CIV.—*The Constitution of the so-called "Nitrogen Iodide."*

By FREDERICK D. CHATTAWAY, M.A., Christ Church, Oxford.

FROM the beginning of the present century, the black explosive compound, formed when a solution of ammonia acts on iodine, has almost continuously engaged the attention of chemists. No definite conclusion, however, as to its constitution has been arrived at, although from time to time different formulæ have been assigned to it; whilst on account of its apparently variable composition several distinct compounds have been assumed to exist.

The so-called iodide of nitrogen was first prepared by Bernard Courtois,* the discoverer of iodine. It was almost the first derivative of iodine made, and was described in the paper announcing the discovery of the element, read before the Institute, on November 29th, 1813.

Courtois being too much occupied, as a chemical manufacturer, to take up the systematic investigation of iodine, this was undertaken by Gay Lussac, and in his laboratory and under his direction nitrogen iodide was first studied by Colin. Colin, adopting Gay Lussac's views, regarded it as a substitution derivative of ammonia of the formula NI_3 , and Gay Lussac himself, in his great memoir on iodine, explains its formation on the assumption that it has this formula. The compound, about this time, was also investigated by Vauquelin and Davy, and their conclusions agree with that of

* References to the bibliography of the subject are collected at the end of the paper.

Gay Lussac. They both regard it as analogous to nitrogen chloride, that is, as ammonia in which all the hydrogen has been replaced by iodine. Mitscherlich, later, was led to assign to it the formula NI from the observation that it and ammonium chloride were produced by the action of iodine trichloride on ammonia.

Serullas, who next studied it, concerned himself mainly with some of its reactions, and expressed no opinion as to its constitution. Soon after this, Millon, who observed that hydrochloric acid added to an excess of nitrogen iodide was neutralised, and Marchand who showed that the dry compound, on explosion, yielded small quantities of ammonium iodide, came independently to the conclusion that it must contain hydrogen, and agree in considering the formula, NH_2I , as the most probable.

Bineau, however, showed that this must be incorrect and that the formula should rather be NHI_2 , since in the compound the nitrogen and iodine were present in the ratio of one atom of nitrogen to two of iodine. He did this by decomposing the compound with hydrogen sulphide, and noting that two molecules of hydriodic acid were formed to one of ammonia. He also decomposed it by ammonium sulphite, and found the same ratio.

Gladstone, some years afterwards, repeated Bineau's observations, using, however, sulphurous acid in place of ammonium sulphite, and confirmed his results.

Bunsen, about the same time, investigated the substance, adopting a slightly different method of analysis. He definitely states that nothing but iodide of nitrogen and ammonium iodide is formed in the action between ammonia and iodine, and that consequently nitrogen iodide must be a substitution derivative. From this and the result of his analyses, he concludes that the black substance has the formula NH_3NI_3 , and that it is composed of a molecule of ammonia with the whole of its hydrogen replaced by iodine, united with a molecule of unsubstituted ammonia. Bunsen, however, found that the composition varied with the mode of preparation, and believed that several allied substances of different compositions existed.

Gladstone thereupon repeated his analyses, and still found one molecule of ammonia to two atoms of iodine among the decomposition products of the substance.

Schönbein, in a very interesting study of the reaction between ammonia solution and iodine, showed that Bunsen's statement was incorrect, and that ammonium hypoiodite as well as ammonium iodide was formed in the reaction, and suggested that the formation of the black iodide depended on this.

All the researches of this period, though differing in certain

points, agree in regarding hydrogen as a constituent of the compound.

A little later, Stahlschmidt, from the results of a few analyses, revived the statement that under certain circumstances the simple triiodide NI_3 could be formed, but he also obtained another product containing less iodine.

After some years, Mallet took up the investigation. He analysed products prepared in various ways from iodine and ammonia, and also found that the composition varied with differences in the mode of preparation. From his own and other previous analyses, he concluded that a series of compounds existed, each containing two pentad nitrogen atoms doubly linked together, that they were in fact substitution derivatives of a hypothetical substance, $\text{H}_3\text{N}:\text{NH}_3$, with the hydrogen more or less replaced by iodine in one or both —NH_3 groups.

