1892

Derivatives of hydroxylamine

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Thesis by
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Derivatives of Hydroxylamine.

Hydroxylamine, when pure, is a white, odorless, needle-shaped crystal which melts at 38°. When brought in contact with the flame, it explodes, giving an intense yellow light. It is slightly soluble in chloroform, benzene, carbon disulfide, and ether. It is soluble in water, in fact, it is so deliquescent that very often the crystals become liquid when exposed to the air, even for a short time. Strong aqueous solutions can be kept formal.
ment when protected from the air and from the action of alkalies. Hydroxylamine solutions decompose with the evolution of ammonia. When concentrated, quite rapidly, but gradually, when dilute:

\[ \text{NH}_2\text{(OH)}_2 = \text{NH}_2 + \text{PH}_3 + \text{H}_2\text{O} \]

Probably the presence of water in the solution aids in the decomposition, so instead of using water as a solvent, absolute methyl alcohol can be employed. The ligand then undergoes but slight decomposition. The solution of free hydroxylamine is strongly alkaline, when distilled no residue remains, and the
distillate contains ammonium and undecomposed hydroxylammonium. It is a powerful reducing agent and precipitates silver, gold, and mercury from solutions and throws down cuprous oxide from a hot solution of cupric sulphate. Perhaps it shall be useful as an alkaline developer in photography if it can be prepared cheaply enough. Cork and cellulose are strongly attacked by it, and nitrogen and iodine act with it quite violently. Hydroxylammonium behaves very similarly to ammonium — and it is supposed that it is ammonium in which one part of hydrogen is replac-
ed by the hydroxyl group (OH).

Separation of Hydroxylamine. — The compound hydroxylamine was first discovered by Losenz in the reduction of ethyl nitrate by guic acid hydrochloric acid. Now several methods for its formation are used.

One of them is to allow nitric oxide to pass through a series of flasks containing granulated zinc and hydrochloric acid. Hydrogen will escape, and as platinum chloride is added metallic platinum will be precipitated on the tin. After the action is set up for two hours, the liquid...
is poured off and the tin is precipitated by the hydrogen sulphide, the sulphide is filtered off and the solution is evaporated. The residue is then heated with alcohol which dissolves the hydro-chlorides of hydroxylamine, leaving the sal-ammoniac undissolved. Platinum chloride is now added to free the solution from sal-ammoniac, — the precipitate is filtered off and the filtrate is evaporated to dryness. The residue, now consisting of hydrochloride of hydroxylamine (\(\text{H}_2\text{N}\cdot\text{OH}\cdot\text{Cl}\)) is treated with dilute sulphuric acid and the solution is evaporated. Paraffin water is
added to the sulphate of hydroglamine until all of the sulphate is precipitated, leaving an aqueous solution of hydroglamine.

It may also be formed when nitric acid is added to a mixture of tin and hydrochloric acid, the hydrogen produced by the action of the tin on the hydrochloric acid reducing the nitric acid.

Another method is to decompose silver nitrite and mercurous nitrite with sulphurous acid and added in moderate excess. This yields an insoluble sulphide of the metal and some nitric oxide with sulphuric acid.
After boiling away the excess of sulphurous acid, the solution will give as a test for hydroxylamine, a precipitate of cuprous oxide with an alkaline and copper sulphate. Should there be much sulphurous acid present, this test will not apply as the sulphurous acid destroys the hydroxylamine. The potassium salt of hydroxylamine dисульфо acid is formed by mixing solutions of potassium nitrite and potassium sulphite in such pro-portions that the mixture shall contain one molecule of the first to more than four molecules of the second. After thorough boiling, the whole is allowed
to cool when long light transparent crystal form. These crystal form when boiled with water, hydroxylamine potas.

$\text{CuSO}_4 \cdot \text{H}_2\text{O} + \text{H}_2\text{O} = \text{Cu(OH)}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{SO}_4$.

This salt when boiled with caustic potash decomposed into ammonia, potas.

sulfate and nitrous oxide.

$4\text{Cu(OH)}_2 \cdot \text{H}_2\text{O} + 4\text{KOH} = \frac{3}{2}\text{O} + 2\text{H}_2\text{O} + 4\text{K}_2\text{SO}_4 + 3\text{H}_2\text{O}$.

