IX.—*The Constitution of Nitrogen Iodide.*

By Oswald Silberrad, Ph.D.

Since its discovery in 1812 by Courtois, the explosive compound produced by the action of ammonia on iodine has been repeatedly investigated, with a view to establishing its chemical constitution, but many of the results given in the older chemical literature have been subsequently shown to be erroneous. The difficulties experienced by all workers in investigating the constitution of nitrogen iodide are mainly due to the extreme sensitiveness of the compound in the dry state. Originally, the compound was believed to be simply an iodide of nitrogen containing no other element. Marchand showed, however (*J. pr. Chem.*, 1840, **19**, 1), that when nitrogen iodide was detonated, ammonium iodide was one of the products, thus proving the presence of hydrogen. By combustion over heated lead chromate, he showed that the percentage of hydrogen must be very small.

Bunsen showed (*Annalen*, 1852, **84**, 1) that nitrogen iodide could be prepared from ammonia and iodine in the complete absence of water, thus proving that oxygen was not present. He also showed that the only by-product formed was hydrogen iodide, from which it follows that the reaction is one of direct substitution, and that nitrogen iodide is still a compound of the ammonia type.

The observation of Gladstone (*Chem. Gazette*, 1851, **9**, 269) that ammonia is set free in the preparation of nitrogen iodide from ammonium iodide and bleaching powder does not give any definite indication as to the formula of the compound, although Gladstone considered it an argument in favour of the formula NHI_2.

Szuhay found (*Ber.*, 1893, **26**, 1933) that when ammonia interacted

with iodine, half the iodine was converted into nitrogen iodide, the other half being found as ammonium iodide. This gives no information as to the composition of the nitrogen iodide, however, but only shows that nitrogen iodide is a direct substitution product of ammonia, that is, one molecule of hydrogen iodide (and hence of ammonium iodide) is formed for each atom of iodine which enters into combination with the nitrogen.

Thus, taking, for instance, the formula $N_2H_3I_3$, the formation of nitrogen iodide would be represented by the equation

$$5NH_3 + 3I_2 = N_2H_3I_3 + 3NH_4I.$$

Chattaway's experiments, in which nitrogen iodide was slowly decomposed by a stream of water and the residue analysed, can hardly be regarded as evidence for one formula more than another. In this connection it should be pointed out, firstly, that the ratio of 1 : 2·54 found by him is very little nearer to 1 : 3, which would favour the formation of Stahlschmidt's compound, NI_3 (*Poggendorff's Ann.*, 1862, **115**, 653), than it is to the ratio 1 : 2, which agrees with Szuhay's formula, NHI_2 (*loc. cit.*), and, secondly, that the quantity of free iodine increased so much during the progress of the decomposition (amounting to 44·8 per cent. in the example quoted by Chattaway) that it could probably only be very imperfectly allowed for by the differential method of analysis employed.

The analyses of the products obtained by different workers have led to a number of different formulæ, the following having been put forward by certain of the earlier workers :

NI_3 (Gay-Lussac, Stahlschmidt, Mallet).
NHI_2 (Bineau, Gladstone, Raschig, Szuhay, Seliwanoff).
NH_2I (Millon, Marchand).
$N_2H_3I_3$ and $N_5H_3I_{12}$ (Bunsen).
$N_5H_5I_{10}$ and $N_8H_9I_{15}$ (Guyard).

The conflicting results arrived at by different workers led to the belief that several iodides of nitrogen existed. Indeed, certain investigators found that under different conditions the composition of the products varied. Thus, Stahlschmidt (*loc. cit.*) believed that he produced from aqueous ammonia and an alcoholic solution of iodine a compound having the formula NI_3, whereas from alcoholic ammonia and iodine he obtained a product which he formulated as NHI_2. Mallet (*Chem. News*, 1879, **39**, 257) stated that the concentration of the aqueous ammonia employed influenced the composition of the final product.

Later work has shown that the varying results obtained by different workers were chiefly due to impurities present in the nitrogen iodide

owing to the unsuitable experimental conditions and to the decomposing action of light. Besides this, however, the analytical methods employed were in most instances faulty, and this added to the uncertainty of the results obtained.

