Preparation of Hydroxylamine Using Liquid Sulfur Dioxide

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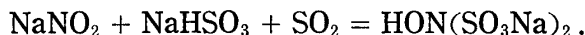
Synopsis

In order to prepare hydroxylamine from sodium nitrite, sodium bisulfite, and sulfur dioxide, liquid sulfur dioxide was used instead of gaseous one and the optimum condition for getting maximum yield was studied by rather quickly adding the dioxide. The best mole ratio of the material is as follows: $NaNO_2 : NaHSO_3 : SO_2 = 1.0 : 1.0 : 0.95 \sim 0.97$. Even the excess of any component results less yield. The preparing time of sodium hydroxylamine disulfonate was reduced to $1/10 \sim 1/20$ by quickly adding liquid sulfur dioxide. But it was perceived that the yield was independent of the adding velocity of the sulfur dioxide. On the hydrolysis of the disulfonate in presence of sulfuric acid by direct heating, the hydrolyzing time was shortened. In total, the preparing time of hydroxylamine was shortened by about one tenth.

I. Introduction

There is a method to prepare hydroxylamine from sodium nitrite, sodium bisulfite, and sulfur dioxide.[1] Namely, sodium hydroxylamine disulfonate is formed by gradually passing sulfur dioxide into a cooled mixed solution of the nitrite and the bisulfite:

$$NaNO_2 + NaHSO_3 + SO_2 = HON(SO_3Na)_2 .$$

By hydrolyzing the product, hydroxylamine is produced as its sulfate:

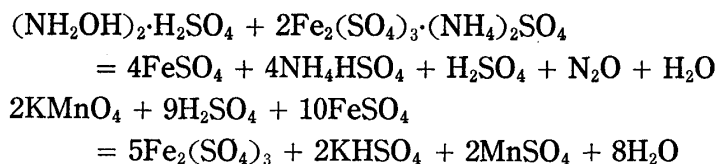$$2HON(SO_3Na)_2 + 4H_2O = (NH_2OH)_2 \cdot H_2SO_4 + Na_2SO_4 + 2NaHSO_4 .$$

There has been almost no study on the passing velocity of sulfur dioxide, but it has been said that the gas to be passed gradually.[1]~[5] In the present study, liquid sulfur dioxide was used instead of gaseous one and the optimum condition for getting maximum yield was studied by rather quickly adding the dioxide. For comparison, experiment on the gradual addition of the gaseous dioxide has also been conducted.

II. Analytical method

Although many quantitative analytical methods of hydroxylamine have been reported,[6] no reliable one was found. Some methods have been studied, taking a method utilizing its reducing property as a main one. The ferric salt method stated by W. C, Bray[7] is here designated as A-method, in which hydroxylamine

(1) G. K. Rollefson and C.F. Oldershaw, J. Amer. Chem. Soc., **54** (1932), 977.
(2) E. Divers and T. Haga, J. Chem. Soc., **69** (1896), 1665.
(3) R. Adams and O. Kamm, J. Amer. Chem. Soc., **40** (1918), 1283.
(4) W. L. Semon, ibid., **45** (1923), 188.
(5) Collected Reports, Toyo Rayon & Company, 3, No. 2 (1948), 43.
(6) Gmelins Handbuch der anorganischen Chemie, System-Number **23** (1936), 582.
(7) W. C. Bray, M. E. Simpson and A. A. Mackenzie, J. Amer. Chem. Soc., **41** (1919), 1363.

is added into a mixed solution of ferric ammonium alum and sulfuric acid, strongly boiled and titrated with potassium permanganate:

$$(NH_2OH)_2 \cdot H_2SO_4 + 2Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4$$
$$= 4FeSO_4 + 4NH_4HSO_4 + H_2SO_4 + N_2O + H_2O$$
$$2KMnO_4 + 9H_2SO_4 + 10FeSO_4$$
$$= 5Fe_2(SO_4)_3 + 2KHSO_4 + 2MnSO_4 + 8H_2O$$

The analytical result using a commercial product of the first grade as the sample is shown in Table 1, which shows that the analytical result differs according to the used amount of ferric ammonium alum.

