1892

Derivatives of hydroxylamine

Agnes Elizabeth Otto
State University of Iowa

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Derivatives of Hydroxylamine

Thesis by

Agnes E. Otto

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Derivatives of Hydroxylamine.

Hydroxylamine, when pure, appears as white odorless needles-shaped crystals which melt at 30°. When brought in contact with the flame, it explodes, giving an intense yellow light. It is slightly soluble in chloroform, benzene, carbon disulphide, 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:

\[ \text{NH}_2(\text{OH})_2 \rightarrow \text{NH}_2 + \text{NH}_4 + \text{H}_2\text{O} \]

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 liquid then undergoes but slight decomposition.

The solution of free hydroxylamine is strongly alkaline, when distilled no residue remains, and the
distillate contains ammonia and
undecomposed hydroxylamine. It is
a powerful reducing agent and pre-
cipitates silver, gold and mercury
from solutions and throws down
cuprous oxide from a hot solution
of cuprous sulphate. Perhaps it shall
be useful as an alkaline developer
in photography if it can be pre-
fpared cheaply enough. Cork and
cellulose are strongly attacked by it,
and bromine and iodine act with it
quite violently. Hydroxylamine
behaves very similarly to ammonia — and it is
supposed that it is ammonia in
which one part of hydrogen is replac-
by the hydroxyl group (-OH).

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

One of these 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 guic...
as 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 hydrochlorides 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 hydrochlorides of hydroxylamine \((\text{NH}_2\text{OH})\) is treated with dilute sulphuric acid and the solution is evaporated. Paraffin water is
added to the sulphate of hydroxylamine until all of the sulphate is precipitated, leaving an aqueous solution of hydroxylamine.

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 nitrate and mercurous nitrate with sulphurous acid added in moderate excess. This yields an insoluble sulphite 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 disulphonic acid is formed by mixing solutions of potassium nitrite and potassium sulphite in such proportions that the mixture shall contain one molecule of the first to less than four molecules of the second. After thorough boiling, the whole is allowed
to cool when long light transparent crystal form. These crystals form when boiled with water, hydroxyamine potash, gum monosulphonate \((\text{CH}_2\text{OH})\text{SO}_3\text{K})\), \((\text{CH}_2\text{SO}_3\text{K})_2 + 4\text{H}_2\text{O} = 2\text{CH}_2\text{OH}\text{H}_2\text{O} + 2\text{KHSO}_4\).

This salt when boiled with caustic potash decomposes into ammonia, potash, gum sulphate and nitrous oxide:
\[2\text{CH}_2\text{OH}\text{H}_2\text{O} + 4\text{KOH} = 2\text{K}_2\text{O} + 2\text{NH}_3 + 2\text{KHSO}_4 + 3\text{H}_2\text{O}.

Perhaps the best results can be obtained by mixing solutions of sodium nitrite 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 acid, which is added very carefully, and 20° escape with effervescence. If other proportions of the salt are taken, much less hydrochloric acid 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 hydroglaucumonum sulphate remains. The hydroglaucumonum sulphate is separated from the mixed residue by alcohol—that is, the alcohol dissolves the hydroglaucumonum.
sulphate leaving the residue of sodium sulphate. The solution after filtration is allowed to evaporate very slowly. Hydroxyplammonium sulphate crystallizes from the alcohol in short opicular crystals quite soluble in water. When sodium metasulphite ($Na_2S_2O_5$) is added to sodium nitrite, the temperature of the mixture rises but escape of gas accompanied it. The mixture shows no presence of hydroxyplammonium until after boiling when it is acidified and again thoroughly boiled. In order to obtain the hydroxyplammonium free in solution, barium hydroxide ($Ba(OH)_2$) can be added to the solution of
hydroxyammonium sulphate until all of the sulphate is precipitated as barium sulphate — the aqueous solution of hydroxyammonium is formed.