The main difficulty in the determination of the composition of nitrogen iodide is due to the fact that the dry substance can only be handled with extreme caution. For this reason, direct analyses with weighed quantities of the dry compound have only recently been carried out. In all the earlier investigations, unknown quantities were treated in various ways, and conclusions were drawn from the ratios between the quantities of the different products. The reagents mainly employed for the decomposition were hydrogen sulphide and sulphurous acid.

Thus Bineau (*Compt. rend.*, 1844, **19**, 764) and, later, Gladstone (*loc. cit.*) used hydrogen sulphide and determined the relative quantities of hydriodic acid and ammonia formed. Bunsen (*Annalen*, 1852, **84**, 1) decomposed the compound with hydrochloric acid and estimated the relative amounts of ammonia and hydriodic acid produced. Mallet (*loc. cit.*) used a solution of sodium sulphite and estimated the nitrogen as ammonia and the iodine as silver iodide. Szuhay (*Ber.*, 1893, **26**, 1933) used free sulphurous acid of known strength and determined the iodine and ammonia. The above methods are, however, all open to objection, since the reduction to ammonia never takes place quantitatively, a certain amount of free nitrogen being always liberated, as was shown by Chattaway (*Amer. Chem. J.*, 1900, **24**, 138). The most satisfactory method is that adopted by this investigator (*loc. cit.*), in which the nitrogen iodide is treated in the dark with standard sodium sulphite; the excess of sulphite is then titrated with standard iodine solution, and the ammonia is subsequently distilled, after the addition of alkali.

In some experiments, Chattaway used weighed quantities of the dry nitrogen iodide, thus gaining an additional check on the results obtained. By means of a series of analyses carried out on products prepared by different methods, Chattaway showed that the same compound was obtained in every instance (*Amer. Chem. J.*, 1900, **23**, 363, 369; 1901, **24**, 138, 159, 318, 331, 342). He found the composition to agree in all cases with the formula originally assigned by Bunsen, namely, $N_2H_3I_3$, and ascertained further that the iodide is a definite chemical compound, neither iodine nor hydriodic acid being present in loose molecular combination, as in periodides or acid iodides. Each atom of iodine was shown to be univalent and directly linked to nitrogen.

Hugot has shown (*Compt. rend.*, 1900, **130**, 505) that at low temperatures compounds exist having the formulæ $N_3H_6I_3$ and $N_4H_9I_3$.

These are, however, only capable of existence in presence of excess of ammonia at very low temperatures, and dissociate very readily, regenerating ammonia and the compound $N_2H_3I_3$. This compound is thus the only one which need be considered at the ordinary temperature.

Although the empirical formula has been thus established, no investigations have hitherto given any insight into the constitution of nitrogen iodide. Evidence as to the structure of the nitrogen iodide molecule can evidently only be obtained by a study of its derivatives. The conclusions drawn from the metallic derivatives have hitherto been rather misleading than otherwise. The compound formulated by Guyard (*Compt. rend.*, 1884, **97**, 526) as $CuI_2,2NH_2I$ cannot be regarded as evidence in favour of the formula NH_2I for nitrogen iodide, for the number of hydrogen atoms in the molecule is difficult to determine by analysis. Thus, whereas the above compound would theoretically contain 0·66 per cent. of hydrogen, a compound having the formula $Cu_2I_2,2NH_3NI_3$ would contain 0·50 per cent., so that no reliable deductions could be made from Guyard's analyses as to the constitution of the compound (compare the following paper).

Szuhay (*Ber.*, 1893, **26**, 1933) obtained a silver derivative of nitrogen iodide, to which he ascribed the formula $AgNI_2$. This appears to render the formula NHI_2 probable for nitrogen iodide. In the following paper, however, the pure compound is shown to be a direct silver derivative of $N_2H_3I_3$.

The reactions of nitrogen iodide with organic compounds have as yet been very little studied. The experiments of Stahlschmidt (*Poggendorff's Ann.*, 1863, **119**, 421) should be noticed, although the conclusions drawn by him from the results were erroneous. By the action of methyl iodide on nitrogen iodide, he obtained the following products: nitrogen, hydriodic acid, ammonium iodide, tetramethylammonium pentaiodide, iodoform, iodine, and, further, a small quantity of an insoluble compound which was not further investigated. From the mother liquor, on addition of caustic potash, he obtained ammonia and di-iodomethylamine.