Table 1. The effect of the amount of the ferric ammonium alum
in the analysis of hydroxylamine.

No.	0.1N-hydro-xylamine $f=0.9105$(cc)	0.1N–ferric-ammonium alum (cc)	Ferric ammonium alum hydroxylamine (Mole ratio)	12N-sulfuric acid (cc)	0.1N-potassium permanganate (cc)	Purity (%)
1	20	27	3	15	21.85	120.0
2	,,	,,	,,	,,	21.64	118.8
3	,,	36	4	,,	18.49	101.5
4	,,	,,	,,	,,	18.67	102.5
5	,,	45	5	,,	17.44	95.77
6	,,	,,	,,	,,	17.42	95.66
7	,,	54	6	,,	17.31	95.06
8	,,	,,	,,	,,	17.30	95.00
9	,,	63	7	,,	17.26	94.78
10	,,	,,	,,	,,	17.34	95.22
11	,,	72	8	,,	17.30	95.00
12	,,	,,	,,	,,	17.31	95.06

A constant analytical value is obtained when the mole ratio is larger than the following value: ferric ammonium alum: hydoxylamine = 6:1. The purity in the table was expressed with percentages of the ratio of the amount of the amine obtained from the analytical result and that of the sample.

In the above result, the higher purity was obtained as the smaller ratio, which suggested the remaining of intermediate substances, such as N_2O or NOH after boiling. For completing the reaction, the process was modified as follows.

A hydroxylamine solution was boiled, into which a definite amount of ferric ammonium alum was added and the boiling was continued. After adding sulfuric acid, the solution was titrated with potassium permanganate. The process was designated as B-method. The effect of the ferric ammonium salt in this case was shown in Table 2.

In this process, almost definite analytical values were obtained independent of the mole ratio of ferric ammonium alum to the amine, which suggested the effectiveness of the B-method comparing with the A-method. But the purity might be consumed to be smaller than the real value owing to the oxidation of Fe^{++} by oxygen in air.

When the mole ratio was larger than 6, the two methods gave a definite value as the purity of the amine. Namely, their mean values were 95.02 per cent by the A-method and 92.65 per cent by the B-method. For judging the two results, the

Table 2. The effect of an ferric ammonium alum in
the analysis of hydroxylamine.

No.	0.1N-hydro-xylamine $f=0.9105$(cc)	0.1N-ferric-ammonium alum (cc)	Ferric ammonium alum / hydroxylamine (Mole ratio)	12N-sulfuric acid (cc)	0.1N-potassium permanganate (cc)	Purity (%)
1	20	27	3	15	17.33	91.38
2	,,	,,	,,	,,	17.40	91.75
3	,,	36	4	,,	17.34	91.43
4	,,	,,	,,	,,	17.34	91.43
5	,,	45	5	,,	17.42	91.86
6	,,	,,	,,	,,	17.43	91.91
7	,,	54	6	,,	17.55	92.54
8	,,	,,	,,	,,	17.61	92.86
9	,,	63	7	,,	17.51	92.33
10	,,	,,	,,	,,	17.58	92.70
11	,,	72	8	,,	17.58	92.70
12	,,	,,	,,	,,	17.59	92.75

sample was purified as follows and analysed.

As the commercial product was contaminated with free sulfuric acid, it was washed enough with 94 per cent ethyl alcohol and dried. The analysis of the product gave the following value as the purity of the amine : 100.3 per cent by the A-method and 97.74 per cent by the B-method. The other methods gave the following values as mean ones. A method to reduce the amine with Devarda's alloy in a concentrated alkaline solution, 94.32 per cent ; a gravimetric method to determine sulfate radical, 99.75 per cent ; and a method to neutralize the combining sulfuric acid with sodium hydroxide using phenolphthalein as an indicator, 98.65 per cent.

