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A Study of Nitrogen Iodide and Related Compounds
A STUDY OF NITROGEN IODIDE AND RELATED COMPOUNDS

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Mayor Farthing Fogler

ENTITLED A Study of Nitrogen Triiodide and Related Compounds

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Bachelor of Science.

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SUMMARY

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A STUDY OF NITROGEN IODIDE AND RELATED COMPOUNDS

INTRODUCTION

The object of this thesis is to determine the valence of Iodine in the compound nitrogen iodide and if possible to determine it's structure. The method followed is that of verifying former results, in part, and attempting to form similar compounds from other ammonium compounds and their related amines.
HISTORICAL SUMMARY

Nitrogen iodide has been known and studied by a number of investigators for several decades, but its exact empirical formula was not known for a certainty until F. D. Chattaway finished his investigations in 1900. He published a series of articles in the American Chemical Journal. The following is a summary of these articles.

The first publication was made in conjunction with Orton, and was entitled "The Preparation and Properties of Nitrogen Iodide." In this article the methods of preparation are discussed. It was prepared by the action of ammonia on solid iodine; by the action of ammonia and tincture of iodide; by the action of ammonia and iodine monochloride. The product, in every case a black non-crystalline substance, was explosive and decomposed under action of light very rapidly.

The next paper was a study of "The Action of Reducing Agents on Nitrogen Iodide" by Chattaway and Stevens. They found that the iodine contained in nitrogen iodide exerted twice its normal oxidizing power.

The following paper "The Composition of Nitrogen Iodide" showed the empirical formula to be $\text{N}_2\text{H_3I_3}$. Products from all sources of preparation were taken and analyzed, and a consistent ratio of 3 iodine to 2 ammonia was obtained.

In the next paper "Action of Light on Nitrogen Iodide", the composition as determined by light decomposition was given. It was found to decompose under the influence of light into hydroiodic acid and nitrogen, and to be most sensitive to the
infra red wave lengths.

Under the "Action of Alkaline Hydroxides on Nitrogen Iodide" they discuss its decomposition with the liberation of ammonia and the formation of iodide salts.

"The Action of Acids on Nitrogen Iodide" is their sixth paper, and states the way in which nitrogen iodide is decomposed by acids. It seems to be a hydrolysis with the formation of hydroiodic acid and ammonium salts.

The final paper of the series was "The Formation and Constitution of Nitrogen Iodide." This paper discusses the formation and gives probable intermediate reactions and suggests the formula:

\[
\begin{align*}
H & \quad I \\
H & \quad N \quad N \quad I \\
H & \quad I
\end{align*}
\]

as the possible structure. This structure was somewhat confirmed by a decomposition experiment they carried out, in which they permitted water to percolate slowly through nitrogen iodide. Samples of the solution from time to time for several days, and of the residual substance were analyzed. The solution was found to contain ammonia and the original substance approached the composition of HI₃. This suggests a probable splitting of the molecule at the center.
Preparation of Iodine-monochloride.

1. Iodine monochloride may be prepared by the direct union of iodine and chlorine. This is best carried out by passing chlorine gas over solid iodine in a glass tube. A heavy orange colored liquid is formed due to the presence of a small amount of moisture.

2. Iodine monochloride is best prepared by dissolving solid iodine in aqua regia. Almost equal amounts of iodine and chlorine must be present, otherwise iodine trichloride may be formed. It was found that the correct proportions to use are about as follows: 50 grams of iodine, 15 grams of hydrochloric acid, and 2 grams of nitric acid. The acids are placed in an evaporating dish, and the iodine added and heated until all is dissolved. The solution is then boiled to expell nitrosyl chloride and the excess chlorine. A beautiful orange colored liquid remains behind. This is mostly iodine monochloride.

3. Attempts were made to separate out solid iodine monochloride in the following manner. Iodine monochloride was extracted from acid solution and evaporated down, but a violent decomposition took place, with evolution of iodine. This was again tried with slow evaporation, but only iodine crystals were obtained.