Perhaps the best results can be obtained by mixing solutions of soda.

sulphate and sodium sulphite in such proportions that the mixture shall contain one gram molecule of the first to two gram molecules of the second. This solution is then
neutralized with hydrochloric or sulphuric acid, which is added very carefully, and escape with effervescence. If other proportions of the salte are taken, much less hydroglammonium will be produced. After neutralization, the solution is thoroughly boiled and then allowed to cool and evaporate very slowly to dryness. A white residue of long-transparent crystals of sodium sulphate and hydroglammonium sulphate remains. The hydroglammonium sulphate is separated from the mixed residue by alcohol—i.e., the alcohol dissolves the hydroglammonium
sulphate leaving the residue of sodium sulphate. The solution after filtration is allowed to evaporate very slowly. Hydroxylammonium sulphate crystallizes from the alcohol in short opicular crystals quite soluble in water. When sodium metasulphite (Na$_2$SO$_3$) is added to sodium nitrite, the temperature of the mixture rises but escape of gas accompanied it. The mixture shows no presence of hydroxylamine until after boiling when it is acidified and again thoroughly boiled. In order to obtain the hydroxylamine free in solution, barium hydrate $Ba(OH)_2$ can be added to the solution of
hydroxylammonium sulphate until all of the sulphate is precipitated as barium sulphate, the aqueous solution of hydroxylammonium re-formed.

Trout, to obtain the hydroxylammonium monosulphonates pure for the preparation of salts, neutralized the hydrolyzed solution with ammonia. He then added Barium water which threw down a precipitate of a di-barium oxy-amidosulphonate. After thorough washing the salt can easily be decomposed by adding just enough sulphuric acid to combine with the barium. The filtered solution of the mixture can then be used in the
preparation of salts by combining it with corresponding bases.

Hydrophilic Compounds

Like ammonia, hydrophilic combines directly with acids to form crystallizable salts which decompose with effervescence, the nitrate yielding nitric oxide gas and water:

\[ \text{NH}_2 \text{OH} + 2 	ext{H}_2 \text{SO}_4 = 2 \text{H}_2 \text{O} + 2 \text{H}_2 \text{SO}_4 \text{NO}_3 \]

Hydrophilic derivatives containing three acid radicals can be formed by the action of benzyl chloride on the silver salt of the dihydrophilic acids. These compounds formed are insoluble in water and slightly
so in alcohols.

Hydroxyammonium chloride, \((\text{NH}_3\text{Cl})\),
can be obtained from a solution
of sodium molybdate and sodium
sulphite (one gram-molecule of the
first and two gram-molecules of the
second Saei used) which is neutralized
with hydrochloric acid. This is the
reaction which takes place:

\[ \text{Na}_2\text{WO}_4 + 2\text{NaHSO}_3 + 2\text{HCl} = \text{H}_2\text{WO}_4 \cdot \text{HCl} + 3\text{NaCl} + 2\text{Na}_2\text{SO}_4 \]

It crystallizes from a hot alcoholic
solution in large monoclinic prisms
which are quite soluble in water.

When a concentrated solution of
This salt is brought in contact with a hydrochloric solution in alcohol \( (\text{H}_3\text{O}^+)\text{HCl} \) is thrown down. Also when \( (\text{H}_3\text{O}^+)\text{HCl} \) is mixed with the normal salt large crystals of \( (\text{H}_3\text{O}^+)\text{HCl} \) are formed. The normal salt decomposes by heat with evolution of gas into nitrogen, ammonium chloride, water and hydrochloric acid.

Hydrogenaminium sulphate
\( (\text{H}_3\text{O}^+)\text{SO}_4^+ \) is formed by neutralizing the mixed solution of sodium nitrate and sodium sulphite with dilute sulphuric acid. It is separated from the residue by alcohol from which it crystallizes in the form of little
white needles.

\textit{Hydroxylammonium nitrate} \(\text{H}_3\text{ON}^+\) at ordinary temperatures is liquid which solidifies at \(-18^\circ\). It is formed by decomposing a chloride with silver nitrate. Its aqueous solution decomposed with the evolution of red vapour.

Sodium hydroxylammonium sulphamate is also liquid, rather gummy. It shows no sign of crystallization or solidification.