Excepting the ferric salt method (B) and Devearda method, the results of the other three methods were in coincidental with each other in the range of 1.7 per cent error. As an analytical method to be used in the preparing experiments, the Devarda method would not give a correct value when other nitrogen compound was mixed in the product. The method would also give low value because nitrogen of hydroxylamine itself was not completely reduced to ammonia by the method.

As sodium sulfate and sodium bisulfate are produced as by-products with hydroxylamine, the gravimetric method is not applicable. In the neutralization method, free sulfuric acid, if present, must be previously determined using methyl orange as an indicator, at which the end point is ambiguous. The ferric salt method (A) gives a slightly larger value, but is in coincidental with those of the gravimetric and neutralization methods. This method was therefore adopted as the analytical one in the present study, because the accuracy to be obtained by the method would be sufficient for our purpose.

III. Experimental apparatus and procedure

In preparing sodium hydroxylamine disulfonate by adding sulfur dioxide into a mixed solution of sodium nitrite and sodium bisulfite cooled at below 0°C, a pressure-proof glass bomb containing liquid sulfur dioxide was invertly fixed on a reaction vessel as shown in Fig. 1 and the content was quickly added into the

flask. The adding velocity was 5–13 g. SO_2/min. and the method was designated as liquid method. In another method, designated as gas method, sulfur dioxide gas was gradually introduced into a 1-liter flask containing the mixed solution through a glass tube dipped in the solution at the velocity of 0.3–0.6g. SO_2/min. The flask was equipped with an agitator rotated by the velocity of 700 r. p. m. In case of the liquid method, the flask was vigorously shaked with hands.
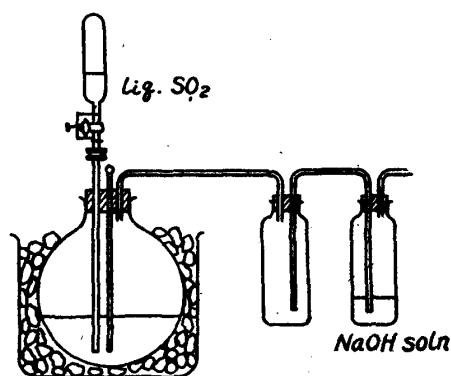

Fig. 1. Apparatus for the liquid method.

IV. Experimental results and discussion

1. The relation between the mole ratio, SO_2 : $NaNO_2$, and pH

The change of pH during the process of the formation of sodium hydroxylamine disulfonate by passing sulfur dioxide gas into a cooled mixture of sodium nitrite and sodium bisulfite was examined.

The reaction was conducted by passing sulfur dioxide gas at the velocity of 60 ~120 cc./min. into a 300 cc. solution containing 20.000 g. of sodium nitrite (purity : 99.98 %) and 30.403 g. of $Na_2S_2O_5$ (purity 90.60%) cooled at 0~−5°C. The result was shown in Table 3 and Fig. 2.

Table 3.

No.	SO_2(g)	SO_2/$NaNO_2$ in mole ratio	pH
1	0	0	7.1
2	3.70	0.199	7.0
3	5.35	0.288	7.2
4	6.55	0.353	6.7
5	6.91	0.372	6.7
6	9.80	0.528	6.5
7	10.44	0.562	6.5
8	12.44	0.670	5.9
9	12.44	0.670	6.4
10	14.58	0.785	6.0
11	14.67	0.790	5.5
12	15.63	0.842	6.4
13	15.93	0.858	5.7
14	16.00	0.862	4.8
15	16.52	0.890	4.1
16	17.34	0.934	1.4
17	17.39	0.937	3.2
18	17.45	0.940	4.4
19	18.10	0.975	2.2
20	21.73	1.17	1.3
21	22.28	1.20	1.1
22	28.96	1.56	0.6