The substance has more recently been studied by Guyard, Raschig, Szuhay, and Seliwanoff. But few new facts have been brought forward by these observers, although all agree in assuming the existence of a series of compounds; they agree also in regarding all these as substitution products of ammonia, the last-named considering them to be amides of hypoiodous acid.

Nitrogen iodide having always been looked on as a substitution product of ammonia, it seemed probable that a synthesis of hydrazine derivatives might be effected by its agency, and a series of experiments was made with that object. These experiments, giving in every case a negative result, threw some doubt on the usually accepted views as to its constitution, and led to the present research.

It is very remarkable that almost all conclusions as to the constitution of this substance have been drawn from the ratio between the amounts of ammonia and of iodine that could be obtained from it, scarcely any attempt having been made to deduce its constitution from its reactions.

The author therefore undertook the re-examination of the substance, and has especially studied the various reactions in which it takes part.

Owing to the extremely unstable nature of nitrogen iodide, it cannot be obtained dry in a condition suitable for analysis, and on that account and from the fact that it is not crystallisable, no criterion of its purity or constancy of composition is available. When dry, it can hardly be manipulated at all, exploding violently as it does at the slightest touch, and even when moist, it is very unstable. In certain conditions, it explodes violently on friction under water, and when wet and in the state of a thin pulp, the impact of a jet of water from a wash bottle is frequently sufficient to cause it to

detonate. As a consequence, all experiments with the substance have to be conducted on an unknown quantity and in presence of water, which frequently introduces complications.

Nitrogen iodide, to use the name by which it has long been known, is best prepared by pouring a concentrated solution of iodine in potassium iodide into a strong solution of ammonia; the substance is then precipitated as a soft, black powder, which is best washed first with a weak solution of ammonia, and finally rapidly with very cold water until the filtrate is no longer alkaline. These operations should be conducted entirely in the dark.

Alcoholic solutions of iodine or ammonia should be avoided altogether, as alcohol rapidly decomposes the compound, forming iodoform, which is not easy to remove. The method of digesting finely powdered iodine with strong ammonia is also not a very suitable one, for the iodine being in particles of some size is not only slowly acted on, and iodine superficially coated thus with the iodide is difficult to remove, but the product being more compact is very liable to explode on being touched. Any method, however, may be used and will give the same substance, provided sufficient precautions are taken to remove iodoform or any ammonia or iodine that may be in excess.

As the substance cannot be weighed, only the ratio between the nitrogen and the iodine in an unknown quantity can be determined, leaving the structure of the molecule to be decided by its various reactions. Several methods of analysis have been made use of in this research, the most convenient being based upon the decomposition of the substance by a solution of sodium thiosulphate. When a solution of sodium thiosulphate acts on iodide of nitrogen suspended in water, all the iodine in the compound reacts as if it were free iodine, whilst all the nitrogen is liberated as ammonia.

To obtain exact results, the solutions must be sufficiently dilute, and the decomposition must be conducted rapidly in a dark room. The operation is best carried out as follows: A small quantity of moist iodide of nitrogen is brought into a measured quantity of a dilute solution of sodium thiosulphate more than sufficient to decompose it, and shaken till black grains have entirely disappeared. The ammonia is then titrated with standard acid, and finally the excess of thiosulphate is estimated by a standard solution of iodine. The results, if necessary, can be confirmed by distilling one part of the solution with iron alum, and sulphuric or hydrochloric acid, and another part with caustic potash, and estimating the iodine and ammonia liberated. In some cases, the compound has been decomposed by hydrogen sulphide or by sodium sulphite, and the iodine and ammonia distilled off as above and estimated volumetrically. Many

specimens of the black substance, prepared in various ways, have been analysed, and always with the same result if adequate precautions have been taken to free them completely from uncombined iodine and ammonia. The proportion between the ammonia and the iodine found is always very nearly that of one molecule of ammonia to two atoms of iodine. Practically, all previously published analyses have given this ratio, or have found the proportion of iodine to be larger than this, only one observer having obtained a less proportion of iodine. The discrepancies, however, are very probably due to imperfectly washed or partially decomposed products having been used in the analyses.