Potassium hydroxylammonium sulphenate crystallizes in large plates, usually six-sided, but sometimes they are square. By very rapid evaporation extremely
large crystals can be obtained. When the solution of this salt shows a tendency to supersaturate, it is difficult to crystallize it. The crystals when obtained can be kept permanently if kept dry. When heated they suddenly decompose with violence.

Barium hydroxylamido-sulphonate is formed by adding sulphuric acid to the barium salt to remove half of the barium. The crystals of this salt are very soluble. They are quite hard and in the form of small brilliant square prisms. They contain water of crystallization and readily decompose. When heated to 100° they
quickly and violently decomposed. 

Sodium hydroxylamido sulphonate is a crystalline salt having an alkaline reaction and quite insoluble in water. It dissolves readily in hydrochloric acid. It is formed from one equivalent of the acid and two equivalents of benzene. This is its formula: 

$\text{Na} \left(C\#_8\right)_2$
Experimental Work.

Hydroxylammonium aluminium sulphate, \( \text{H}_2\text{(OH)}_2\text{AlSO}_4 \), is prepared by mixing solutions of aluminium sulphate (\( \text{Al}_2\text{(SO}_4\) and hydroxylammonium sulphate (\( \text{H}_2\text{(OH)}_2\text{SO}_4 \)) in such proportions that the mixture contains one gram molecule of each.

\( \text{Al}_2\text{(SO}_4\) + \( \text{H}_2\text{(OH)}_2\text{SO}_4 = \text{H}_2\text{(OH)}_2\text{AlSO}_4 \) + \( \text{Al}_2\text{(OH)}_2\text{SO}_4 \)

After thorough boiling, the solution is transferred to a crystallizing dish and allowed to crystallize very slowly.

The crystals are large, flat, transparent and many sided.
heated they melt in their water of crystallization, lose it gradually and finally become a white, amorphous mass.

Analysis of this compound.

Determination of aluminum. A hot solution of the compound is mixed with ammonium chloride solution in excess. The mixture is then boiled until alkaline, when the precipitate has thoroughly settled it is filtered and when quite dry is ignited and weighed.

\[
\text{Height of } \text{Al}_2(\text{SO}_4)\cdot(\text{H}_2\text{O})_2 \text{ and tube} = 13.96 \text{ g}\text{.}
\]

\[
\text{tube} = 121.8164 \text{ g}
\]

\[
\text{Residue} = 1.1382 \text{ g}
\]
Weight of crucible — 11.6926 gr.
... residue and crucible ignition — 11.8163 "
... residue — 11.8163 "
... residue — .1207 "

The percent of aluminium: — the
weight of aluminium in $\text{Al}_2\text{O}_3$ is

$$ \frac{.0605}{11.1362} = .005408 $$

5.408% of aluminium

III

Height of substance and tube — 12.8164 gr.
... tube — 11.6175 "
... substance — 1.1989 "
... crucible and crucible residue ignition — 11.8309 ,
... 2" — 11.8256 ,
... 9" — 11.8212 ,
... 4" — 11.8212 "
Weight of crucible: 11.6926 g.

\[ \text{Al}_2 \text{O}_3 \] 128.6 g.

The percent of aluminium: the weight of aluminium in \[ \text{Al}_2 \text{O}_3 \] is \[ \frac{57.48}{101.96} \] of 128.6 g. - 0.0682 g - \[ \frac{0.0682}{1.1989} \] = 0.769 - 0.149% - of aluminium.

Average percent of II and III = 0.76%.

Molecular weight of: \[ \text{Al}_2(\text{SO}_4)_3 + 24 \text{H}_2\text{O} \]

= 936.5 g.

Theoretical percent of aluminium = 5.74%

Determination of hydroxylamine:
A solution of the compound is mixed with Fehling solution in excess so as to precipitate all of the copper oxide. This reaction takes
\[ \text{Al}_2(\text{ OH}_2) \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O} + 2\text{Ba}(\text{OH})_2 = \text{Al}_2(\text{OH})_3 + 2\text{BaSO}_4 + 2\text{H}_2\text{O} + 2\text{H}_2\text{SO}_4 \]

\[ (\text{CuH}_2\text{O})_2 \cdot \text{SO}_4 + 4\text{CuO} = 2\text{CuO} + 4\text{Cu}_2\text{O} + \text{SO}_2 + 4\text{H}_2\text{O} \]

The precipitate when dry is ignited very strongly. These are the results.