SO_2/$NaNO_2$ in mole ratio
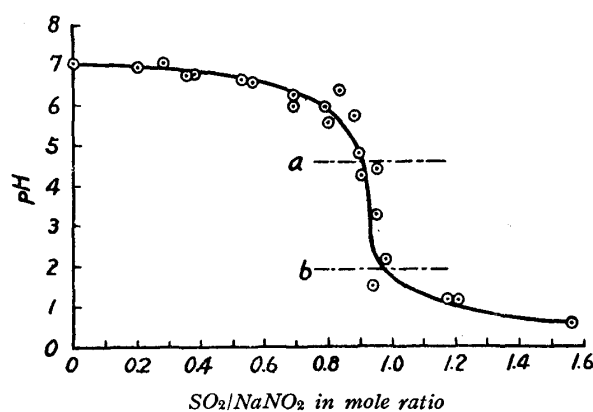
Fig. 2.

At first, pH of the solution was about 7, being neutral. When the mole ratio of SO_2/$NaNO_2$ became about 0.9, the pH became smaller and the acidity increased. The appearance of the solution seen from outside also changed. At the position of

a-line in the Figure, i. e., the mole ratio being about 0.9, the solution was gradually tinged with yellow color, then denser, reddish brown and then lighter again. The color disappeared at the position of b-line, i. e., the mole ratio being about 0.97, evolving sulfur dioxide odor. If the reaction proceeded as shown by the reaction formula, it should be completed at the point of the mole ratio 1, producing sodium hydroxylamine disulfonate. But the reaction would proceed as follows. As the mole ratio became larger than 0.9, the acidity of the solution due to sulfur dioxide increased and a nitrogen oxide would be produced by the decomposition of sodium nitrite.

The process would cause the loss of nitrogen during the preparing process of hydroxylamine.

2. The relation between the mole ratio, $SO_2 : NaNO_2$, and the yield

20.000 g. of $NaNO_2$ and 30.403 g. of $Na_2S_2O_5$ were dissolved in 300 cc. of distilled water and their concentrations were made to be 1.0 M/1000 g. H_2O respectively. Sulfur dioxide was introduced into a solution containing sodium bisulfite and sodium nitrite in equal mole ratio according to mole ratio of $SO_2 : NaNO_2$ in the liquid and gas methods. The produced sodium hydroxylamine disulfonate was hydrolyzed with 0.3N sulfuric acid by gentle boiling with direct heating for 5 hours under reflux, producing hydroxylamine sulfate. The relation between the mole ratio, $SO_2 : NaNO_2$ and the yield for $NaNO_2$ was shown in Tadle 4 and Fig. 3.

Table 4.

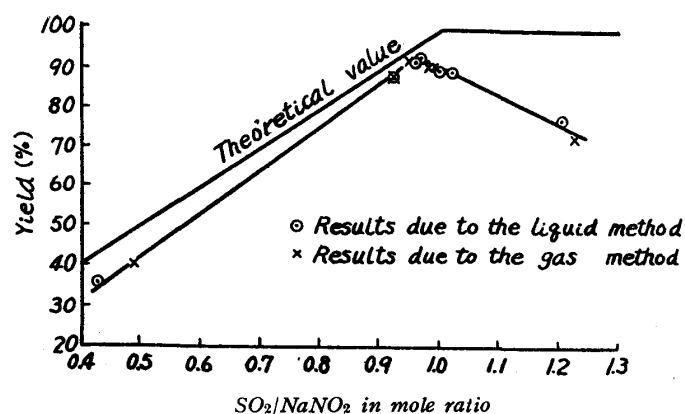| No.	Liquid method		Gas method	
	$SO_2/NaNO_2$ in mole ratio	Yield (%)	$SO_2/NaNO_2$ in mole ratio	Yield (%)
1	0.43	36.2	0.49	40.2
2	0.92	88.9	0.92	88.0
3	0.96	91.8	0.95	91.9
4	0.97	92.5	0.97	91.3
5	1.00	89.8	0.98	90.1
6	1.02	90.0	0.99	90.8
7	1.21	78.3	1.25	72.6