In view of the conflicting evidence as to the constitution of nitrogen iodide obtained by different authors, the preparation of direct substitution products, which should leave no doubt as to the constitution of this compound, was desirable. The problem has now been definitely solved by a study of the interaction of zinc ethyl and nitrogen iodide. In this way, the formula $NH_3{\cdot}NI_3$ has been established.

Before carrying out this work, the question of the applicability of magnesium alkyl iodides was also considered, as their use would probably be experimentally easier; but since the complete exclusion of alkyl iodides is of great importance, their application was regarded as

unsatisfactory. For the magnesium alkyl iodides may contain traces of alkyl iodide, or may possibly themselves act in an analogous manner to alkyl iodides, which would greatly complicate the reaction. By using zinc ethyl, which could be obtained completely free from iodine compounds, on the other hand, this objection was satisfactorily overcome.

It was established by Chattaway's work that the empirical formula of the compound was $N_2H_3I_3$. From this it is seen that only two different constitutional formulæ are probable, namely, $NH_2I{:}NHI_2$ and $NH_3{:}NI_3$. These two compounds may be assumed to react with zinc ethyl in the manner represented by the equations:

I. $2NH_2I{:}NHI_2 + 6Zn(C_2H_5)_2 = 6Zn(C_2H_5)I + 2C_2H_5{\cdot}NH_2 + 2NH(C_2H_5)_2$.

II. $2NH_3NI_3 + 6Zn(C_2H_5)_2 = 6Zn(C_2H_5)I + 2NH_3 + 2N(C_2H_5)_3$.

The latter of these equations was proved to be correct by the identification of ammonia and triethylamine as the products of the reaction.

Experimental.

Preparation of Nitrogen Iodide.—The nitrogen iodide required for this investigation was prepared by allowing iodine chloride to act on aqueous ammonia (compare Bloxam's Chemistry, 4th edition, 1880, p. 180, and also Chattaway and Orton, *J. Amer. Chem. Soc.*, 1900, **23**, 363).

Action of Zinc Ethyl on Nitrogen Iodide.—In the first place, it was necessary to find a solvent for zinc ethyl which would not interact in any way with nitrogen iodide, and preliminary experiments showed that ether was the best suited to the purpose, whilst from the following results it will be seen that the pure solvent is entirely without action on nitrogen iodide. In each experiment, 100 c.c. of ether were used and allowed to remain at 0° for various periods, after which the nitrogen iodide was filtered off and the uncombined iodine in solution shaken out with excess of $N/10$ sodium thiosulphate and estimated. The combined iodine was then estimated by boiling the ether for 24 hours with finely granulated sodium, dissolving the latter in water, and determining the iodine with silver nitrate.

Time during which nitrogen iodide and ether were left together.	Unchanged nitrogen iodide removed (titrated in filtered residue).	Free iodine.	Combined iodine.
(*a*) With methylated ether (sp. gr. 0·720) which had been left for three weeks over ground caustic soda and subsequently distilled.			
1 hour	1·358 grams	0·118	0·0013
4 hours	1·570 ,,	0·135	0·0015
48 ,,	1·326 ,,	0·446	0·0055
(*b*) With the above ether further purified by boiling for twenty-four hours with finely granulated sodium (this ether was used in Experiments 1—4 described below).			
24 hours	5 grams	Not estimated.	Less than 0·0003
(*c*) With ether purified as described below and used in Experiment 5.			
48 hours	5 grams	—	No coloration with starch solution.

On repeating this first series of experiments and allowing the ether to evaporate spontaneously, iodoform was readily detected by its odour; from this it would appear probable that the reaction observed with less carefully purified ether is due to traces of alcohol. Indeed, the reaction appears to lend itself to the detection of very minute traces of alcohol in ether. A suitable diluent having been thus obtained, it became necessary to ascertain the nature of the reaction. To this end, a series of preliminary experiments was carried out with very small quantities of nitrogen iodide, which established the following points:

(*a*) That it is impracticable to work with dry nitrogen iodide in any quantity, as explosions cannot be avoided; it was therefore used under ether.

(*b*) That ammonia is among the products.

(*c*) That the reaction proceeds quietly and slowly, and that even a slight evolution of heat was noticeable only during the addition of the first portion of zinc ethyl.