Height of substance and U tube: 11. 59. 79 g.
Tube: 10. 88. 68.
Substance: 7609.
Crucible residue, ignition: 11. 78. 61.
Crucible: 11. 78. 68.
Crucible: 11. 78. 68.
Residue: 11. 69. 39.
Residue: 0. 07. 19.
Molecular weight of $\text{N}_2\text{H}_4\text{O}_4$ = 108.98

$\text{Cu}_2\text{O}$ = 2.84.24

Height of $\text{Cu}_2\text{O}$ = 0.719 grams.

($0.83\text{ gr.}$) = 0.831 gr. = 100% = 2.84.24

Height of $\text{N}_2\text{H}_4\text{O}_4$ = 0.831 gr.

Hydroxyplammine = $\frac{\text{.9994 gr.}}{\text{100.76}}$ = 0.0994 gr.

$\text{KOH}$ = 0.0478 gr. = 0.93% = 6.02

6.02% of hydroxyplammine

III

Height of substance in tube = 10.8068 gr.

Tube = 9.7072

Substance = 1.1296

 Crucible = 11.6946

Reduced ignition = 10.0810

= 10.0295
Height of crucible + residue 3" ignition = 12.027 g.

" " " 4" = 12.0275 g.

" " " 5" = 12.027 g.

Height of residue = 3.252 g.

$(1.2047 g) \times 0.2382 g = 100.76$.

Height of $(26.40 g) S_4O_6 = 1.2047 g.$

" hydroxyamine $= \frac{59.94}{100.76} \times 1.2047 g.$

or $= 6.814 g.$

$\frac{6.814}{1.1276} = 6.11$.

6.11% of hydroxyamine.

Average percent of $\text{N}_{2} \text{O}_{5} = 6.066%$.

Theoretical percent of hydroxyamine = 6.43%.

Hydroxyammonium iodate. Parain hydrate, is added to a solution of hydroxyamine sulphate until all of the sulphate is precipitated as basic hydroxyamine.
um sulphate, the filtrate then contains free hydroxylamine:

\[(\text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O})_{\text{aq}} + \text{Ba(OH)}_2 = \text{K}_2\text{BaSO}_4 + \text{H}_2\text{O}\]

The solution should be kept as concentrated as possible so as to avoid loss of substance. Peric acid is added to the filtrate until it becomes neutral, after which it is allowed to crystallize:

\[(\text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}) + \text{C}_6\text{H}_2(\text{O})_3 = \text{C}_6\text{H}_2(\text{O}_2)\text{(O)}_{\text{aq}} + \text{H}_2\text{O}\]

The crystals of hydroxylamine picrate are of a beautiful golden yellow, minute and acicular. They are sob
soluble in water and slightly so in alcohol. Like many of the ferriates, they explode when heated, suddenly and violently.

Analysis:

To a solution of hydroxyamine ferriate add potassium carbonate in excess and alcohol. The hydroxyamine ferriate then decomposes:

\[ 2 \text{C}_6\text{H}_5\text{H}_2\text{O}_3\text{Fe} + 4\text{K}_2\text{CO}_3 \rightarrow 2\text{C}_6\text{H}_5\text{H}_2\text{O}_3\text{K}_2 + 4\text{H}_2\text{O} + \text{O}_2 \]

\[ 2\text{C}_6\text{H}_5\text{H}_2\text{O}_3\text{K}_2 + 4\text{H}_2\text{O} + 2\text{O}_2 \]

Height of substance and tube — — 9.0988 gr.

" tube — — 9.2062 gr.

substance — — 1871"
Height of U-socket and paper = 67 0.0 gr.

Paper = .67 10

U-socket = 1694

Molecular weight of U-socket = 288.60

Hydroammonium sulphate = 213.04

Hydroammonium = .3877 - weight f = .02 08 gr.

.02 08 = 12. 708

12. 708% of hydroammonium

III

Height of substance in tube = 9. 20 62 gr.

Tube = 8. 99 48

Substance = 2. 32 0

U-socket and paper = 11 80

Paper = 11 30

Paper = 30 21
Height of Supercal - 210.9 gr.

hydroxylamine - .0299 gr.

\[
\frac{.0299}{.2326} = 12.88 - 12.88 \text{ gr. of } \text{hydroxylamine.}
\]

Average percent - 12.26\%.