The substance retains some of the ammonia, in presence of which it is thrown down, with great persistence, and when this is removed, it is exceedingly unstable. In presence of water, it decomposes very rapidly, especially on exposure to light; even diffused light very much accelerates the decomposition. It is only when the washing is carried just to the point when the filtrate is no longer alkaline that the ratio of the nitrogen to iodine is 1 : 2. If the washing be pushed beyond this point, the compound begins at once to decompose, and this progresses continuously during the washing. When decomposition begins, the wash water becomes slightly yellow, and the compound acquires a strong odour of iodine.

If a considerable quantity of the substance be subjected to systematic washing for many hours, and if portions be removed at regular intervals and analysed, the ratio between the ammonia and iodine becomes progressively less and less, until after some days a small quantity of practically pure iodine alone remains. This appears to be a sufficient explanation of the variations of composition observed; they are probably due to a decomposition of greater or less extent having taken place during the treatment of the substance after precipitation. Obviously any composition is possible, from that yielding one molecule of ammonia and two atoms of iodine, to pure iodine. At any stage of the operation, if the iodine formed be removed, the undecomposed nitrogen iodide is found still to have its normal composition. This seems to show that only a single compound really exists in which two atoms of iodine are associated with one atom of nitrogen, and that the compounds of other compositions which have been described are really admixtures of this with iodine.

Nitrogen iodide has always been assumed to be a substitution derivative of ammonia, mainly on the ground that in its preparation from iodine and ammonia, a large amount of ammonium iodide is formed, the amount being supposed to be proportional to the amount of nitrogen iodide produced. It has been frequently stated that it is

the only other product, and equations have been given representing its formation, thus :

This fundamental statement is, however, incorrect. Ammonium iodide is not the only other product of the reaction, nor are the amounts produced dependent on the amount of nitrogen iodide thrown down, but depend on the dilution of the solutions, and on the conditions under which the precipitation is effected. When very dilute solutions of iodine and ammonia are mixed, they form a perfectly clear liquid ; no nitrogen iodide is precipitated, but ammonium iodide and ammonium hypoiodite are formed, according to the equation,

and although the hypoiodite is unstable, the iodine used can nearly all be set free again by the addition of excess of acid.

If somewhat stronger solutions are mixed, a slight precipitation of nitrogen iodide takes place, and the amount formed increases with the concentration of the solutions, up to a certain point, proportionally decreasing amounts of ammonium iodide and hypoiodite being produced. The amounts of the various products are affected, however, very noticeably by the conditions under which the solutions are brought together ; solutions which will give a copious precipitate of nitrogen iodide if the solution of iodine in potassium iodide be added to the ammonia, fail to give any turbidity when the ammonia is added to the iodine. Further, as each drop of iodine solution falls into the ammonia, an immediate local precipitation of nitrogen iodide takes place ; this, however, at first disappears on shaking, not being permanent until a certain amount of iodine has been added. These effects are due to the presence of water, potassium iodide, and ammonia, all of which are able to decompose the nitrogen iodide. The amount of hypoiodite found after the nitrogen iodide has been precipitated is seldom equivalent in amount to the ammonium iodide, as it seems to decompose some of the nitrogen iodide with liberation of nitrogen. This behaviour indicates that the compound may not be a substitution product of ammonia at all. If it were a substitution product, whatever its formula, the nitrogen iodide produced could never contain more than half the total quantity of iodine used, as the remaining half would form hydriodic acid, which would combine with the excess of ammonia present, according to the equation,

Now, even using a comparatively weak solution of iodine, for example, a decinormal solution, considerably more than half the

iodine employed can be obtained, under proper conditions, in the nitrogen iodide precipitated. The yield depends to a large extent on the iodine being dissolved in the least possible quantity of potassium iodide, and on the solution being rapidly mixed with the ammonia, and, up to a certain point, is increased by using an excess of very strong ammonia. This, again, seems to show that the black explosive compound cannot be a substitution product.