Firstly, to obtain the hydroxy-

amine-monosulphonate pure for the preparation of salts, neutralize the hydrolyzed solution with ammonia. He then added aqua rara which threw down a precipitate of a di-bar-

ium oxy-amidocarboxylate. 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 new acid can then be used in the
preparation of salts by combining it
with corresponding bases.

Hydroxyplammonium Compounds:

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

\[ \text{HO}_4^- + \text{HO}_4^- = 2 \text{HO} + \text{H}_2 \text{O} \]

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

Hydrazo-hydrazine chloride, \( \text{H}_4 \text{OCL} \),
can be obtained from a solution of sodium mithite and sodium
sulphite (one gram-molecule of the
first and two gram-molecules of the
second Saez used) which is neutralized
with hydrochloric acid. This is the
reaction which takes place:

\[
2\text{S}_2\text{O}_5^2- + 2\text{Na}_2\text{S}_2\text{O}_3 + 4\text{HCl} = 4\text{Cl}_2 + 2\text{H}_2\text{O} + 3\text{NaCl} + 2\text{Na}_2\text{SO}_4
\]

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 hydroxylamine solution in alcohol (\(\text{NH}_2\text{OH}\)). HCl is thrown down. Also when (\(\text{H}_3\text{O}\)) HCl is mixed with the normal salt, large crystals of (\(\text{H}_3\text{O}\)) HCl are formed. The normal salt decomposes by heat with evolution of gas into nitrogen, ammonium chloride, water, and hydrochloric acid.

Hydroxylammonium sulphate (\(\text{NH}_2\text{H}_2\text{O}\text{SO}_4\)) 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.

\[ \text{Hydroxyaluminum nitrate } \text{H}_4\text{AlO}_4(\text{NO}_3) \]

at ordinary temperatures is liquid
which solidifies at \(-15^\circ\). It is formed by decomposing a chloride
with silver nitrate. Its aqueous solution decomposed with the evolution of red vapours.

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

Potassium hydroxyalumino sulphonate
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 sud-
ddenly 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 in the form of small bil-
liant square prisms. They contain
water of crystallization and readily
decompose. When heated to 100° they
quickly and violently decomposed.

Di-Ionic hydrochloride 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 Benzoic acid. This is its formula:

\[ \text{P} (\text{C} \# \#) (\text{O} \# \# \# \#) \]
Experimental Work.

Hydroxylammonium aluminium sulphate, \( \text{Al}_2(\text{OH})_3\text{SO}_4 \), is prepared by mixing solutions of aluminium sulphate (\( \text{Al}_2\text{SO}_4 \)) and hydroxylammonium sulphate (\( (\text{NH}_3\text{OH})_2\text{SO}_4 \)) in such proportions that the mixture contains one gram-molecule of each.

\( \text{Al}_2\text{SO}_4 + (\text{NH}_3\text{OH})_2\text{SO}_4 = \text{Al}_2(\text{OH})_3\text{SO}_4 \)

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 voluminous 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.

mass of $\text{Al}_2\left(OH\right)_3(OH)\cdot O\left(H_2O\right)$ and tube = 13.56456 gr.

mass tube = 121.8164 gr.

mass substance = 1.13 gr.
Height of crucible — ———— 11.6926 gr.

... residue and crucible ignition 11.8163 "

... " " " " 2" 11.8163 "

... residue — ———— 1207 "

The percent of aluminium: — the weight of aluminium in \( \text{H}_2\text{O}_3 \) is \( \frac{54.08}{101.96} \)

\( 0.6077 \text{ gr.} - 0.1207 \text{ gr.} \)

\( \frac{0.6077}{1.1362} = 0.5372 \)  6.7% of aluminium

---

Height of substance and tube — 12.8164 gr.

