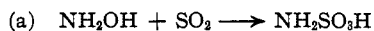


[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Preparation of Sulfamic Acid by the Hydroxylamine-Sulfur Dioxide Reaction

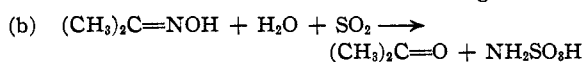
BY H. H. SISLER AND L. F. AUDRIETH

The reaction of hydroxylamine with sulfur dioxide (or sulfurous acid) is one of the few reactions in which the hydroxylamine molecule plays the role of an augmenting agent,¹ for in this reaction the sulfur dioxide is nitridized to sulfamic acid.



It is not surprising, however, that hydroxylamine should behave in this manner in certain of its reactions, for it is an aquo ammono analog of hydrogen peroxide,² just as the sulfamic acid which is formed is an aquo ammono sulfuric acid.

In addition to its interest from a theoretical point of view, the nitridation of sulfur dioxide by hydroxylamine salts represents one of the best known laboratory methods for the preparation of sulfamic acid.³ An analogous reaction of acetoxime with aqueous solutions of sulfur dioxide also has been recorded.⁴ It is interesting to note



that normal sulfites do not react with hydroxylamine derivatives in this way.⁵

Hitherto, these nitridation reactions always have been carried out either by saturating an aqueous solution of the hydroxylamine derivative with sulfur dioxide and allowing it to stand in the cold for an extended period of time, or by bubbling sulfur dioxide through the solution for about forty-eight hours. These procedures have two disadvantages: (1) low yields are obtained, and (2) a relatively long period of time is required to carry out such preparations.

A study of the hydroxylamine-sulfur dioxide reaction was undertaken primarily in an effort to obtain experimental facts which would permit an elucidation of the mechanism of the reaction. The procedure for preparation also was improved and modified by carrying out the reaction under pressure. The experimental portion of this paper deals with the effects of such variables as the concentrations of the hydroxylamine salt, and of hy-

dronium ion, and time upon the yield of sulfamic acid. The reaction between acetoxime, as an example of a hydroxylamine-yielding compound, and sulfur dioxide was also subjected to investigation.

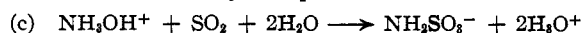
Experimental

Reaction of Hydroxylamine Sulfate with Sulfur Dioxide.—An aqueous solution of hydroxylamine sulfate was cooled to approximately -80° in a dry-ice-acetone mixture. An excess of sulfur dioxide was then condensed in the container. The container was transferred to an autoclave and allowed to warm to room temperature. Under these conditions, the reaction mixture was subject to a pressure of 3.5–4 atmospheres, approximately equal to the vapor pressure of sulfur dioxide at room temperature. After a certain time interval, the pressure was released, and the excess sulfur dioxide allowed to escape. The sulfamic acid which had crystallized was removed by filtration, and the adhering liquid removed as completely as possible by suction on a Buchner funnel. The product was dried by washing with alcohol and ether, and was found to contain only a small trace of sulfate. To recover the sulfamic acid remaining in the solution, the filtrate was treated with concentrated sulfuric acid and cooled in an ice-salt mixture. In typical experiments such as are recorded in Table I, two factors were varied: (1) the reaction time, and (2) the concentration of hydroxylamine sulfate solution.

TABLE I
REACTION OF HYDROXYLAMINE SULFATE WITH SULFUR DIOXIDE UNDER PRESSURE

$(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4$, g.	H_2O , g.	Concn., equivs.		Time, hr.	Temp., $^\circ\text{C}$.	$\text{NH}_2\text{SO}_2\text{H}$ obtained, g.	Yield, %
		$(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4$, per 1000 g. H_2O	SO_2				
1	41	50	10.0	18.3	0	15.5	32
2	16.5	50	4.0	23	25	14	72
3	17	50	4.1	6	25	13	65
4	16.5	20	10.1	15	25	3	15
5	16.5	35	5.7	15	25	11	56
6	16.5	50	4.0	15	25	13	67

Examination of the data listed in Table I shows that the reaction of sulfur dioxide with highly concentrated solutions of hydroxylamine sulfate goes much more slowly than with more dilute solutions. It was thought that this phenomenon might be due to the high concentration of hydronium ions which would be built up under these circumstances as illustrated by the equation



This hypothesis was substantiated by means of the following experiments. A mixture of 16.8 g. of hydroxylamine sulfate, 25 g. of water, and 75 g. of 98% sulfuric acid was sealed in the autoclave with a large excess of sulfur dioxide and allowed to remain at room temperature for sixty-six

(1) Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Corporation, New York, N. Y., p. 212.

(2) Sisler and Audrieth, *Proc. Ill. Acad. Sci.*, **31**, 145 (1938).

(3) Raschig, *Ann.*, **241**, 161 (1887).

(4) Schmidt, *J. prakt. Chem.*, **44**, 513 (1891).

(5) Raschig, "Schwefel und Stickstoff Studien," Verlag Chemie, G. m. b. H., Berlin, p. 225.

hours. No sulfamic acid was obtained. A similar result was obtained when a solution of 16.8 g. of hydroxylamine sulfate in 50 g. of 98% sulfuric acid and 50 ml. of water was treated with sulfur dioxide under pressure for forty-six hours. Sulfamic acid was obtained in both cases by subsequent neutralization and further treatment with sulfur dioxide.