Preparation of Nitrogen Iodide.

If a dilute ice cold solution of iodine monochloride is slowly poured into an ice cold solution of ammonia, a black, amorphous precipitate separates out. This precipitate is
nitrogen tri-iodide. This reaction must be carried out in the cold, and in the dark, as both heat and light cause a rapid decomposition. It must be kept in an ammonical solution, otherwise it will dry and become very explosive, or if placed in a water solution it will undergo decomposition by hydrolysis.

Analysis of Nitrogen Iodide.

The black precipitate was filtered and washed with water, and dumped into flasks containing strong sodium hydroxide, and distilled to drive over ammonia which was collected in a standard solution of hydrochloric acid. The excess acid was titrated back to determine exact amount of ammonia present in sample.

The liquor remaining in the flask was treated with ferric and ferrous sulphate, and sulphuric acid; and the iodine was driven off by heat, and collected in a solution of potassium iodide and titrated against standard sodium thiosulphate. In this way the ratio of iodine to ammonia in each sample was obtained. If iodine is taken as 3, the following results are obtained.
First Sample of Nitrogen Iodide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>cc. Normal Acid</th>
<th>cc. Normal Thiosulphate</th>
<th>Iodine</th>
<th>Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.42</td>
<td>8.16</td>
<td>3</td>
<td>1.99</td>
</tr>
<tr>
<td>2</td>
<td>4.53</td>
<td>6.82</td>
<td>3</td>
<td>2.00-</td>
</tr>
<tr>
<td>3</td>
<td>4.52</td>
<td>6.32</td>
<td>3</td>
<td>2.04</td>
</tr>
<tr>
<td>4</td>
<td>4.22</td>
<td>6.30</td>
<td>3</td>
<td>2.00-</td>
</tr>
</tbody>
</table>

Second Sample of Nitrogen Iodide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>cc. Normal Acid</th>
<th>cc. Normal Thiosulphate</th>
<th>Iodine</th>
<th>Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.12</td>
<td>3.20</td>
<td>3</td>
<td>1.99</td>
</tr>
<tr>
<td>2</td>
<td>3.86</td>
<td>5.76</td>
<td>3</td>
<td>2.00</td>
</tr>
<tr>
<td>3</td>
<td>3.30</td>
<td>4.88</td>
<td>3</td>
<td>2.01</td>
</tr>
<tr>
<td>4</td>
<td>2.52</td>
<td>3.77</td>
<td>3</td>
<td>2.00-</td>
</tr>
</tbody>
</table>

Another sample was taken, filtered, washed, and dried in a dessicator, in an atmosphere of ammonia. The dried product was weighed and analyzed for iodine.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight of Sample</th>
<th>cc. Normal Thiosulphate</th>
<th>Theoretical Wgt. of Iod.</th>
<th>Iod. by Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.4148</td>
<td>3.05</td>
<td>.3823</td>
<td>.3620</td>
</tr>
<tr>
<td>2</td>
<td>.3910</td>
<td>2.84</td>
<td>.3621</td>
<td>.3610</td>
</tr>
<tr>
<td>3</td>
<td>.5112</td>
<td>3.78</td>
<td>.4740</td>
<td>.4800</td>
</tr>
</tbody>
</table>
These results check closely enough to verify the formula as found by others as \( H_2H_3I_3 \).

The next analysis was attempted with the point in view, that it decomposes rapidly under the action of sunlight. An apparatus was set up and the nitrogen liberated was collected in a burette, but owing to the tendency of the gas to dissolve in the solution, and its lodging on the sides of the apparatus no consistent results could be obtained by this method.

**Action of Copper Ammonium Salts and Iodine Monochloride.**

Copper ammonium sulphate was dissolved in water and then ice was added. An ice solution of iodine monochloride was added, and a black brown precipitate separated out. A few qualitative tests were run with the following results. It was soluble in nitric, hydrochloric, and sulphuric acids, and iodine was liberated in each case on heating. It dissolved partially in alcohol and a brown precipitate was observed in a red solution, the iodine probably dissolved giving the red solution. It was also partially soluble in sodium hydroxide.