... tube — ———— 11.8170 "

... substance — ———— 1.1984 "

... crucible and residue ignition — 11.8309 "

... " " " " 2" 11.8256 "

... " " " " 3" 11.8212 "

... " " " " 4" 11.8212 "
\[
\text{Place: -} \\
\text{Al}_2(\text{OH})_3(\text{SO}_4) + 6 \text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{Al}_2\text{O}_3 + 6\text{H}_2\text{O} + 3\text{SO}_2 + 3\text{H}_2\text{SO}_4.
\]

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

Height of substance and tube - 11.6979 gr.
   " " tube - 10.8868.
   " " substance - 7609.
   " " crucible + residue - ignition - 11.7861 gr.
   " " crucible - 11.7768.
   " " residue - 0.719.
Molecular weight of \( \text{H}_2 \text{SO}_4 \) = 108.18

\( \text{Cu}_2 \text{O} \) = 2.84.24

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

\( \text{Cu}_2 \text{O} \times \frac{0.831 \text{ g}}{100} \times 76 = 2.84.24 \)

Height of \( \text{Na}_2 \text{SO}_4 \) = 0.831 g.

Hydroxylamine = \( \frac{99.94 \times 0.831 \text{ g}}{100 \times 76} \)

\( 0.24 g \text{ g} = \frac{0.24}{0.9} = 6.02 \)

6.02% of hydroxylamine.

---

Height of substance in tube = 10.8868 g.

Tube = 9.7072

Substance = 1.1296

Crucible = 11.6940

Reduction ignition = 11.0810

\( 11.0810 - 11.6940 = -0.6130 \)
Height of crucible

residue on ignition: 121.027 g

- 4 " = 12.027 g

- 5 " = 12.027 g

Height of residue = 13.232 g

\((1.2047 \text{ g}) \times 323.829 \text{ g} = 105.76 \times 0.84.24\)

Height of \((26.04) \text{ g}\) = 1.2047 g

\(\text{hydroxylamine} = \frac{59.94}{105.76}\)

\(= \frac{0.814}{1.1276} = 0.71\)

6.11% of hydroxylamine

Average percent of \(\text{Fe}^{3+}\) = 6.066%

Theoretical percent of hydroxylamine = 6.45%

Hydroxylammonium ferric nitrate \(\text{Fe}^{3+}\) nitrate
hydrate is added to a solution of hydroxylamine sulphate until all of the sulphate is precipitated as ferric.
um sulphate, the filtrate then contains free hydroxylamine: 

\[(K_2C_2O_4)_2 \cdot 3H_2O + Ba(OH)_2 \rightarrow 2KOH \cdot 3H_2O + BaC_2O_4 + 2H_2O\]

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

\[(K_2C_2O_4)_2 + C_6H_2(OH)_3 \rightarrow C_6H_2(OH)_3 \cdot 3H_2O + K_2CO_3 + H_2O\]

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

Analysis:

To a solution of hydroxyflamme picrate add potassium carbonate in excess and alcohol. The hydroxyflamme picrate then decomposed:

$$2\text{C}_6\text{H}_5\text{H}_3\text{O}^-\text{K}^+\text{C}_6\text{H}_4\text{O}_4^-\text{H}_2\text{O} = 2\text{C}_6\text{H}_5\text{H}_3\text{O}^-\text{K}^+\text{C}_6\text{H}_4\text{O}_4^- + \text{C}_6\text{H}_5\text{CO}_2\text{H}_2 + 2\text{H}_2\text{O}.$$

Height of substance and tube — — 9.0933 gr.

tube — — — — 9.2062.

substance — — — — 1871.
Height of H-ferrate in tube = 2.2062 gr.

Tube = 8.9742 gr.

Substance = 2.3320 gr.

H-ferrate in paper = 0.180 gr.

Paper = 0.021 gr.
Height of Supericate — 2109 g

Hydroxylamine — 0.297 g

\[
\frac{0.297}{2.326} = 12.88\% 
\]

12.88% of hydroxylamine.