The following experiments were then carried out, the work being always conducted in red light:

Expt. 1.—Eleven grams of nitrogen iodide (prepared from 100 c.c. of a 14 per cent. solution of iodine chloride) were thoroughly washed by decantation, first with dilute ammonia, then ten times with absolute alcohol, until the latter gave no coloration with anhydrous copper sulphate, and after that as many times with absolute ether which had been prepared by leaving methylated ether (sp. gr. 0·720) over ground caustic soda for three weeks and then boiling for 24 hours with finely granulated sodium. A fresh quantity of absolute ether (50 c.c.) was run in, and then 14 grams of zinc ethyl dissolved in

25 c.c. of ether were introduced. The whole was then left for 48 hours in the dark, after which the mixture was worked up in the manner described below.

On distilling into water the product obtained by the action of the bases on ethyl oxalate, the latter became strongly alkaline. Since ammonia, mono- and di-ethylamines all react with ethyl oxalate, it appeared probable that this base was triethylamine. The quantity, however, was too small to establish its identity.

Expt. 2.—A duplicate experiment was therefore made with 120 grams of nitrogen iodide, and on this occasion the reaction was accompanied by a distinct effervescence, the product showing signs of clogging together, so that it was found necessary to leave the mixture for four days before it could be worked up with safety. On doing so, however, a distinct quantity of the alkaline distillate, which failed to react with ethyl oxalate, was obtained. This was concentrated with excess of hydrochloric acid and treated with a drop of very concentrated platinic chloride solution, when a readily soluble platinichloride was obtained.

0·01677 gave 0·00561 Pt. Pt = 33·45.

$[NH(C_2H_5)_3]_2PtCl_6$ requires Pt = 31·84.

$[NH_2(C_2H_5)_2]_2PtCl_6$ requires Pt = 35·06 per cent.

The quantity was, however, so small that the analytical results were not of sufficient accuracy to be regarded as establishing the nature of the compound.

Expt. 3.—The foregoing experiment was repeated, but in this case the flask was fitted with stirring gear. Unfortunately, the stirrer slipped before many c.c. of the zinc ethyl solution had been added, and, falling on some unchanged nitrogen iodide, caused a violent explosion and considerable conflagration.

Expt. 4.—The experiment was accordingly repeated, and this time successfully; but on working up the product of the action of ethyl oxalate on the bases no better results were obtained.

Expt. 5.—Finally it was decided to work with 1 kilogram of nitrogen iodide, as this, judging from Experiment 2, should yield 0·14 gram of the platinichloride, which ought to be sufficient to obtain a reliable analysis.

It had been noticed throughout that a slight evolution of heat occurred during the addition of the first portions of the zinc ethyl, but as the reaction between zinc ethyl and nitrogen iodide is so slow, the evolution of heat could hardly be traced to this cause; indeed, it appeared far more likely that it was due to the presence of some impurities either in the ether or in the nitrogen iodide. It was therefore decided to exercise the utmost care in order to ensure the

highest degree of purity in both these compounds, and to this end the reaction was carried out in red light and in a refrigerator kept approximately at 0°, the following precautions being observed.

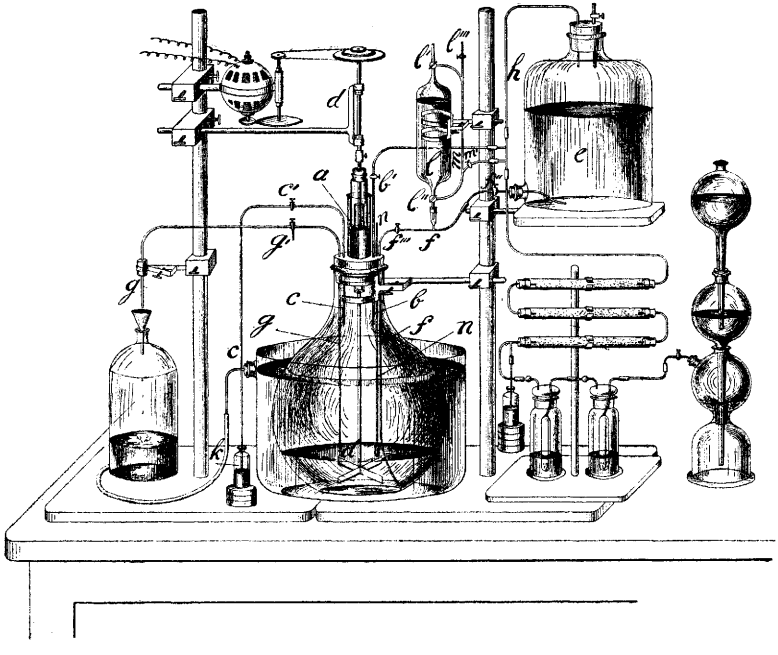
Purification of the Ether.—Two hundred grams of caustic potash, dissolved in 100 c.c. of water, were added to each of 6 "Winchester quarts," each containing 1500 c.c. of methylated ether (sp. gr. 0·720). These bottles were then agitated in a shaking machine for two days, after which the ether was poured on to 1 kilogram of finely ground caustic soda contained in a 10 litre flask immersed in a large water-bath, and the mixture boiled with a reflux condenser for 24 hours. The ether was next decanted into another 10 litre flask, treated with 50 grams of finely granulated sodium, and again boiled for 24 hours, after which it was distilled off. These last two operations were repeated until the ether ceased to tarnish the sodium on boiling for 24 hours. During distillation, the ether was collected in bottles filled with dry carbon dioxide in order to prevent absorption of moisture or auto-oxidation on evaporation.