Fig. 3

As shown above, almost no difference between the yields due to the two different methods, the gas and liquid methods, was observed. Namely, the adding velocity of sulfur dioxide gave almost no influence on the formation of hydroxylamine. When the mole ratio, $SO_2 : NaNO_2$, was 1 : 1, the yield should be maximum in theory, but it was 0.95~0.97 in reality, which would be due to the decomposition of sodinm nitrite by the increase of acidity before the mole ratio reached 1 : 1 and also to the reaction between the disulfonate and sodium bisulfite during the hydrolysis. When sulfur dioxide was added in excess, less yield was resulted, which would be due to the reaction between the disulfonate and sulfur dioxide. The maximum yield for sulfur dioxide was 95~97 per cent when the mole ratio was 0.92~0.97.

The end point of the formation of sodium hydroxylamine disulfonate would be perceived by the disappearance of brown color appearing near the completion of the reaction. Attention should be payed for the elevation of temperature of the reacting solution by the evolved heat, when it was colored.

3. The relation between the mole ratio, $NaHSO_3 : NaNO_2$, and the yield

The present experiment was conducted for examining the effect of NO_2^- and HSO_3^- in excess for the producing process of hydroxylamine, although the amount of sodium bisulfite and sodium nitrite necessary for the reaction should theoretically be 1 : 1 in their mole ratio. The experimental condition was same with the former one. Sulfur dioxide was added into the reacting solution in the condition of $SO_2 : NaNO_2 = 0.96 : 1$ in mole ratio. The yield was expressed with the value for nitrogen. The result was shown in Table 5 and Fig. 4.

Table 5.

No.	NaHSO₃/NaNO₂ in mole ratio	Yield (%)
1	0.80	69.1
2	0.90	81.9
3	1.00	91.8
4	1.20	80.0
5	1.43	61.6

NaHSO₃/NaNO₂ in mole ratio
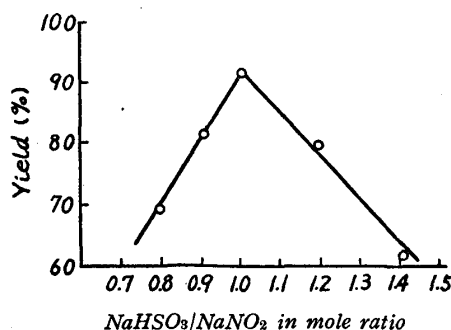
Fig. 4.

The yield rapidly decreased although either one was excess. The maximum yield, 91.8 per cent, was obtained when the mole ratio, $NaHSO_3 : NaNO_2$, was 1 : 1. The excess of NO_2^- and HSO_3^- decreased the yield, reacting with produced sodium hydroxylamine disulfonate and hydroxylamine themselves.

4. The effect of the concentration of the material

The former experiment was conducted using sodium nitrite and sodium bisulfite in about $1.0 M/1000$ g. H_2O concentration and the mole ratio, $NaNO_2 : NaHSO_3$, was 1 : 1. Hereafter, the concentration of the nitrite and the bisulfite were expressed separately. And their effects on the yield were examined. The mole ratio, $SO_2 : NaNO_2$, was 0.95 : 1, and the hydrolysis was conducted for 5 hours in 0.3N sulfuric

acid by direct heating (marked with × mark in Fig. 5). When the concentration of the material was 3.3 M/1000 g. H_2O, the hydrolysis was conducted in a water bath for 24 hours differing from the other cases (marked with ⊙ mark in Fig. 5). The result was shown in Table 6 and Fig. 5.

Table 6.