Average percent — 12.76%

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 proportions of substance. Boil thoroughly and allow to crystallize slowly. The following equation expresses the reaction which takes place:

—
This compound crystallized 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 the ferrous iron, in the solution of hydroxyflammonium iron sulphate has been reduced to ferric iron, add ammonia in excess. Ferric hydrate is then precipitated as a dark red gelat.
After thoroughly washed and dry it is ignited. These are the results:

\[ \text{Weight of substance and tube} = 13.0290 \, \text{g} \]
\[ \text{tube} = 10.9\,\text{g} \]
\[ \text{parting of substance} = 1.069\,\% \]
\[ \text{crucible and residue together} = 11.9843 \, \text{g} \]
\[ \text{crucible} = 11.6872 \, \text{g} \]
\[ \text{residue} = 2.96 \, \% \]

Molecular weight of \( \text{Fe}_2\text{O}_3 = 169.64 \)
\[ \text{Fe}_2\text{O}_3 = 71.84 \]

There is twice as much iron in \( \text{Fe}_2\text{O}_3 \) as in \( \text{FeO} \); hence:
20.21 gr. (x) = 29.76 gr. = 140.09 = 169.64 - 20.21 gr. = 2FeO, then 1 FeO = 12.63 gr.

\[
\frac{12.63}{1.069} = 11.98
\]

11.93 gr. of iron

---

twight of substance and tube = 10.92 gr.

tube

substance

crucible with losses after ignition 12.0258

crucible

residue 0.8417 gr.

14.1 gr. (x) = 28.92 gr. = 169.64 = 140.68 - 28.92 gr. = 2FeO - 1 FeO = 14.46 gr. - 1.2161

11.60% of iron
Method of Direct Ignition

Weight of substance and crucible — 12.4038 gr.
   " crucible — — — — 11.6873 gr.
   " substance — — — — .7206 gr.
   after first ignition — — — 11.9693 gr.
   second — — — 11.9664 gr.
   third — — — 11.9640 gr.
   residue — — — .2792 gr.

\[ \frac{.2792 \text{ gr}}{.2866 \text{ gr}} = 16.04 \% \]

16.41 % of iron

IV

Weight of substance and crucible — 12.0293 gr.
   " crucible — — — — 11.6892 gr.
   " substance — — — — .6601 gr.
Weight of unbleached residue: 1st injection - 11.93 g.

2nd " - 11.947 g.

3rd " - 11.948 g.

4th " - 11.94 g.

5th " - 11.948 g.

residue - 20.86 g.

20.86 g (x 2180) = 169.64 x 48.68 =

De = ¹/₂ of 2180 g - 1090 grams

1090 / 66.28 = 16.39% - 16.39% of iron

Average percent of Fe: \( \sqrt{\text{IV} \times \text{V}} = 16.48\%

Theoretical percent = 16.38% of -

Determination of hydroxylamide. To a solution of hydroxylammonium and sulphate add sodium carbonate to precipitate the ion as -
Ferrous sulphate –

\( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} + 6\text{H}_2\text{O} + 2\text{CuO} = 2\text{FeO} \cdot \text{OH} \)

+ 2\text{Na}_2\text{SO}_4 + 2\text{NaOH} + \text{CO}_2

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

\( \text{Na}_2\text{O} \cdot \text{H}_2\text{O} + 2\text{CuSO}_4 = 2\text{Cu}_2\text{O} + 2\text{NaOH} + \text{H}_2\text{SO}_4 \)

Wash the residue thoroughly and ignite.

These are the results obtained.

II

Height of substance tube – 10.79 grs.

" " tube – 9.64 grs.

" " substance – 1.15 grs.

" " crucible – 11.68 cc

" and residue ignition 12.16 cc
Height of crinkle Tresidue ignition = 12.1489

= 12.0780

= 12.0780

= 12.0780

acende = 3868

L. Cu. = 3868 gr. hydroxyamines = 1842 gr.

1842

16.001 - 16.001 - 16.001 of hydroxy-

amine

Height of substance tube = 9.5489 gr.

tube = 8.7928

substance = 6.759

crinkle Tresidue ignition = 11.9462

= 11.9094

= 11.9094

= 11.9094
Relation of Hydroxyamine to the nitrate.