Some of the solid was taken and allowed to dry, iodine was given off and copper sulphate left behind. When quickly dried and rubbed, it did not explode, but free iodine was present in it. It did not decompose under the influence of light on standing in ammonia water.

A quantitative analysis was run on the precipitate, but no consistent results were obtained. This points to the fact that no definite compound was formed, but a mixture of substances was formed.
Cadmium Ammonium Salts and Iodine Monochloride.

Cadmium chloride was dissolved in ammonia water and evaporated to dryness and Cd(NH₃)₂Cl₂H₂O was formed. The compound was identified by determining the percentage of ammonia present. The results follow:

<table>
<thead>
<tr>
<th>Weight of Cd Complex</th>
<th>cc. Normal Acid</th>
<th>Wgt. of NH₃</th>
<th>% NH₃ by Weight</th>
<th>Theoretical percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8560</td>
<td>15.95</td>
<td>.2720</td>
<td>14.65</td>
<td>14.45</td>
</tr>
<tr>
<td>2.0005</td>
<td>17.25</td>
<td>.2940</td>
<td>14.70</td>
<td>14.45</td>
</tr>
</tbody>
</table>

Another product was formed by allowing cadmium chloride to dissolve in ammonia solution and skimming the crystals off the top. It's analysis follows:

Cd(NH₃)₂Cl₂·H₂O

<table>
<thead>
<tr>
<th>Weight of Cd Complex</th>
<th>cc. Normal Acid</th>
<th>Wgt. of NH₃</th>
<th>% NH₃ by Weight</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1987</td>
<td>1.64</td>
<td>.0279</td>
<td>14.1</td>
<td>2</td>
</tr>
<tr>
<td>.6118</td>
<td>5.11</td>
<td>.0870</td>
<td>14.05</td>
<td>2</td>
</tr>
</tbody>
</table>

These analyses show the cadmium compounds to be identical.

When iodine monochloride was added to a solution of this salt no precipitate appeared, on boiling CdCl₂ separated out. No compounds of the nature desired were formed from the iodine.
**Action of Phosphine and Iodine-Monochloride.**

Since phosphine and ammonia seem to be somewhat related, it was thought that it might be possible to form a compound analogous to nitrogen iodide from phosphine and iodine monochloride.

Phosphine was prepared by the action of sodium hydroxide on yellow phosphorus. The phosphine was collected over water and thoroughly washed to remove the anydride $\text{P}_2\text{H}_4$, which is spontaneously inflammable on being brought into contact with air in this pure phosphine.

This phosphine was passed through iodine monochloride, but no reaction occurred. This was then tried under pressure, but a violent explosion occurred. This was tried over ice solution and a like explosion occurred. These were due to free halogens present. In order to eliminate, an ether solution of ICl was tried under pressure, but after several weeks no reaction occurred.

**Action of Hydrazine and Iodine Monochloride.**

Hydrazine sulphate was first treated with iodine and only a slight absorption took place. It was then treated with iodine monochloride. A decomposition took place with an evolution of iodine and an apparent absorption of chlorine. Because of the difficulty encountered in preparing hydrazine, this was not attempted, and no reactions between hydrazine and iodine monochloride were obtained.

**Action of Methyl Amine and Iodine Monochloride.**

A solution of methyl amine in absolute alcohol was treated with iodine monochloride, and a red precipitate was obtained, which decomposed rather rapidly. This gave no constant results
on quantitative analysis. This was thought to be due to a probable oxidation of the alcohol present.

This was avoided by taking methyl amine hydrochloride, and recrystallizing it from absolute alcohol, in order to remove all ammonium chloride present. This pure methyl amine hydrochloride was treated with strong sodium hydroxide and distilled. The methyl amine was collected in distilled water. A product was thus obtained presumably free from ammonia.

