## XXVIII.—On the Iodide of lodammonium.

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Tree symbol II is employed to express isotypism ; the symbol III to denote idiotypism :* thus-

HCl III KCl III KI III NaI , \&c.
HCl II $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{Cl}$ II $\mathrm{C}_{10} \mathrm{H}_{11} \mathrm{I}$, \&c.
$\mathrm{NH}_{3}$ II $\mathrm{NH}_{2} \mathrm{C}_{2} \mathrm{H}_{3}$ II $\mathrm{NH} \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{C}_{4} \mathrm{H}_{5}$, \&c.
The explosive body produced by the action of aqueous ammonia upon iodine, sometimes called "iodide of nitrogen," has been shown by Bineau to be an ammonia, in which two equivalents of hydrogen have been replaced by two equivalents of iodine-

$$
N\left\{\begin{array}{lll}
\mathrm{H} & & \mathrm{~N} \\
\mathrm{I} & \text { III } & \mathrm{N} \\
\mathrm{I}
\end{array} \mathbf{H} \begin{array}{l}
\mathrm{H} \\
\mathrm{H}
\end{array}\right.
$$

By the action of ammonia upon an alcoholic solution of iodine, Bunsen $\ddagger$ obtained a body, to which he assigned the formula

$$
\mathrm{NH}_{3} \mathrm{NI}_{3}
$$

- Chem. Soc. Qu. J., xiii, 35.
$\dagger$ Comptes rendus, xix, 764.
$\ddagger$ Ann. Ch. Phys. Ixxxiv., 1.

This formula may be brought under the same type*-

$$
\mathbf{N}\left\{\begin{array} { l } 
{ \mathrm { H } } \\
{ \mathrm { H } }
\end{array} \left\{\begin{array} { l } 
{ \mathrm { H } } \\
{ \mathrm { I } } \\
{ \mathrm { I } } \\
{ \mathrm { I } }
\end{array} \quad \text { III } \quad \mathrm { N } \left\{\begin{array} { l } 
{ \mathrm { H } } \\
{ \mathrm { H } } \\
{ \mathrm { N } }
\end{array} \left\{\begin{array} { l } 
{ \mathrm { H } } \\
{ \mathrm { H } } \\
{ \mathrm { H } } \\
{ \mathrm { H } }
\end{array} \quad \text { II } \quad \mathrm { N } \left\{\begin{array}{l}
\mathrm{H} \\
\mathrm{H} \\
\mathrm{H}
\end{array}\right.\right.\right.\right.\right.
$$

namely, by viewing it as an ammonia, in which one equivalent of hydrogen is replaced by an ammonium, in which three equivalents of hydrogen are replaced by three equivalents of iodine.

Yet Gladstone $\dagger$ finds, that the body produced by acting with ammonia upon an alcoholic solution of iodine has the composition assigned by Bineau to his compound.

The discrepancy in the results obtained by these chemists may arise from the difference in the conditions of their experiments, having given rise to bodies in reality differently constituted.

By the action of dry ammonia upon iodine, a body is obtained, to which Millon gives the formula $\mathrm{NH}_{3} \mathrm{I}$, and to which Bineau has given the formula $3 \mathrm{NH}_{3} \cdot \mathrm{I}_{2}$. The first of these formulæ would obviously be that of iodammonium, a body to which, with perhaps the exception of nitroxine, no antitype is known; the formula of Bineau is that of iodide of iodammonammonammonium.

## Iodide of Ammonia.



* For a similar formulation of polynitrides, see Phil. Mag., September, 1857, p. 185.
$\dagger$ Chem. Soc. Qu. J. v., 34 ; vii., 51.

The conditions under which iodine and ammonia are brought together, do therefore in truth greatly modify the composition and properties of the resulting product, and may, as will be shown immediately, give rise to a product different from all those above described.

