogen is briskly evolved. When excessively strong soda-solution is employed, nearly the whole of the nitrogen is readily obtained as gas. The mean of two experiments gave 98.0 per cent. of the total nitrogen of the urea, no heat being applied to the vessel, and the gas being measured at the end of 15 minutes. The objection to the use of such viscid solutions has already been noticed.

When the soda-solution is of the strength recommended by Knop (10 grams in 25 c.c. of liquid), there is a deficiency of nitrogen. In their experiments on this subject, Drs. Russell and West employed Knop's strength of solution, and found, from a large number of experiments, that there was a deficiency of 8 per cent. of the total nitrogen of the urea. Their results have been confirmed by several other chemists.

The mean of three experiments with soda-solution of about the normal strength gave me 92.3 per cent. of the total nitrogen at the end of 15 minutes without the application of heat.

A large number of experiments have been made with various strengths of hypobromite solution, which show that with the stronger solutions there is a greater yield of nitrogen than with the weaker ones,

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and that with normal solutions there is a deficiency of about 8 per cent. of the total nitrogen.

Action of Alkaline Hypobromite on Oxamide.

In some unpublished experiments of Dr. Russell's, this reaction has been briefly studied. When oxamide is added to the alkaline hypobromite, decomposition at once commences, is attended with a brisk evolution of nitrogen gas. In consequence of the light and insoluble character of the oxamide, it is advisable to employ a vessel which admits of being easily agitated. If the agitation during decomposition be neglected, some time is required before the last portions of oxamide disappear. The strength of the alkaline hypobromite is a matter of some importance. When the hypobromite is of the normal strength, the decomposition progresses slowly, even on the application of heat, and at the end of some minutes there are generally small quantities of white powder still remaining, which is no doubt unaltered oxamide. When the freshly prepared normal alkaline hypobromite is diluted with about an equal volume of water and then subjected to the action of the oxamide, the mixture effervesces readily on agitation, giving off gaseous nitrogen, whilst the temperature of the vessel rises in a very marked degree. This elevation of temperature facilitates the decomposition of the oxamide, and generally results in a perfectly bright solution at the end of four or five minutes. In some cases, it is advisable to apply heat to the containing vessel in order to complete the reaction. In the presence of excess of the hypobromite no odour of ammonia can be detected.

The experiments for determining the amount of nitrogen evolved as gas, were made in the form of urea apparatus, such as has been suggested by Dupré and Apjohn. This consists of a small test-tube attached to the lower side of an indiarubber plug which accurately fits the neck of a small flask. Through the plug passes a piece of glass tubing attached to a graduated receiver for collecting and measuring the gas evolved in an experiment. The oxamide having been weighed, is placed in the test-tube, and a small quantity of water added. The freshly prepared hypobromite solution is then placed in the flask and the plug with attached tube containing the oxamide is then inserted, and the whole apparatus left for a few minutes to assume the temperature of the apartment, the level of the water in the measuring-tube being afterwards carefully adjusted. All being now ready, the flask is gently tilted and shaken alternately, so as to cause the admixture of the oxamide and hypobromite, the receiver at the same time being gradually raised so as to keep the level of the water inside and outside the measuring tube as nearly equal as possible.

When the decomposition is complete, which is known by the solution being perfectly bright, and still having a distinctly yellow colour, the whole apparatus is cooled down to the original temperature, and the increased volume of gas in the tube is determined. This number is then corrected in the ordinary way for temperature and pressure.

The following four experiments are illustrations of the experimental numbers which have been obtained :—

Oxamide taken in grams.	c.c. of gas evolved uncorrected.	Percentage of nitrogen obtained from oxamide as gas.	Percentage of total nitrogen of oxamide evolved as gas.
·245	51·00	24·3	76·0
·222	44·75	23·5	74·0
·247	52·00	24·0	75·5
·201	40·25	23·5	74·0

The mean of the four experiments gives 74·87 as the percentage of the total nitrogen which can be obtained in the gaseous form in this way. Oxamide contains 31·8 per cent. of nitrogen.

After satisfying myself of the perfectly regular yield of nitrogen under these conditions, attempts were made to ascertain the state of the suppressed nitrogen, amounting to 25 per cent. of the total quantity present in the original oxamide. The perfectly bright solution at the close of an experiment on the amount of gas evolved was then transferred to a large clean flask containing a considerable quantity of the "copper-couple," and distilled. Ammonia appeared in the condensed liquid very slowly, so that on distilling for three or four hours and collecting about 300 c.c. of distillate, not more than one quarter of the suppressed nitrogen could be accounted for. On allowing the flask and its contents to stand over night and commencing the distillation in the morning, the first portions coming over were relatively richer in ammonia than those of the previous day. Ammonia continued to come over after distilling for three or four hours on the second day of the experiment, and owing to the fracture of the flask towards the close of each of several experiments, I have not yet pushed the distillation far enough to yield me a distillate free from ammonia. However, I have recovered more than two-thirds of the suppressed nitrogen as ammonia, and I have no doubt that the whole of it can be recovered in this way.

Operating on ·223 gram of oxamide, I have obtained ·0124 of nitrogen as ammonia, the amount to be accounted for being ·0177.

The slow reduction of the nitrogen compound by the copper-couple in a boiling alkaline solution led to the belief that it existed as a

nitrate. Some of the sodium hypobromite was then treated with an insufficiency of oxamide, evaporated to dryness, fused and kept in that condition for some minutes. The fused mass was then dissolved in water and starch-solution, iodide of potassium, and tartaric acid added in excess. Under these circumstances an intense blue colour was always produced.

The soda employed in these investigations was purchased as that made from metallic sodium, but experiments made to test its purity show that it contained traces of something which yields excessively minute quantities of ammonia when boiled with the copper-couple. When converted into hypobromite, fused, and afterwards treated with starch-solution as above, the results have been generally negative, but not uniformly so. I am therefore at present unable to state the precise condition of the suppressed nitrogen. The experimental evidence is in favour of the notion that it is converted into nitrate, whilst, from general considerations of the decomposition-products of oxamide, one would rather expect to find it in the condition of cyanate. This latter view finds further support in the experiments recently made by Mr. Fenton, who has found that a portion of the nitrogen of urea is converted into cyanate, under somewhat similar circumstances.

I am not inclined to regard the evolution of three-fourths of the nitrogen of the oxamide as accidental, the result of a particular strength of alkaline hypobromite only. The results obtained would rather favour the view that all the nitrogen in the oxamide molecule is not similarly situated, and in depicting the behaviour of oxamide in this reaction, I would suggest the formula—

It is my intention to have some pure sodium hydrate prepared, and then settle the most interesting part of this inquiry—the condition of the suppressed nitrogen in the experiments described.

I also propose investigating the action of hypobromite on acetamide and other bodies.