Theoretical percent - 12.61\%.

Hydroxylammonium and sulphate is obtained by mixing solutions of ferrous sulphate and hydroxylammonium sulphate in such a manner that each contains the same portions of substance. Boil thoroughly and allow to crystallize slowly. The following equation expresses the reaction which takes place:
\[ \text{Fe}_7 + 4\text{H}_2 \text{O} + (\text{H}_4\text{Fe})_2\text{SO}_4 = 2\text{H}_2\text{(OH)}_2 + 2\text{H}_2\text{O} + 6\text{Fe}_3\text{O}_4. \]

This compound crystallizes in small beautiful green regular octahedra or cubes. When subjected to heat, they behave very similarly to alum, they melt in their water of crystallization, gradually lose it and become a greyish voluminous mass.

**Analysis:**

From: When the ferrous iron, in the solution of hydroxylammonium iron sulphate has been reduced to ferrous iron, add ammonia in excess. Ferric hydrate is then precipitated as a dark red gelat.
Second sample. After thorough
washing and drying it is ignited.
Here are the results:

Weight of substance and tube - 121.0219095 g.
Tube - 10.9104 g.
Substance - 11.0091 g.
Crucible and residue fraction - 11.9858 g.
Crucible - 11.6872 g.
Residue - 2.96 g.

Molecular weight of Fe₂O₃ = 169.64.
FeO = 71.84.
There is twice as much iron in Fe₂O₃
as in FeO, hence...
\[ \text{FeO} \times 12.60 = 11.98 \]
\[ \frac{1.05}{1.05} = 11.98 \]
\[ \text{11.98 g of iron} \]

\[ \text{Height of substance and tube} = \text{10.794 g} \]
\[ \text{Tube} = 9.942 \text{ g} \]
\[ \text{Substance} = 1.211 \text{ g} \]
\[ \text{Crucible + remainder after ignition} = 12.025 \text{ g} \]
\[ \text{Crucible} = 12.039 \text{ g} \]
\[ \text{Residue} = 11.68 \text{ g} \]
\[ \text{As above} = 1.211 \text{ g} \]
\[ 3 + 14 \text{ g, 1 x 14 g} = 28.92 \text{ g} \]
\[ 169.64 : 148.68 = 1.1466 \text{ g} \]
\[ 28.92 \text{ g} = \text{FeO} \]
\[ 17.66 = 11.60 \]
\[ \text{11.60% of iron} \]
Method of Direct Ignition

Weight of substance and crucible

- crucible: 12.4983 gr.
- substance: 11.6878 gr.
- after first ignition: 11.9693 gr.
- second: 11.9664 gr.
- third: 11.9664 gr.
- residue: 0.0192 gr.

\[
\text{final weight} = \left( \frac{12.4983 - 11.9693}{12.4983} \right) \times 100 = 4.164 \%
\]

IV

Weight of substance and crucible: 12.0398 gr.
- crucible: 11.6878 gr.
- substance: 0.6604 gr.
Weight of volatile residue — ignition

1. 998882 g.

2°  "  "  "  "  "  "  "  "  "  "  "  "  11. 9471 g.

3°  "  "  "  "  "  "  "  "  "  "  "  "  11. 9471

4°  "  "  "  "  "  "  "  "  "  "  "  "  11. 9408 g.

5°  "  "  "  "  "  "  "  "  "  "  "  "  11. 9408 g.

residue  —  —  —  —  —  —  —  —  —  —  —  —  20. 86 g.

20. 86 g. (x 2/3 2180) = 169. 64 148. 68

Fe = ½ of  2180  2180  1090  gram

1090  —  16. 39 %  —  16. 39 % of iron.