Purification of the Nitrogen Iodide.—One kilogram of well washed nitrogen iodide was transferred to a 10 litre flask by means of absolute alcohol; it was then further washed 9 times with this solvent, until the liquid gave no coloration with anhydrous copper sulphate, and then ten times with purified ether, 1 litre being used for each washing. The ether used for the last three washings contained no combined iodine, and gave no reaction with nitrogen iodide on standing for 48 hours.

The flask containing 1 kilogram of nitrogen iodide and about 1 litre of ether was then fitted up as shown in the diagram and all the air displaced by means of dry carbon dioxide. The stirrer, *d*, was then set in motion with just sufficient rapidity to cause the nitrogen iodide lying on the bottom of the flask to change its position continuously. A slow stream of pure ether was allowed to flow in from the vessel, *e*, through the tube, *f*, and out through the tube, *g*, the pressures on the surface of the liquid in the flask and in the ether reservoir being rendered identical by means of the carbon dioxide generator, which was connected to the ether reservoir through the tube, *h*, and to the flask through *b*. The tap, *b'*, was so adjusted that a few bubbles of carbon dioxide passed, from time to time, slowly up the tube, *g*, together with the spent ether. The level of the liquid in the flask was thus kept constant. The washing with ether was continued for 4 hours, during which time about 4 litres of pure ether were passed through the flask. The spent ether, after filtration from a few grams of nitrogen iodide which had been carried over, was found to contain very minute traces of free iodine, but no combined iodine whatever.

Action of Zinc Ethyl on the Purified Nitrogen Iodide.—The tube through which the ether made its exit was then closed by means of the cock, c', $2\frac{1}{2}$ litres of pure ether were run into the flask, the displaced carbon dioxide being allowed to escape through the mercury trap, k, by means of the tube, c, the cock, c', having been previously opened for this purpose.

The flask was then surrounded with a freezing mixture, and as soon as the temperature of its contents had fallen to $-5°$ the addition of zinc ethyl was commenced. In this manner, 1300 grams of zinc ethyl dissolved in $2\frac{1}{2}$ litres of pure ether were added from the con-



tainer, l.* From time to time during the addition of the zinc ethyl, and also at subsequent stages of the experiment, samples were run off by

* The advantages of the piece of apparatus l will be obvious from the diagram; it was so constructed that ether could be forced in from the reservoir e by means of the carbon dioxide pressure on its surface, and that the whole apparatus could readily be connected with the carbon dioxide system through $m\,m'$, so that the dry gas displaced the zinc ethyl solution as it flowed through the cock l''. The cock l''' was attached in order to render it possible to refill the apparatus with zinc ethyl solution, as it was not large enough to hold the complete charge; in doing so, the charge enters through the tap l''' and l'', whilst the displaced carbon dioxide passes out through l'.

means of the three-way cork, *c'*. In every instance, even after the first addition of a few c.c. of the zinc ethyl, it was found that unaltered zinc ethyl was present in the solution.

The stirring was continued for 48 hours; during the first 24 hours, the refrigerator was kept at 0°, but subsequently was allowed to warm up to the ordinary temperature. The black nitrogen iodide slowly changed into a white, amorphous powder. The reaction proceeded quite quietly, and no evolution of heat was noticeable, indeed, the thermometers in the flask and in the cooling-bath indicated the same temperature during the whole of this period. Half a litre of ether, which had previously been shaken with water, was then added, and as this produced no effervescence it was concluded that the reaction was completed, and excess of water was accordingly added and the mixture again stirred for 24 hours. Excess of hydrochloric acid was then run in and the ether removed by distillation.

