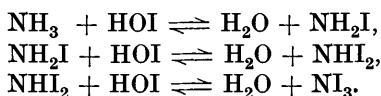# CCCLXVIII.—*Nitrogen Tri-iodide.*

By Herbert William Cremer and Donald Russell Duncan.

Ever since Courtois in 1813 obtained the black explosive compound commonly known as nitrogen iodide, the composition of this material has been a subject of controversy. It is usually prepared by the action of ammonia on iodine dissolved in a suitable solvent. In the reaction ammonium iodide is formed; consequently, solvents in which ammonium iodide is soluble have been employed, *e.g.*, water, alcohols, and aqueous potassium iodide. Nitrogen iodide is also precipitated when ammonia is added to a solution of a polyhalide such as potassium dibromoiodide ($KIBr_2$) or of a hypoiodite.

The disadvantages of these methods are (1) the difficulty of removing the solvent from the extremely unstable nitrogen iodide without decomposing the latter; (2) the fact that nitrogen iodide reacts slowly with an excess of almost any of the reagents employed, and also with the solvents; (3) the possibility, suggested by many of the investigators, that the nitrogen iodide is not formed by the direct substitution reaction $3I_2 + NH_3 = NI_3 + 3HI$ (which would not occur readily, since free iodine is not a strong iodinating agent), but generally by the iodinating action of hypoiodous acid, thus :

$$NH_3 + HOI \rightleftharpoons H_2O + NH_2I,$$
$$NH_2I + HOI \rightleftharpoons H_2O + NHI_2,$$
$$NHI_2 + HOI \rightleftharpoons H_2O + NI_3.$$

From this point of view it seems unlikely that the ammonia would be completely iodinated unless there were present a high concentration of hypoiodous acid; but the latter is unstable and not capable of existing in concentrated solution; hence the conditions appear unfavourable to the production of pure nitrogen tri-iodide of the formula NI_3.

Owing, perhaps, partly to these causes and partly to the difficulties of analysing a highly explosive compound, the published analytical figures vary considerably. Gay-Lussac and Davy assumed, from analogy with nitrogen trichloride, that the material had the formula NI_3, but analyses by later workers have led to other suggestions, such as NHI_2, NH_2I, $N_5H_5I_{10}$, $N_8H_9I_{15}$, $N_2H_3I_3$, $N_5H_3I_{12}$, N_2HI_5, and NH_3I_2. All except the last, proposed by Chattaway (J., 1896, **69**, 1572), may be regarded as ammonia in which the hydrogen has been partly replaced by iodine, or as additive compounds of nitrogen tri-iodide with ammonia. The formulæ most favoured are NH_2I and $N_2H_3I_3$. The former may be regarded as the amide of hypoiodous acid, and the latter as NI_3,NH_3. It is, however, quite possible that the investigators have not isolated pure compounds at all, and, even if they have done so, this does not preclude the possibility of preparing the compound NI_3 by more suitable methods. A full bibliography of the subject is given by Mellor (" Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1922, Vol. II, p. 611).

In the course of experiments on the preparation and properties of the polyhalides, the authors have encountered another type of reaction in which nitrogen iodide is formed, and in this case it appears that the product has the formula NI_3. The iodinating agent is iodine monobromide, the reaction being essentially $4NH_3 + 3IBr = NI_3 + 3NH_4Br$, which occurs in the vapour phase at room temperature in the absence of a solvent, the nitrogen tri-iodide being obtained as a black solid mixed with ammonium bromide.

Iodine monobromide vapour, however, is not conveniently obtained from the solid substance, since this gives off a vapour rich in bromine and leaves a solid containing an excess of iodine. On the other hand, the dibromoiodides provide a convenient method of supplying a known quantity of iodine monobromide vapour at a definite concentration. This type of polyhalide dissociates according to equations such as

$$KIBr_2 \rightleftharpoons KBr + IBr.$$
$$\text{solid} \qquad \text{solid} \quad \text{vapour}$$
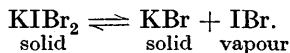
Dissociation continues until the partial pressure of iodine monobromide vapour reaches an equilibrium value, which represents the dissociation pressure of the polyhalide at the given temperature. This value varies considerably for different dibromoiodides. For example, according to determinations made by the authors and not yet published, the value for the potassium salt is approximately 1000 times greater than that for the tetramethylammonium derivative at room temperature. It is evident that, when iodine mono-

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bromide is removed in any reaction, the dissociation of the poly-halide may proceed to completion, but, during the reaction, the partial pressure of iodine monobromide vapour will not exceed the dissociation pressure of the compound.

The more stable dibromoiodides, viz., those of very low dissociation pressure, such as the tetramethylammonium and trimethyl-sulphonium salts, do not react with ammonia to form nitrogen iodide but form instead additive compounds with 2 mols. of ammonia, e.g., $(CH_3)_4NIBr_2(NH_3)_2$. This fact was discovered by Dobbin and Masson (J., 1886, **49**, 848; J. pr. Chem., 1885, **31**, 37), and has been confirmed by the authors. It is necessary to use dry ammonia, since the additive products are decomposed by water with formation of nitrogen iodide. Since, according to investigations of the authors (compare Reade, J., 1929, 853), aqueous solutions of dibromoiodides contain hypoiodous acid, it is probable that the nitrogen iodide is in this case formed at least partly by the action of hypoiodous acid on ammonia, and this method, for reasons already given, is not recommended for the preparation.