Average percent of iron  16. 45%

Theoretical percent  16. 38 %

Determination of hydroxyamine. To a solution of hydroxyaminommonium and sulphate add sodium carbonate to precipitate the ion as
Ferrous sulphate

\[(\text{FeSO}_4 \cdot \text{H}_2\text{O}) + 2\text{Na}_2\text{SO}_4 + 6\text{H}_2\text{O} + \text{Cu}_2\text{O} \rightarrow \text{Fe}_2\text{O}_4 \cdot \text{H}_2\text{O} + 2\text{Na}_2\text{SO}_4 + 2\text{OH}_2\text{O} + \text{CO}_2\]

FeClig solution is then added in excess so as to precipitate all of the copper in the filtrate as cuprous oxide.

\[\text{FeCl}_{2} \cdot \text{H}_2\text{O} + \text{CuCl}_2 \rightarrow \text{Cu}_{2}\text{Cl}_2 + \text{FeCl}_2 + \text{H}_2\text{O}\]

Wash the residue thoroughly and ignite. These are the results obtained:

- Height of substance tube: 10.79
- Tube: 9.6468
- Substance: 1.167
- crucible: 11.6871
- and residue ignition: 12.1651
Height of crumbly T. residue ignition. 11.1403 gal.

0"  = 12.0750".

4"  = 12.0840".

6"  = 12.0840".

Residue = 3.860 gal.

$\text{CaO} = 3.860$ gal. Hydroxylamine = .1842 gal.

$\frac{18.42}{1.841} = 16.001$.

16.001% of hydroxylamine.

Height of substance tube. = 9.6480 gal.

T. tube = 8.9028".

Substance = 6.795".

Crumbly T. residue ignition = 11.9462 gal.

2"  = 11.9094 gal.

6"  = 11.9094 gal.

4"  = 11.7078 gal.
If \( \text{On} = 0.22069 \), hydroxylamine = 10.83% \\
\( \frac{6.82}{6.86} \) = 0.08% \\
16.08% of hydroxylamine

Average percent = 16.0405%

Theoretical percent = 16.1087%

Relation of Hydroxylamine to the nitrate. By the removal of one of the atoms of oxygen, nitric acid (\( \text{HNO}_3 \)) is converted into nitrous acid (\( \text{HNO}_2 \)). By still further reduction this acid is converted into hyponiitrous acid (\( \text{H}_2\text{NO}_2 \)), and by continued action the hyponitrous acid is converted into hydroxylamine. The reactions are represented by these equations:
\[ \text{HN}_6 + \text{H}_2 \rightarrow \text{H}_2\text{O}_6 + \text{H}_2 \text{O} \]
\[ \text{N}_2 + \text{H}_2 \rightarrow \text{H}_2\text{N}_2 + \text{H}_2 \text{O} \]
\[ \text{HN}_6 + \text{H}_2 \rightarrow 2\text{H}_2\text{N}_2(\text{OH}) \]
\[ 2\text{H}_2\text{N}_2(\text{OH}) + \text{H}_2 \rightarrow 2\text{H}_2\text{N}_3 + \text{H}_2 \text{O} \]

Hydrosyphonine behaves very differently than ammonia, towards the halogens. Hydrosyphonine, when in the liquid state, dissolves salt, and on evaporation the salt is thrown down. For example, B. Chrismen found that on heating jodochloride and hydrosyphonine, \( \text{J}_2\text{H}_2\text{OS}_2 \), the J, distilled off could be condensed in an ice receiver.
Reduction of Nitrates to Hydromagnesia

by Hydrogen Sulphide - A solution of an alkaline nitrate, saturated with hydrogen sulphide and acidified with hydrochloric acid yields sulphur nitric oxide and ammonia but no hydromagnesia.

But if silver nitrate is suspended in water and treated with hydrogen sulphide, hydromagnesia is produced together with sulphur, nitric oxide and ammonia. On adding hydrochloric acid to the filtrate and evaporating to depress a mixture of ammonium and hydromagnesinium.
chloride. If the filtrate be heated before adding the acid, the hydroxyplamime will be destroyed by the action of hydrogen sulphide. Estimates have been made of the quantity of hydroxyplamime produced after heating with hydrochloric acid. In one case 69.26 grams of silver nitrate yielded about one sixth of the nitrogen as hydroxyplamime, and in another 0.644 gram yielded about three elevenths of the nitrogen as hydroxyplamime. Mercurous nitrite, though a little more difficult to decompose, yields the same results as silver nitrite. When mercurous nitrite is heated
with nitric oxide or alkali nitrite and hydrogen sulfide, mercury nitrite is formed, and hydroxylamine only by hydrogen sulfide reducing the nitrite.