A number of other facts support this conclusion. If nitrogen iodide were a substitution derivative of ammonia, one would expect to be able by suitable reagents to replace the iodine by other groups, no such replacement, however, has ever been observed. One would expect, for example, to be able to replace the iodine by hydroxyl by the action of water or caustic alkalis, or moist oxides of silver or lead, obtaining $\text{NH}_2\cdot\text{OH}$, $\text{NH}(\text{OH})_2$, $\text{N}(\text{OH})_3$, or products formed from these by loss of water, according as one, two, or three of the hydrogen atoms were replaced. No hydroxylamine, hyponitrous acid, or nitrous acid has ever been detected among the products of such reactions, indeed, they follow an entirely different course. This seems the more convincing, because nitrogen chloride, which on many grounds must be regarded as having the formula NCl_3 , always yields nitric acid in such reactions.

Further, iodine only substitutes with extraordinary difficulty, if at all, and yet here we have an almost instantaneous substitution, and in a group into which iodine is not known otherwise to enter. For example, iodine does not substitute in the NH_2 group, either in aniline, or urea, or hydroxylamine, although all are basic.

The conclusion is again strengthened by the difference in behaviour of the two elements, chlorine and iodine, towards ammonia and ammonium compounds. Nitrogen chloride is only formed when chlorine acts on an ammonium salt; as long as free ammonia is present, nitrogen is liberated. On the other hand, iodine forms nitrogen iodide only in the presence of free ammonia, and it has no substituting action on any ammonium salt, even in presence of iodic acid.

Again, one would hardly expect ammonium iodide to be formed as one of the products of its detonation if it were a substitution product. Also, if the compound NI_3 , which has often been supposed to exist, were possible, one would expect it to be formed when a solution of potassium iodide acts on nitrogen chloride. Actually no such compound is formed, but nitrogen is evolved, and iodine liberated.

Some of the strongest arguments in favour of the view that it is not a substitution product, are found in the reactions of the compound, which do not admit of any simple explanation on the theory

of substitution. Whenever the substance is decomposed, ammonia and iodine are always liberated. According to the conditions of the reaction, these may be free, or partially combined, or they may react with the agent effecting the decomposition. This seems to show that the substance may really be formed by the direct union of ammonia and iodine, and considering the ratio found between the ammonia and iodine, that it may be iodo-ammonium iodide, NH_3I_2 .*

This view of its constitution not only agrees with its composition and modes of formation, but gives the simplest explanation possible of its entire chemical behaviour. The decomposition of the substance by water is very characteristic. If it be placed in a large quantity of water, light being excluded, it slowly disappears, forming a clear brown solution containing free iodine. If to this solution an excess of acid be added, a further quantity of iodine is liberated approximately equal in amount to that already free in the liquid.

If, however, light be admitted, the decomposition is much more rapid, and nitrogen is evolved, the rapidity of its evolution being determined by the intensity of the light; somewhat more iodine is then set free in the liquid, but on adding an acid the further amount liberated is not so great. These actions seem best explained thus. The iodo-ammonium iodide reacts slowly with water, liberating iodine, and forming ammonium iodide and ammonium hypoiodite, half the total amount of iodine present in the compound being set free.

On the addition of acid, the hydriodic and hypoiodous acids formed immediately react, liberating a second portion of iodine, equal in amount to that at first set free.

If light be admitted, some of the compound decomposes, forming ammonium iodide, setting nitrogen and iodine free.

The hypoiodite formed at first, however, really seems to oxidise some of the undecomposed compound.

* Guthrie (*J. Chem. Soc.*, 1863, **16**, 239) assigns this formula to a liquid obtained by adding finely powdered iodine to a saturated solution of some easily soluble ammonium salt, partially decomposed by about one-third of the equivalent quantity of caustic potash. Neither the mode of purification nor the analytical results, however, justify the assumption that a single pure substance is thus obtained. A similar liquefaction of iodine is noticed when the solid is added to a solution already containing free iodine and free ammonia, obtained by heating the black explosive compound with strong aqueous ammonia.

This decomposition by water may be the action by which the ammonium iodide and hypoiodite are obtained in the preparation of the compound. This is rendered probable by the rapid disappearance, on standing or shaking, of the black compound first produced when a dilute solution of iodine is added to a dilute solution of ammonia.