By the removal of one of the atoms of oxygen, nitric acid (HNO₃) is converted into nitrous acid (HNO₂). By still further reduction this acid is converted into hyponitrous acid (H₂N₂O), and by continued action the hyponitrous acid is converted into hydroxyamine.

The reactions are represented by these equations:
$$\begin{align*}
4\text{H}_2\text{O} + 3\text{H}_2 &= 4\text{H}_2\text{O}_2 + 2\text{H}_2 \text{O} \\
\text{H}_2\text{O} + \text{H}_2 &= \text{H}_2\text{O} + \text{H}_2\text{O} \\
4\text{H}_2\text{O} + \text{H}_2 &= 2\text{H}_2\text{O}_2 \text{(CH)} \\
\text{H}_2\text{O}_2 \text{(CH)} + \text{H}_2 &= 2\text{H}_2 + \text{H}_2\text{O}.
\end{align*}$$

Hydroxylamine behaves very differently from ammonia towards the halogens. Hydroxylamine, when in the liquid state, dissolves salt and on evaporation the salt is thrown down. For example, B. C. tsimer found that, on heating 
\text{C}_{\text{H}}\text{H}_2\text{ClO}, the face distilled off could be condensed in a receiver.
Reduction of Nitrates to Hydroxylamine by Hydrogen Sulphide. A solution of an alkali nitrate, saturated with hydrogen sulphide and acidified with hydrochloric acid yields sulphur nitric oxide and ammonia but no hydroxylamine.

But if silver nitrate is suspended in water and treated with hydrogen sulphide, hydroxylamine is produced together with sulphur, nitric oxide and ammonia. On adding hydrochloric acid to the filtrate and evaporating to dryness a mixture of ammonium and hydroxylammonium...
chloride. If the filtrate be heated before adding the acid, the hydroxylamine will be destroyed by the action of hydrogen sulphide. Estimates have been made of the quantity of hydroxylamine produced after heating with hydrochloric acid. In one case 0.049 gram of silver nitrate yielded about one sixth of the nitrogen as hydroxylamine, and in another 0.064 gram yielded about three eleventh of the nitrogen as hydroxylamine. Mersuronic nitrite, though a little more difficult to decompose, yields the same results as silver nitrate. When mersuronic nitrite is heated
with nitric oxide or alkali nitrite and hydrogen sulfide, mercury nitrite is formed, and hydroxylamine only by hydrogen sulfide reduces 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 hydroxylamines. Hydrogen sulfide decomposes them 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:

\[ 4\text{Ag}_2\text{S} \cdot \text{H}_2\text{O} \rightarrow 4\text{Ag} + 2\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O} \]

\[ 2\text{Ag} + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} + \text{H}_2\]

The action of the gum-birch catkin
convert nitric acid into ammonium 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 alkaline nitrite brought suddenly in contact with hydrochloric acid and
gives yields a little hydroxyglamine.

The reaction of sulphites and nitrites when other metals than potassium is used. When Claudius worked on Trena's series of potassium salts, he discovered that by adding potassium nitrite to potassium sulphite, a salt was formed having the composition \( \text{KHSO}_4 \cdot \text{K}_2 \text{SO}_3 \), which when heated in solution yielded \( \text{K}_2 \text{O} \cdot \text{KHSO}_4 \cdot \text{K}_2 \text{SO}_3 \) with potassium hydrogen sulphate. Claus found the former salt to be hydroxyglamine deisulphomate and Claus found the latter to be potas-
sium hydroxyamine - monosulphonate.

Preece found that by heating potassium hydroxyamine sulphonate with water, changed it into the acid sulphate of potas-
sium and hydroxyamine. The sulphonate can be used as a cheap source of hydroxyamine.