At the commencement of the distillation, a large quantity of inflammable gas passed over. A sample of this was collected over mercury, freed from ether vapour, and analysed. It was not absorbed by fuming sulphuric acid or concentrated nitric acid, and proved to be a mixture of paraffins, evidently butane and ethane.

Dry gas before explosion at 99·2° and 757 mm. = 3·2 c.c.
„ „ together with oxygen added at 99·2° and 769 mm. = 53·2 c.c.
Moist gas after explosion at 17·5° and 757 mm. = 36·8 c.c.
„ „ „ absorbing carbon dioxide with caustic potash at 17·5° and 757 mm. = 29·0 c.c.

The volumetric composition of the gas corresponds with 46 per cent. of butane and 54 per cent. of ethane.

It was foreseen that zinc ethyl would first form double zinc amides with the amines formed (except tertiary amines) with evolution of ethane (Frankland, *Jahresber.*, 1857, 418). These zinc amides hydrolyse readily, however, with hydrochloric acid to zinc chloride and the original amines. Thus the solution contained the hydrochlorides of the amines formed. From these, the bases were liberated with alkali and distilled into hydrochloric acid. The mixture of chlorides obtained on evaporation was then extracted several times with alcohol, in which all the ethylamine hydrochlorides are much more readily soluble than ammonium chloride. The least soluble fraction was recrystallised from water, after which a small portion was converted into its platinichloride and analysed.

0·1182 gave 0·0517 Pt. Pt = 43·74.
$(NH_4)_2PtCl_6$ requires Pt = 43·91 per cent.

The yield of ammonium chloride was 125 grams, or 95 per cent. of the theoretical. For the identification of the organic amines present, Hoffmann and Wallach's method of separation was adopted (*Jahresber.*, 1861, 495; *Annalen*, 1876, **184**, 33). The alcoholic extract of the hydrochlorides was evaporated, distilled with very concentrated caustic soda, and the distillate collected in absolute alcohol at 0°. A slight excess of ethyl oxalate was added and the mixture allowed to remain at a low temperature for 15 hours. On distillation from a water-bath, a strongly alkaline distillate passed over, which proved to be triethylamine.

A crystalline deposit, which formed in the distilling flask, was recrystallised from alcohol, and in this way separated into two compounds. The major portion consisted of ethyl oxamate, melting at 114°.

0·0983 gave 10·4 c.c. moist nitrogen at 16° and 753 mm. N = 12·28.
$CONH_2 \cdot CO_2 \cdot C_2H_5$ requires N = 12·0 per cent.

The second product, which was sparingly soluble in alcohol, occurred only in a very small quantity; it melted at 210—211° and probably consisted of oxamic acid. The formation of ethyl oxamate confirmed the presence of ammonia in the original product. The oxamic acid was evidently produced as a by-product of the same reaction. Derivatives of primary or secondary amines were entirely absent.

Since only the tertiary amines are unacted on by ethyl oxalate, it was to be expected that the distillate from the product obtained by the action of the amines on this ester would consist of triethylamine.

The yield was far greater than was expected, and in order to determine it the distillate was made up to 250 c.c. and an aliquot portion titrated with *N*/10 acid with the following result: 3 c.c. required 9·3 c.c. *N*/10 hydrochloric acid; the yield was therefore 7·8 grams or 3·5 per cent.

In order to establish the identity of the base, the remainder of the distillate was acidified with excess of hydrochloric acid, concentrated to a small bulk, and the hydrochloride converted into the readily soluble platinichloride.

0·3704 gave 0·11843 Pt. Pt = 31·98.
$[NH(C_2H_5)_3]_2PtCl_6$ requires Pt = 31·84 per cent.

It thus becomes evident that the reaction is greatly dependent on the experimental conditions. The fact that the success of the reaction demands the entire absence of impurities is a definite proof that the formation of triethylamine is due to the interaction of zinc ethyl on nitrogen iodide, indeed in no other manner can the entire

absence of mono- or di-ethylamine in the presence of so large an excess of ammonia be explained.

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