It also explains the decomposition of the substance by prolonged washing, and the accompanying accumulation of iodine in the residue; the ammonium iodide and hypoiodite formed can dissolve a little of the liberated iodine, and therefore the wash water is always somewhat yellow, but some of the iodine produced cannot thus be taken into solution, and consequently remains adhering to the undecomposed compound; the percentage of iodine in the residue, therefore, continually increases, and ultimately only a small quantity of practically pure iodine is left.

A solution of potassium iodide appears to decompose the black iodide very readily; this, however, is only apparent; it has no action on it other than facilitating the action of water by dissolving the iodine as it is formed, so that the decomposition is much more rapid and less water is required.

A solution of ammonia of moderate strength seems to render the compound somewhat more stable, but if the solution be very dilute, or, on the other hand, if a very large excess be present, the decomposition is still rapid, the liberated iodine forming with the ammonium hydrate, ammonium hypoiodite, and ammonium iodide.

The hydrates of sodium and potassium very rapidly decompose the compound, liberating ammonia and forming iodide and hypoiodite, or, if the solution be heated, iodide and iodate.

The oxides of lead and silver in presence of water similarly decompose the substance on standing or warming, setting ammonia free, and forming iodide and iodate of the metal.

Finely divided metals, such as silver, copper, or zinc, suspended together with the compound in water, assist the action of the water by combining with the liberated iodine, a further action sometimes taking place between the ammonium hypoiodite and the iodide of the metal.

The action of acids, generally speaking, appears to be to decompose the compound, setting the iodine free and combining with the ammonia; thus, sulphuric acid and hydriodic acid liberate iodine, and form ammonium sulphate and ammonium iodide.

The action of hydrochloric acid is, however, peculiar; the sub-

stance dissolves, giving a pale yellow solution, which appears to contain only ammonium iodide and iodine chloride; no iodine is set free at first, although, on standing, the colour of the solution deepens, and the free element makes its appearance. If excess of potassium iodide be added, iodine is at once set free. It appears at first sight unlikely that iodine chloride and ammonium iodide should exist together in solution; it may, however, be that a combination with the iodine of the ammonium iodide really takes place, and that we have in solution a compound, $\text{NH}_4\text{I} < \overset{\text{I}}{\text{Cl}}$, similar to that formed by chlorine with iodobenzene, $\text{C}_6\text{H}_5\text{I} < \overset{\text{Cl}}{\text{I}}$. This is not, however, absolutely necessary, for in the course of the research many instances have been met with of uncombined substances existing together in solution which are able to react at once if an excess of one or the other is present. Thus, iodine can exist under certain circumstances in presence of a very large excess of ammonia, and it can also exist as iodine in the presence of a very considerable excess of caustic soda or potash.

The black explosive compound is at once acted on by all substances capable of reacting with iodine, for instance, when hydrogen sulphide is passed through water containing it in suspension, it is rapidly decomposed, sulphur being deposited, and the solution becoming strongly acid, whilst ammonium iodide and hydriodic acid are formed.

Sulphurous acid and sulphites also readily decompose it, a sulphate and an iodide or hydriodic acid being formed. In all decompositions, however, which take place in presence of an acid, or in which an acid is formed, a further and more complicated action appears also to take place.

Sodium thiosulphate very readily reacts with the compound, liberating ammonia, and forming sodium iodide and sodium tetrathionate. This reaction under proper conditions affords a ready method of analysis.

If the compound be suspended in water containing arsenites in solution, they are oxidised to arsenates, hydriodic acid and ammonia being formed. Alkaline solutions of antimony trioxide also decompose the compound, antimony pentoxide and hydriodic acid being formed.

Potassium cyanide in solution also at once decomposes the substance, ammonia being liberated, and potassium iodide and cyanogen iodide formed.