It was extremely difficult for Frenz to obtain sodium compounds corresponding with the potassium compounds. This must be observed that when solutions of sodium sulphite and sodium nitrite are mixed, the crystal do not occur 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.

\[ \text{Na}_2\text{V}_2\text{O}_5 + 2\text{SO}_3 \text{H}_2 + 3\text{CO}_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4(\text{Na}_2\text{H}_2\text{O})_2 + 3\text{CO}_2 \text{gast.} \]
\[ 2\text{Na}_2\text{SO}_3 \text{H}_2 + 8\text{H}_2\text{O} + 2\text{CO}_2 = 2\{\text{Na}_2\text{H}_2\text{O}\}_2 + 6\text{CO}_2 \text{gast.} \]

The constitution of hypomuriates is explained by the decomposition of hydroxylammonium-mono-sulphate.
Fleming found that potassium hydroxy-
plamine sulphamate decomposed
into acid sulphate and hydroxy-
plamine salt. The change takes
place when the solution is boiled;
this is the formula:

\[ S + O_{18} K + H_2 O \cdot K_2 + S \cdot O_8 K_2 H_2 O. \]

The decomposition of hydroxyplamine
monosulphenate into sulphate and
hypomnitrite show that as hypomnitrite
must have its oxygen between
nitrogen and metal. Some
chemists admit that as 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 \( \text{Hg}_2(\text{OH})_2 \) or \( \text{[Hg(OH)]}_2 \), the \( \text{OH} \) and itself as hydroxymanganate, \( \text{[Hg(OH)]}_2 \) being the radicle.

**Oxidation of Hydroxylaminic sulfonates byBasic Reagents**—Chains of manganese dioxide dissolved as manganese and salt as hydroxylaminic sulphonie 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 nitrous oxide instead of oxygen. The potassium salt
reduce salts of copper, gold, and silver. The copper must be excepted 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 sulphinate is converted into sulphite and sulphate, the copper oxide is just half what it would be were hydroxylamine first formed.
The hyposulphurous acid is resolved into nitrous oxide and water. If hydrochloric acid is added after this 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 colour will be produced, but no presence of cuprous oxide.
The alkaline solution does not contain hydroxyglaminic 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 hydroxyglaminic sulphonate 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 cuprous oxide, weigh rapidly and weigh the reduced oxide. Silver and mercuric oxide behave just like cupric hydroxide and yield much sulphate, in an alkaline solution.

Decomposition of Hydroxylamine sulphonate and Alkaline Base.

The hydroxylamine sulphonate undergoes decomposition when treated with alkalies as with acids. An unheated alkaline solution of hydroxylamine sulphonimic acid is really a solution of free hydroxylamine, the quantity of which can be esti-
mated from the amount of acid taken. The hydroxylamine sulphonates are hydroxylamine derivatives which hydrolyze in acid solution into hydroxylamine and sulphate. In alkaline solution this is not the case, neither sulphate nor hydroxylamine nor even the decomposition products of hydroxylamine are given. The hydroxylamine sulphonates decompose with potassium hydroxide into sulphite and hypernitrite and the decomposition products of hypernitrite. No ammonia is formed, no sulphate or nitrogen. Hydroxylamine cannot 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 hypochlorite, the solution must be allowed to remain for some time in the cold with strong potassium hydrosulphite, or be heated for a short time with strong alkali. Decomposition of the hypochlorite 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
ponitrite and reduced silver. The silver hypoponitrite forms potassium
celow sulphite. This latter change can be avoided by using the
tarium salt instead of the potas
sium salt.

In preparing hypoponitrite it is
not really necessary that the
hydroxalumine sulphamate be pure.
Because of the decomposition of
much of the pottassium hypoponitrite
into hydromel and nitrous oxide,
the determination of the hypoponitrite.
does not prove the formation of this salt is, the only decomposition of the hydroxylamine sulphonate. This is the reaction:

\[ \text{H}_2\text{N}+\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2\text{H}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{SO}_4 \]

When hydroxylamine monosulphonate is evaporated to dryness on a water bath with potassium or sodium carbonate, sulphite is yielded, evolution of carbonic anhydride accompanied 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 decomposed in the presence of hot acid:

\[2HNO + SO_3 \cdot H_2O \rightarrow (HOC)SO_4 + H_2SO_4\]

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