The new body has the composition$\mathrm{NH}_{3} \mathrm{I}_{2}$
being idiotypic with pentachloride of phosphorus or chloride of ammonium.

$$
\begin{aligned}
& \mathrm{P}\left\{\begin{array} { l } 
{ \mathrm { Cl } } \\
{ \mathrm { Cl } } \\
{ \mathrm { Cl } } \\
{ \mathrm { Cl } } \\
{ \mathrm { Cl } }
\end{array} \text { III } \quad \mathrm { N } \left\{\begin{array} { l } 
{ \mathrm { H } } \\
{ \mathrm { H } } \\
{ \mathrm { H } } \\
{ \mathrm { H } } \\
{ \mathrm { Cl } }
\end{array} \quad \text { III } \quad \mathrm { N } \left\{\begin{array}{l}
\mathrm{H} \\
\mathrm{H} \\
\mathrm{H} \\
\mathrm{I} \\
\mathrm{I}
\end{array}\right.\right.\right. \\
& \text { or, } \\
& P\left\{\begin{array}{l}
\mathrm{Cl} \\
\mathrm{Cl} \\
\mathrm{Cl} \\
\mathrm{Cl}
\end{array}\right\} \mathrm{Cl} \quad \text { III } \quad \mathrm{N}\left\{\begin{array}{l}
\mathrm{H} \\
\mathrm{H} \\
\mathrm{H} \\
\mathrm{H}
\end{array}\right\} \mathrm{Cl} \quad \text { III } \quad \mathrm{N}\left\{\begin{array}{l}
\mathrm{H} \\
\mathrm{H} \\
\mathrm{H} \\
\mathrm{I}
\end{array}\right\} I
\end{aligned}
$$

This body, which may be called the iodide of iodammonium, is readily formed in the following manner. A saturated solution of some very soluble salt of ammonia (the nitrate or carbonate) is treated with about $\frac{1}{3} \mathrm{rd}$ of an equivalent of hydrate of potash, so that all the potash is neutralised, and the ammoniacal salt is in excess.* To the clear solution, finely powdered iodine is added in small quantities, with constant agitation. The iodine appears to be immediately and perfectly liquified; no appreciable heat is evolved. The iodine, in uniting with the elements of ammonia, presents itself as a thoroughly mobile brownish-black liquid. The supernatant saline solution remains almost colourless. $\boldsymbol{A}$ few bubbles of gas rise from the lower liquid and drag portions of it to the surface of the upper one. The iodine is used in deficiency to ensure its complete conversion. The iodide of iodammonium is separated by a pipette from the saline solution. Its properties are briefly as follow :-

[^0]Exposed in the dry state to the air, it decomposes spontaneously into ammonia and iodine, no permanent gas being evolved. On agitating it in a eudiometer-tube with mercury, iodide of mercury is formed, and the mercury is depressed by the liberated ammonia, which latter is completely absorbed by water-

$$
\mathrm{NH}_{3} \mathrm{I}_{2}+2 \mathrm{Hg}=\mathrm{NH}_{3}+2 \mathrm{HgI} .
$$

Treated with water, it is decomposed, colours the water red-dish-brown, evolves a permanent gas, and gives rise to a residue which explodes spontaneously under water.

A few grammes of the iodide of iodammonium in a capsule being placed under water in a basin and covered with an inverted test-tube of water, a gas collects in the tube, which, after washing to remove ammonia, is found to be pure nitrogen :

$$
\begin{aligned}
2 \mathrm{NH}_{3} \mathrm{I}_{2}+\mathrm{HO} & =\mathrm{NHI}_{2}+\mathrm{NH}_{4} \mathrm{I}+\mathrm{HI}+\mathrm{HO} . \\
& =\mathrm{N}+2 \mathrm{HI}+\mathrm{I}+\mathrm{NH}_{4} \mathrm{I}+\mathrm{HO}
\end{aligned}
$$

The coloration of the water is due to the solution of the iodine in the hydriodic acid and iodide of ammonium.

The formation of the biniodammonia (iodide of nitrogen) is more rapid than its decomposition, so that some of it is left after the original compound is completely broken up.

The part which the water plays in this decomposition seems to be whoily due to its solvent power for hydriodic acid and iodide of ammonium. The water determines the formation of the things which it can dissolve, according to a well-known corollary of Berthollet's law. Doubtless, for the same reason, the decomposition of the body is stopped almost completely by the addition of saturated solutions of many neutral salts.

Comparing the decompositions wrought by water and air, it is seen that each medium effects the resolution of the compound into those constituents which most readily dissolve in the medium.

The caustic alkalies effect the same decomposition as water, but act more energetically, on account of the greater affinity of their metals for the iodine.