It is very necessary to note that most of these reactions are not quantitative. The substance is so very unstable that results which differ considerably are obtained when working under apparently

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similar conditions. Some approach near to the equations required by the formula NH_3I_2 ; others, again, agree better with the assumption that the compound is a substitution derivative. If that were the case, however, the reactions would not be so simple, and water would have to be assumed to take part in every reaction. Certain facts, too, seem to show that this introduction of water into the equations is inadmissible. For example, if water be assumed to take part in the reaction with sodium thiosulphate, it must be expressed thus:

This would explain the decomposition of the substance and the production of ammonia, sodium iodide, and sodium tetrathionate. But in this case the solution would be alkaline after distilling off the ammonia, whilst actually it is always found to be neutral or slightly acid, and the amount of alkali indicated by direct titration is obtained as ammonia on distillation with potash. It appears more probable that the variations from theory are due to the peculiar chemical behaviour of iodine.

If the substance be regarded as an additive product, the manner of its formation with liberation of ammonia, when a solution of calcium hypochlorite acts on ammonium iodide, is clear; the calcium hypochlorite oxidises some of the hydriodic acid combined with the ammonia, liberating iodine which is able to combine with half of the ammonia present to form the explosive substance, leaving the other half free.

The action described by Willgerodt, where nitrogen iodide suspended in water is used as an agent to substitute iodine in various phenols, can also be explained. In presence of the water used, a hypoiodite is produced, which is almost certainly the active agent in the substitution. That this is so is shown by the work of Messinger and Vortmann (*Ber.*, 1889, **22**, 2314), who obtained a similar substitution in phenols by using a solution of iodine in caustic alkali. Here, again, hypoiodite is formed, and the action in both cases is probably analogous to the well known substituting action of hypochlorites.

The view brought forward as to the constitution of the explosive compound receives considerable support from the fact recently observed by Remsen and Norris (*Amer. Chem. J.*, 1896, **18**, 90), that, with iodine, trimethylamine yields an additive product, $\text{N}(\text{CH}_3)_3\text{I}_2$, which can be weighed and analysed, and which resembles the ammonia compound in many of its reactions.

On the whole, therefore, it seems that only one compound is formed by the action of ammonia on iodine, and that in this, one atom of nitrogen is associated with two atoms of iodine. Whether the simplest molecular formula that can be given to the substance must be NH_3I_2 or NHI_2 can only be finally settled by a prolonged and careful investigation of all its reactions under the most varied conditions; but at present the formula NH_3I_2 seems best to accord with the reactions of the compound as a whole, and best to group all the known facts regarding it. A further investigation of the reactions of the compound is proceeding.

Appended is a list of previous researches on the subject.

Courtois, *Ann. de Chimie*, 1813, **88**, 304; Vauquelin, *ibid.*, 1814, **90**, 239; Gay-Lussac, *ibid.*, 1814, **91**, 5; Colin, *Ann. de Chimie*, 1814, **91**, 252; Davy, *Ann. de Chimie*, **92**, 89, and *Trans. Roy. Soc.*, 1814, 86; Serullas, *Ann. Chim. Phys.*, 1825, [2], **22**, 172, and 1829, **42**, 200; Mitscherlich, *Gmelin's Chemistry*, vol. 2, 465; Andre, *Journ. Pharm.*, 1836, **22**, 137; Millon, *Ann. Chim. Phys.*, 1838, [2], **69**, 78; Marchand, *J. pr. Chem.*, 1840, **19**, 1; Bineau, *Ann. Chim. Phys.*, 1838 [2], **67**, 225, and 1845, [3], **15**, 71; Bunsen, *Annalen*, 1852, **84**, 1; Gladstone, *Chem. Soc. J.*, 1852, **4**, 34, and 1853, **7**, 51; Schönbein, *J. pr. Chem.*, 1861, **84**, 385; Stahl-schmidt, *Ann. Phys. Chem.*, 1863, **29**, 421; Champion et Pellet, *Bull. Soc. Chim.*, 1875, [2], **24**, 447; Mallet, *Amer. Chem. J.*, 1879-1880, **1**, 4; Guyard, *Compt. rend.*, 1883, **97**, 526, and *Ann. Chim. Phys.*, 1884 [6], **1**, 358; Raschig, *Annalen*, 1885, **230**, 212; Willgerodt, *J. pr. Chem.*, 1888, **145**, 446; Szuhay, *Ber.*, 1893, **26**, 1933; Seliwanow, *Ber.*, 1894, **27**, 1012.