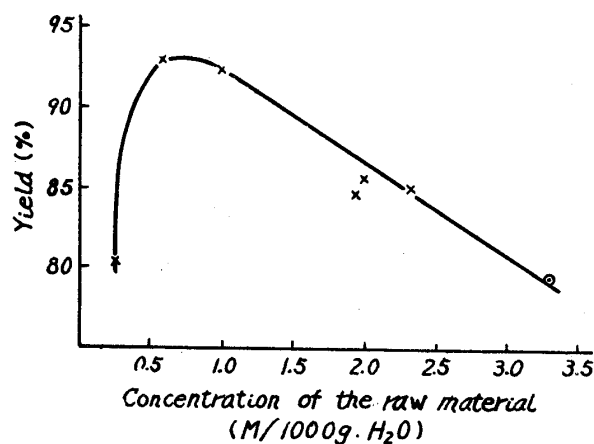| No.	Concentration of the matarial (moles/1000 g. H_2O)	Yield (%)
1	0.25	80.3
2	0.58	93.1
3	1.00	92.3
4	1.96	84.6
5	2.00	85.5
6	2.37	85.0
7	⊙ 3.31	77.0

Fig. 5.

When the concentration of the material was less than about 2.3 M/1000 g. H_2O and the indirect heating was continued for 5 hours, the yield was less than the value given in the Table by about 1~4 per cent. But, by increasing the heating hour, it became almost same with that in Table. For example, the yield was 89.5 per cent in case of 5 hours' indirect heating in the concentration of 1.0 M/1000 g. H_2O, which was however increased to 92.1 per cent by 20 hours' heating.

When the concentration was 2.3 M/1000 g. H_2O, the yield was 84.6 per cent by 18 hours' indirect heating. Moreover, the yield was 73.2 per cent by 5 hours' direct heating in the concentration of 3.3 M/1000 g. H_2O which was less than that obtained by the indirect heating, contrary to the case of lower concentration, in that case the yield of the direct heating was higher. It would be due to the decomposition of the product by boiling point elevation owing to high concentration in the presence of sulfuric acid. In case of hydrolysis of the disulfonate in 0.3N sulfuric acid, the material concentration, in which no decomposition might be caused by the boiling point elevation, would be about 2.3M/1000g. H_2O at its limit. The maximum yield was obtained in the concentration-range of the material of 0.5~1.0M/1000g. H_2O.

5. Extraction as solid hydroxylamine hydrochloride

After the hydrolysis, there remained hydroxylamine sulfate, sodium bisulfate and sodium sulfate in the resulting solution. As it was difficult to extract the sulfate from the solution in high purity, the amine was extracted as its hydrochloride by the following process. By adding a barium chloride solution into the resulting solution, sulfate radical was precipitated as barium sulfate and the amine was changed into its hydrochloride. It was filtered and the filtrate was evaporated to dryness and the hydrochloride was extracted with ethyl alcohol using Soxllet's extractor, separating from sodium chloride. The mean yield for sulfate was 81.29 per cent and that for the raw material sodium nitrite was 75.2 per cent.

Summary

For getting the optimum condition of the preparation of hydroxylamine:

（1） The best mole ratio of the material is as follows: $NaNO_2 : NaHSO_3 : SO_2$ $= 1.0 : 1.0 : 0.95 \sim 0.97$. Even the excess of any component results less yield and pH of the end point lies between $2 \sim 4$.

（2） Taking the concentration of the material, sodium nitrite and sodium bisulfite, as $1.0 M/1000 g. H_2O$, sulfur dioxide was added at the rate of $0.3 \sim 0.6 g./min.$ in the gas method and $5 \sim 13 g./min.$ in the liquid method, the yields by the two methods were almost same. By the result, it was perceived that the yield was independent of the adding velocity of sulfur dioxide.

（3） Using the material in the concentration of less than $2.3 M/1000 g. H_2O$, the hydrolysis of the disulfonate was conducted in the concentration as it is and in 0.3N sulfuric acid by direct heating for 5 hours, which was sufficient time and concentration.

From the above result, the preparing time of sodium hydroxylamine disulfonate was reduced to $1/10 \sim 1/20$ by quickly adding liquid sulfur dioxide. On the hydrolysis of the disulfonate in presence of sulfuric acid by direct heating, the hydrolyzing time was shortened. In total, the preparing time of hydroxylamine was shortened by about one tenth.