This solution was taken and treated with iodine monochloride and a black amorphous precipitate separated out. This precipitate was found to be explosive and contained iodine and methyl amine in equal proportions.
Reactions and Their Indications.

Nitrogen iodide was first obtained by the action of ammonia on solid iodine. In this reaction one half of the iodine goes to form nitrogen iodide, and the other half to form ammonium iodide. The reaction for the formation of nitrogen iodide is thought to be as follows:

\[
\begin{align*}
I^+ & \rightarrow \text{NH}_4\text{OH} \rightarrow \text{NH}_4\text{OI} \\
I^- & \rightarrow \text{NH}_4\text{I} \rightarrow \text{HOH} \rightarrow \text{NH}_3\text{HIO} \rightarrow \text{NI}_3 \rightarrow \text{NH}_5\text{H}_3\text{I}_3
\end{align*}
\]

It is seen that the positive part of the iodine molecule goes to the \(\text{NH}_4\text{Cl}\), and the negative to the \(\text{NH}_4\text{I}\). The \(\text{NH}_4\text{Cl}\) is hydrolyzed to ammonia and hypoiodous acid. These products immediately react again to form \(\text{NI}_3\), which in the presence of an extra molecule of ammonia forms \(\text{NH}_5\text{H}_3\text{I}_3\).

The fact that this reaction goes in a similar manner with \(\text{ICl}\) in which the iodine is believed to be positive and the chlorine negative demonstrates that it is positive iodine which goes to form \(\text{NH}_5\text{H}_3\text{I}_3\). The next step of the reaction is probably true, due to the tendency of a salt of a weak base and weak acid to hydrolyze. This is also supported by the direct formation of \(\text{NH}_5\text{H}_3\text{I}_3\) from \(\text{NH}_3\) and \(\text{HCl}\). The next step is place in the reaction because of the fact, that when \(\text{NH}_5\text{H}_3\text{I}_3\) is slowly hydrolyzed, the part carried off by the water is ammonia and the part remaining behind approaches the constitution of \(\text{NI}_3\). It is therefore, only reasonable to suppose that this reaction might be reversible.

The reaction of formation alone does not point to the fact that iodine is positive in nitrogen iodide. When treated with reducing agents it exerts twice it's normal oxidizing power.
I^+ \rightarrow I^- = 2 \text{ equivalents.}

Therefore iodine must be positive.

**Probable Structure of Molecule.**

If we consider NH_3 as nitrogen with only partly satisfied valence with reference to atoms different than itself, we might write the formula as follows:

\[ \begin{array}{c}
\text{H}^+ \\
\text{H}^+ \text{–H –}_3^+
\end{array} \]

In this formula the negative valence satisfies the positive valence. How we might consider the last intermediate in the formation reaction, namely NH_3, as being similarly constructed in which the H has been replaced by the I, thus:

\[ \begin{array}{c}
\text{I}^+ \\
\text{I}^+ \text{–I –}_3^+
\end{array} \]

If these substances were brought together, they might add as follows:

\[ \begin{array}{c}
\text{H}^+ \\
\text{H}^+ \text{–I} \\
\text{I}^+ \\
\text{I}^+ \\
\text{I}
\end{array} \]

That the iodine is all held on one side is borne out by the fact that the compound splits to give ammonia and NI_3.
The empirical formula is evidently $\text{HgHgI}_3$.

Similar compounds from ammonium complex ions are not at all or difficultly formed.

The indications point to the structure given.

The iodine is undoubtedly positive.

The last experiment with methyl amine is indicative of a series of compounds from the related amines which may have a very serious bearing on the structure of nitrogen iodide, and this subject, it is hoped, will be further investigated in the near future.
<table>
<thead>
<tr>
<th></th>
<th>Author(s)</th>
<th>Journal</th>
<th>Volume</th>
<th>Page</th>
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</table>