Acids determine the formation of ammonia-

$$
\begin{aligned}
& \mathrm{NH}_{3} \mathrm{I}_{2}+\mathrm{HCl}=\mathrm{NH}_{4} \mathrm{Cl}+\mathrm{I}_{2} \\
& \mathrm{NH}_{3} \mathrm{I}_{2}+\mathrm{HOSO}_{3}=\mathrm{NH}_{4} \mathrm{OSO}_{3}+\mathrm{I}_{2} \\
& \text { \&c. }
\end{aligned}
$$

The instantaneous recomposition of iodide of iodammonium by acids furnishes the means for its analysis.

Two or three drops of iodide of iodammonium are allowed to fall into a counterpoised flask containing dilute sulphuric acid. The increase in weight gives the amount of substance. The contents of the flask are agitated and thrown upon a filter. The separated iodine is washed with cold dilute sulphuric acid, converted, in the usual way, into iodide of potassium, and determined as iodide of silver. The sulphate of ammonium in the filtrate is converted into chloride of ammonium by the addition of chloride of barium, and the excess of barium being removed by sulphuric acid, the ammonia is determined by means of platinum.

> I.- $\cdot 7236$ grms. of substance, and II. $\cdot 6666$ grms. of substance, gave-

| Calculated. |  | I. | II. |
| :---: | :---: | :---: | :---: |
| $N=14$ | $5 \cdot 17$ | $4 \cdot 88$ | $5 \cdot 43$ |
| $\mathrm{H}_{3}=3$ | $1 \cdot 10$ | 1.04 | $1 \cdot 16$ (calc.) |
| $\mathrm{I}_{2}=254$ | $93 \cdot 73$ | $93 \cdot 47$ | 93.04 |
| 271 | $100 \cdot 00$ | 99.39 | 99.63 |

When a saturated solution of iodine dissolved in iodide of potassium, is added to the mixed solutions of caustic potash and nitrate of ammonia, a similar and probably identical liquid is formed, which separates in minute oily drops. I did not succeed in collecting these drops in a satisfactory state for analysis.

To prove, therefore, that the above analysed iodide of iodammonium is not a mixture of two or more substances, it was submitted to fractional solution in the manner described in the Journal of the Chemical Society, vol. xiv, p. 128. The solvent used was chloroform, in which the iodide of iodammonium is only slightiy soluble. Several grammes of the body having been about half dissolved in dry chloroform, $\cdot 5454$ grms. of the residue were analysed as above, and gave-

$$
\begin{aligned}
\mathrm{N} & =4 \cdot 98 \\
\mathrm{H} & =1 \cdot 07 \text { (calc.) } \\
\mathrm{I} & =91 \cdot 22 \\
& =98 \cdot 27
\end{aligned}
$$

Whence it is clear that the body is homogeneous.
The iodide of iodammonium dissolves in ether, bisulphide of carbon, alcohol, and solution of iodide of potassium.

On being heated, it is partly decomposed into iodine and an iodiferous liquid, which may be distilled without decomposition, and is most probably Millon or Bineau's "Iodide of Ammonia" formed according to one or other of the equations-

$$
\begin{aligned}
\mathrm{NH}_{3} \mathrm{I}_{2} & =\mathrm{I}+\mathrm{NH}_{3} \mathrm{I} \\
3 \mathrm{NH}_{3} \mathrm{I}_{2} & =\mathrm{I}_{4}+3 \mathrm{NH}_{3} \cdot \mathrm{I}_{2}
\end{aligned} \quad \text { (Millon) }
$$

In conclusion, it may be remarked, that we might well, a priori, have predicted the probable existence of the iodide of iodammonium. Its formation is strictly analogous to that of the halides of ammonium by the union of ammonia with hydrhalides.

$$
\begin{gathered}
N\left\{\begin{array}{l}
H \\
H \\
H
\end{array}+H I=N\left\{\begin{array}{l}
H \\
H \\
H \\
H
\end{array}\right\} I\right. \\
N\left\{\begin{array}{l}
H \\
H \\
H
\end{array}+I I=N\left\{\begin{array}{l}
I \\
H \\
H \\
H
\end{array}\right\} I\right.
\end{gathered}
$$

It may also be consistently presumed, that isotypes and idiotypes of the body may be formed, having other equivalents of hydrogen replaced by chemico-negative groups or elements.


[^0]:    * It is noteworthy, in its bearing upon Berthollet's law, that such a solution can be readily filtered through paper without affecting the latter, after the manner of even dilute caustic potash, so unequally are the bases shared, although both remain in the chemical field.