When metallic copper is brought in contact with silver nitrite in water, a thick green solution forms from which hydroxylamine can be obtained by heating with hydrogen sulfide.

The nitrites of the metals—mercury, silver and copper—are capable of being reduced to hydroxylamine. Hydrogen sulfide decomposes these nitrites in such a way as to
yield the products of the decomposition of the acid by water and additional hydrogen sulphide, the remainder acts according to this equation:

\[ \text{AgNO}_2 + 2\text{H}_2\text{S} = \text{Ag}_2\text{S} + 2\text{H}_2\text{O} \]

\[ 2\text{AgNO}_3 + 2\text{H}_2\text{S} = 2\text{H}_2\text{O} + 2\text{H}_2\text{S} + 4\text{Ag}_2\text{S} \]

Pretake of the gum-lin base convert nitric acid into ammonia but not into hydroxylamine when no other acid is present. But hydroxylamine is formed when acting in conjunction with hydrochloric acid or sulphuric acid. An alkali nitrate brought suddenly in contact with hydrochloric acid and
Jew yields a little hydroxylamine.

The Reaction of Sulphite and Nitrites when other metals than Potassium is used. When Cland worked on Freuny's series of potassium salts, he discovered that by adding potassium nitrite to potassium sulphite, a salt was formed having the composition \( \text{K}_2\text{H}_2\text{SO}_4\text{O}_3 \), which when heated in solution yielded \( \text{K}_2\text{O}\text{H}_2\text{SO}_4\text{O}_3 \) with potassium hydrogen sulphate. D. Meyers found the former salt to be hydroxylamine disulphonate and Cland found the latter to be potas-
Pretzsch found that by heating potassium hydroglamine sulphonate with water, it changed it into the acid sulphate of potassium and hydroglamine. The sulphonate can be used as a cheap source of hydroglamine.

It was extremely difficult for them to obtain sodium compounds corresponding with the potassium compound. This must be observed that when solutions of sodium sulphite and sodium nitrite are mixed, the crystals do not form as when the
Potassium salts are used. If performed very quickly, the sulphite can easily be separated from the nitrite by precipitation as barium salt. The metasulphite and nitrite are neutral when separate, but together give an alkaline reaction and absorb carbonic anhydride.

\[ 2\text{K}_2\text{SO}_3 + \text{H}_2\text{SO}_4 + 3\text{CO}_2 + 2\text{H}_2\text{O} = 2\text{K}_2\text{SO}_4 + 3\text{CO}_2 \, \text{prod.} + \text{H}_2\text{O} \]

\[ + 3\text{CO}_2 \, \text{prod.} \]

\[ + 8\text{K}_2\text{SO}_3 + 8\text{H}_2\text{O} + \text{CO}_2 = 2(\text{K}_2\text{SO}_4) + 6\text{CO}_2 \, \text{prod.} \]

The Constitution of Hyponitites is explained by the Decomposition of Hydroammonium-sulphur-sulphide.
Frey found that potassium hydroxylamine sulphamate decomposed into acids, sulphate and hydroxylamine salt. The change takes place when the solution is boiled. This is the formula:

\[ \text{S} \cdot \text{O}_1 \cdot \text{H}_4 \cdot \text{K}_2 + \text{S} \cdot \text{O}_8 \cdot \text{K}_2 \cdot \text{H}_4 \cdot \text{K}_5. \]

The decomposition of hydroxylamine monosulphhenates into sulphites and hyponitrite shows that a hyponitrite must have its oxygen between nitrogen and the metal. Some chemists admit that a few salts of this acid can not be obtained in a pure state. The molecule of the acid contains two atoms
each of its elements, the formula is then written $\text{H}_2\text{S}_2\text{O}_7\text{(SH)}$ or $(\text{H}_2\text{SH})_2$, the acid itself is hydroxymalogen, $(\text{H}_2\text{SH})$ being the radicle.