The less stable dibromoiodides, on the other hand (e.g., those of cæsium, potassium, and pyridinium), react with ammonia, even when thoroughly dried, producing nitrogen tri-iodide, ammonium bromide, and the bromide of the metal or base : $4NH_3 + 3RIBr_2 = 3RBr + NI_3 + 3NH_4Br$. If $R = C_5H_5NH$, a further reaction occurs more slowly, viz., $C_5H_5NHBr + NH_3 = C_5H_5N + NH_4Br$, so that the complete change may be written as follows :

$$7NH_3 + 3C_5H_5NHIBr_2 = 3C_5H_5N + NI_3 + 6NH_4Br.$$
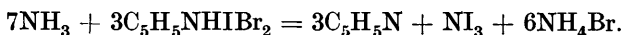
EXPERIMENTAL.

The ammonia for these experiments was prepared by heating aqueous ammonia and dried by passage through towers containing soda–lime and quicklime. The polyhalides were dried in a vacuum desiccator over phosphoric oxide for several days before use. They were weighed out into a boat which was placed in a special weighing bottle during the weighing, so that the materials were exposed to the air as little as possible. The ammonia was passed over the boat containing the materials at room temperature, the boat being weighed at intervals and the passage of ammonia being continued until the mass of the product became constant. The time required was approximately one hour.

Tetramethylammonium dibromoiodide absorbed 9·16% of its mass of ammonia [Calc. for $(CH_3)_4NIBr_2(NH_3)_2$: 9·41%], the observed increase in mass corresponding to 1·95 mols. of ammonia. The properties of this compound were as described by Dobbin and

Masson (*loc. cit.*). It was colourless, but when heated in a sealed tube it became orange and melted sharply at 149°, the same value being obtained on different samples. The original dibromoiodide melts at 190°.

In the case of the alkali dibromoiodides, on the other hand, the increase in mass corresponded to only $1\frac{1}{3}$ mols. of ammonia per mol. of salt taken. For the potassium salt, $KIBr_2$, the increase in mass was 6.96% (mean of three concordant determinations) (Calc. : 6.96%). With the cæsium salt, the gain was 5.52% (equivalent to 1.36 mols.), the theoretical gain being 5.42%. In all the experiments with the alkali derivatives, the final mass was within 0.0002 g. of the theoretical.

These data suggest that 3 mols. of dibromoiodide react with 4 mols. of ammonia, as shown in the equation on p. 2752. The products consisted of a mixture of a black explosive compound with colourless substances. In preliminary experiments, the latter, removed quickly by water, were found to consist of a mixture of potassium and ammonium bromides and to be free from all but traces of iodine in any form. Quantitative estimation of the total bromide was therefore made by titration with standard silver nitrate solution. This was found to agree as well as could be expected with theory as expressed by the above equation; the value found was 2.07 equivs. of bromide formed per mol. of dibromo-iodide taken, theory requiring 2.00 equivs. Moreover, the residue after being washed with water was found to contain nitrogen and iodine in the required atomic ratio :

	Found.	Calculated values.			
Atomic ratio, N : I ...	1 : 3·04	1 : 3	1 : 2	2 : 3	1 : 1
Ratio by mass, N : I	1 : 27·54	1 : 27·18	1 : 18·12	1 : 13·59	1 : 9·06

It may be observed that a slightly high value for the iodine is to be expected, since nitrogen iodide decomposes very slowly in contact with water, liberating iodine.

The iodine was determined by dissolving the nitrogen tri-iodide in acidified potassium iodide solution and titrating the liberated iodine by means of sodium thiosulphate solution : $NI_3 + 4HI = NH_4I + 3I_2$. The ammonia was determined in the resultant solution by the micro-Kjeldahl method.

When ammonia was passed over the pyridine derivative, $C_5H_5NHIBr_2$, the mass increased at first and then decreased until the total loss of the completed reaction was 10.0%, theory requiring a loss of 10.7%. The evolution of pyridine vapour was demonstrated experimentally.

From preliminary experiments it seems that nitrogen tri-iodide

can be sublimed in a vacuum at room temperature, the sublimate being condensed by means of liquid air.

Summary.

Nitrogen tri-iodide, NI_3, is formed when dry ammonia acts on the less stable dibromoiodides, *e.g.*, $3KIBr_2 + 4NH_3 = 3KBr + 3NH_4Br + NI_3$.

The mechanism of the reaction is probably as follows :

$$3KIBr_2 \rightleftharpoons 3KBr + 3IBr,$$
$$3IBr + NH_3 = 3HBr + NI_3,$$
$$3HBr + 3NH_3 = 3NH_4Br.$$
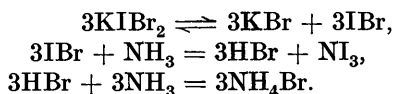
In the case of dibromoiodides of very low dissociation pressure, this reaction does not occur, and additive compounds with two molecules of ammonia are formed, *e. g.*, $(CH_3)_4NIBr_2 + 2NH_3 = (CH_3)_4NIBr_2(NH_3)_2$.