[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

THE REDUCTION OF NITRITES TO HYDROXYLAMINE BY SULFITES

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A common method for the preparation of hydroxylamine has been to pass sulfur dioxide gas slowly into a cold mixture of sodium nitrite and sodium carbonate in water until the solution is just acid to litmus.[1] The hydroxylamine disulfonate ion formed by this process was hydrolyzed by heating the solution, which was then evaporated to dryness and the hydroxylamine extracted as either the sulfate or chloride. The following equations represent the two steps

$$NO_2^- + 2HSO_3^- + H^+ = HON(SO_3)_2^= + H_2O$$
$$HON(SO_3)_2^= + 2H_2O = HONH_3^+ + 2SO_4^= + H^+$$

The yields obtained by following this procedure are usually less than 50% of the theoretical. We have found it possible to obtain a much higher yield by modifying the above procedure so as to eliminate some of the possibilities for side reactions.

The factors to be considered in selecting the optimum conditions for this preparation are: the effect of hydrogen-ion concentration, the effect of temperature, and the effect of excess of either nitrite or sulfite. As a result of a series of tests at various concentrations of hydrogen ion we can say that the rate of formation of the hydroxylamine disulfonate ion becomes very slow if the H^+ falls below 5×10^{-6} but proceeds readily at concentrations between 2×10^{-5} and 5×10^{-5}. At higher concentrations, particularly above 10^{-4}, the evolution of nitric oxide occurs, probably due to the decomposition of the nitrous acid which is formed in such solutions. A favorable H^+ concentration for the reaction is that given by an acetic acid–acetate buffer.

The effect of temperature on the reaction between the nitrite and the sulfite has been investigated by Raschig.[2] His results may be summarized as follows: at temperatures below 0° only the hydroxylamine disulfonate ion is formed, at temperatures above 5° further reduction to the amine trisulfonate ion occurs and the latter reaction becomes rapid at room temperature. From these facts it is evident that the temperature must be kept low during the preparation of the disulfonate and excess sulfite should be removed before hydrolysis.

Excess nitrite should be avoided as Raschig[3] has shown that nitrous

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[1] Divers and Haga, *J. Chem. Soc.*, **69**, 1665 (1896); Adams and Kamm, THIS JOURNAL, **40**, 1283 (1918).

[2] Raschig, "Schwefel- und Stickstoffstudien," Verlag Chemie, Berlin, 1924, p. 8.

[3] Raschig, *ibid.*, p. 7.

oxide is evolved if the disulfonate is hydrolyzed in the presence of nitrites due to a reaction between the monosulfonate and the nitrite. The difficulties due to excess sulfite or nitrite may be avoided by using the potassium salts. The potassium salt of hydroxylamine disulfonic acid is sparingly soluble and precipitates out so that it may be separated from any excess of either reagent.[4] The salt may then be hydrolyzed without danger of side reactions.

The following procedure is recommended for the preparation of hydroxylamine hydrochloride. Weigh out one mole of commercial potassium nitrite and 1.1 to 1.2 moles of potassium acetate. Dissolve these salts in about 200 cc. of ice water and add about 1500 g. of finely chipped ice. Agitate the mixture thoroughly and pass in sulfur dioxide gas until the odor indicates that an excess has been added. During the reaction practically all of the ice will be melted; care should be taken, however, to have some ice present at all times so as to insure keeping the temperature below 0°. Filter out the precipitated potassium hydroxylamine disulfonate with a Büchner funnel and wash the precipitate with ice water. Four washings of about 50 cc. each are usually sufficient to remove all sulfites and acetates from the precipitate. The yields of disulfonate obtained in this way vary with the volume of solution used but are usually approximately 85%. The losses can be accounted for as principally due to the solubility of the salt. The disulfonate is hydrolyzed by placing it in about 1 liter of approximately 0.5 *N* hydrochloric acid and heating to 100° for about two hours. Tests show that under these conditions the hydrolysis is complete in that time; if no acid is added, a longer time should be allowed. The sulfate formed is removed by adding 0.9 mole of barium chloride while the solution is still hot and filtering out the precipitated barium sulfate. The filtrate is evaporated to dryness and the hydroxylamine hydrochloride extracted from the residue by absolute alcohol. The loss of hydroxylamine on hydrolysis by this method is negligible, so the net yield of the hydroxylamine hydrochloride is approximately 85% of the theoretical.

From the results we have obtained with this preparation we may conclude that nitrites react practically quantitatively with bisulfite under the conditions which have been stated to give the hydroxylamine disulfonate ion. Furthermore, the hydrolysis of the disulfonic acid to hydroxylamine is quantitative if carried out in the absence of sulfites or nitrites.

Summary

A method of preparing hydroxylamine from nitrites by the reduction with sulfite so as to give an 85% yield has been described. The high

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[4] An approximate value for the solubility of potassium hydroxylamine disulfonate, $HON(SO_3K)_2 \cdot 2H_2O$, obtained in this Laboratory is 23.0 ± 0.5 g. or 0.075 mole per liter at 0°.

yield is due to the elimination of side reactions by precipitating the potassium salt of hydroxylamine disulfonic acid and separating it from the excess sulfite before hydrolysis.

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THE COMPARATIVE IONIZATION OF SELENIC AND SULFURIC ACIDS

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Introduction

There is much evidence to indicate that sulfuric acid in moderately dilute aqueous solution is substantially completely ionized with respect to its first hydrogen, but only partly with respect to its second. Thus, Sherrill and Noyes,[1] by combining conductance and transference data of sulfuric acid at different concentrations, have estimated the ionization of HSO_4^- ion in sulfuric acid solutions at 25° to vary from 96% at an acid concentration 0.0005 normal to 34.5% at 0.1 normal. The corresponding value of the ionization constant of the HSO_4^- ion was computed to be 0.0115. In making these calculations, it was assumed that the mobility and the activity coefficient of any given ion is, at a definite temperature, determined solely by the ionic strength of the solution.

It is generally assumed that selenic acid closely resembles sulfuric acid in its ionization relations. The physico-chemical evidence of this is very limited, but certain approximate conclusions may be drawn from a comparison of the equivalent conductances of the two acids and their acid salts shown in the following table.[2]

TABLE I

EQUIVALENT CONDUCTANCES AT 25°

Substance	0.002	0.005	0.01	0.02	0.05	0.1	0.20	0.5
Na_2SO_4	122.1	117.3	112.4					
Na_2SeO_4	117.3	113.7	109.4					
H_2SO_4	390.3	364.9	336.4	308.0	272.6	250.8	234.3	222.5
H_2SeO_4	384	366	349	328	295	272	253	233

These values indicate that the mobilities of the sulfate ion and selenate ion are approximately the same, and that in dilute solution the hydrogen-ion concentrations in sulfuric acid and selenic acid solution of the same normality are nearly identical, whereas at higher concentrations, such as 0.2 *N*, the hydrogen-ion concentration is slightly greater in the selenic

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[1] Sherrill and Noyes THIS JOURNAL, **48**, 1870 (1926).

[2] "International Critical Tables," Vol. VI, pp. 242, 236, 247.