Oxidation of Hydroxylamine sulphonates by basic reagents. Oxidation of hydroxylamine sulphonate dissolved in ammonia, and salt in hydroxylamine sulphonate acid, with effervescence, oxygen being given off as a gas. The same reagent causes a brisk effervescence with a solution of potassium salt, but the escaping gas is vitriolic oxide instead of oxygen. The potassium salt
reduce salts of copper, gold, and silver. The copper must be ex-
cepted unless it is present in an alkaline solution. It has been demonstrated that potassium salt in the presence of potassium hydroxide reduces salt of copper and silver in the cold very similarly to hydroxylamine. This is the reaction which takes place: the hydroxylamine sulphamate is converted into sulphite and sulphate, the cuprous oxide is just half what it would be were hydroxylamine first formed.
$$2 \text{HNO}_3(\text{aq}) + \text{CuO} + 2\text{HNO}_3 = \text{Cu(NO}_3)_2 + \text{N}_2\text{O}_4$$

The hyponitrous acid is resolved into nitrous oxide and water. If hydrochloric acid is added after the reduction, much sulphur dioxide will be liberated. The reaction will cease to continue as soon as the solution becomes dilute. If hydroxylamine sulphamate (one gram) is added to water (one litre) with a little of a dilute solution of copper sulphate and potassium hydroxide, an opalescent blue color will be produced, but no presence of cuprous oxide.
The alkaline solution does not contain hydroxylamine, but merely a sulphonic acid which gives sulphites and reducible compounds. It is not an easy matter to measure the amount of sulphite produced because of the oxidation of the very dilute alkaline sulphites by the air and the decomposition of the hydroxygluamine sulphamate is not complete. To measure the amount of copper, it should be reduced, add a slight excess of Fehling solution, quite strong and less alkaline than usual, heat to
boiling, collect the copper oxide, cool rapidly and weigh the reduced oxide. Silver and mercury oxides behave just like cupric hydroxide and yield much sulphate, in an alkaline solution.

Decomposition of Hydroxyamine-sulphonate of Alkaline Daseel.

The hydroxyamine sulphonates undergo decomposition when treated with alkalies as with oxide. An unheated alkaline solution of hydroxyamine sulphonate acid is really a solution of free hydroxyamine, the quantity of which can be exte-
mated from the amount of acid taken. The hydroxyglamine sulphonates are hydroxyglamine derivatives which hydrolyze in acid solutions into hydroxyglamine and sulphate. In alkaline solution this is not the case, neither sulphate nor hydroxyglamine nor even the decomposition products of hydroxyglamine are present. The hydroxyglamine sulphonates decompose with potassium hydroxide into sulphate and hypomonitrite and the decomposition products of hypomonitrite. No ammonia is formed, no sulphate or nitrogen. Hydroxyglamine can not be generated, because
of the absence of ammonia. Cold dilute alkali effects a partial change. But in order to effect a complete change into sulphite and hyponitrite, the solution must be allowed to remain for some time in the cold until strong potassium hydrosulphite, or be heated for a short time with strong alkali. Decomposition of the hyponitrite occurs with effervescence. The escaping gas acts like oxygen; it is nitrous oxide. The alkaline liquid, when acidified gives off sulphur dioxide. Then neutralized with
acetic acid, the solution on treatment with silver nitrate gives silver hyp
pernitrite and reduced silver. The silver hypochlorite forms potassium
silver sulphite. This latter change can be avoided by using the
potassium salt instead of the potas
sium salt.

In preparing hypochlorite it is
not really necessary that the
hydroxyglammic sulphamate be pure.
Because of the decomposition of
much of the potassium hypochlorite
into hydronitride and nitrous oxide,
the determination of the hypochlorite
does not prove the formation of this salt is the only decomposition of the hydroglamine sulphphonate. This is the reaction:

\[ \text{HOSO}_3 + \text{SO}_3 \text{H} \rightarrow \text{KHSO}_4 + \text{H}_2 \text{SO}_4 \]

When hydroglamine monosulphphonate is evaporated to dryness on a water bath with potassium or sodium carbonate, sulphite is yielded, evolution of carbonic anhydride accompanies the reaction. However if left in the cold, the solution will show the presence of a little sulphite. And after evaporation with
potassium acetate, and alkaline mixture containing some sulphite is left.

Hydroxylamine monosulphonate decomposes in the presence of hot acid:

$$2\text{H}_2\text{O} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} = (\text{H}_2\text{O})\text{SO}_3 + \text{H}_2\text{SO}_4$$

In the presence of hydrogen potassium carbonate, this acid reacts with iodine solution as a hydroxylamine salt but much slower.