Reaction of Acetoxime with Sulfur Dioxide.—A solution of 11 g. acetoxime in 10 ml. of water and 30 ml. of ethyl alcohol was saturated at 0° with sulfur dioxide gas, and was kept in a stoppered flask at that temperature for a total of three days. The solid sulfamic acid which formed was removed from time to time by filtration and more sulfur dioxide added as needed to keep the solution saturated. The product was washed with alcohol and ether, and dried in air. A total yield of 11.1 g. of sulfamic acid (corresponding to 76% of the theoretical yield) containing neither sulfate nor oxime was obtained.

In carrying out the reactions of acetoxime with sulfur dioxide under pressure at 0°, an aqueous solution of acetoxime in a glass pressure bottle was cooled to approximately -80° in a dry-ice-acetone mixture. An excess of sulfur dioxide was condensed on the frozen mass, and the bottle sealed. The temperature was allowed to come to 0°, and kept at that point by placing the bottle in an ice-bath. After a certain time had elapsed the bottle was again cooled, opened, and the excess sulfur dioxide allowed to escape. The sulfamic acid which had crystallized from the solution was removed by filtration, and dried by washing with alcohol and ether. The results of a number of typical experiments are listed in Table II. A similar series of experiments was carried out at approximately 25° (in an autoclave). The results of these experiments are also listed in Table II.

TABLE II
REACTION OF ACETOXIME WITH SULFUR DIOXIDE UNDER PRESSURE

(CH ₃) ₂ CNOH, g.	H ₂ O, g.	Temp., °C.	Time, hr.	NH ₂ - SO ₃ H obtained, g.	Yield, %
10	20	0	1.5	9.3	70
20	20	0	3	18.0	68
10	10	0	5.5	10.2	77
14.5	14.5	25	2	14.5	75
10	10	25	5	12.0	90
10	10	25	11.75	12.0	90

Discussion

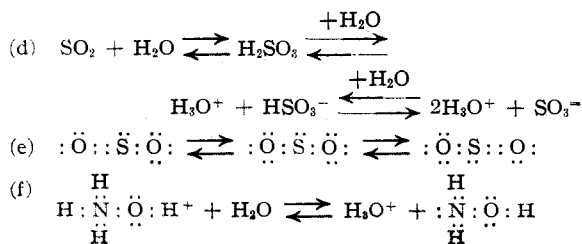
It is evident from the data in Table I that the yield of sulfamic acid from the reaction of hydroxylamine salts with sulfur dioxide is greatly increased and the time required for the reaction decreased by operating under pressure. This is also true of the acetoxime reaction. The results of these experiments also show that the reaction is inhibited by excessive concentrations of hydronium ions. This fact was demonstrated by the failure of hydroxylamine salts to nitridize sulfur dioxide in the presence of concentrated sulfuric

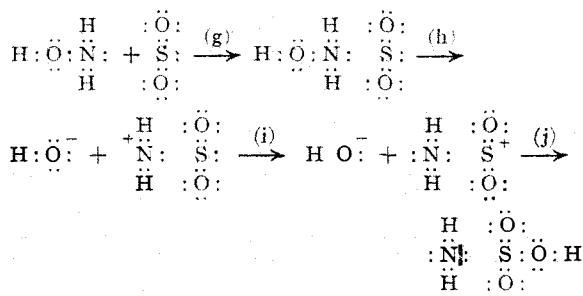
acid, and is further supported by the data from experiments four, five and six in Table I, which show that much lower yields of sulfamic acid are obtained from concentrated solutions of hydroxylamine salts than from more dilute solutions. As may be seen from equation (c), two moles of hydronium ion are released for each mole of hydroxylamine sulfate that reacts. Hence, with concentrated solutions of hydroxylamine sulfate high concentrations of hydronium ions are quickly built up, inhibiting the reaction.

Examination of the data from experiments two, three and six in Table I indicates that the formation of sulfamic acid becomes much slower as the reaction proceeds. Thus, the yield after a six hour reaction time was only 7% less than that after a twenty-three hour period, other conditions being comparable in the two experiments. This effect may be attributed to the formation of hydronium ions as the reaction proceeds, and to the decrease in the amount of hydroxylamine sulfate present.

A comparison of the data presented in Table II with those given in Table I shows that much better yields of sulfamic acid are obtained in a shorter length of time by the reaction of sulfur dioxide with acetoxime than by the corresponding reaction with hydroxylamine sulfate. This is not an altogether unexpected result when considered in the light of the effect of high concentrations of hydronium ions on the reaction. As is shown in equation (b), sulfamic acid is the only product contributing hydronium ions in the acetoxime reaction, and the hydronium ion concentration which can be built up from this source is limited by the relatively low solubility of sulfamic acid. This would seem to explain why, under similar conditions, acetoxime gives 90% yields of sulfamic acid after five hours, whereas hydroxylamine sulfate gives only 72% yields after twenty-three hours.

The nitridation of sulfur dioxide to sulfamic acid by hydroxylamine may be explained by the mechanism





The sulfur dioxide molecule is generally assumed to exist in the resonance forms indicated in (e). The hydroxylammonium ion exists in equilibrium with the hydroxylamine molecule (f). The middle resonance form of the sulfur dioxide molecule, having only six electrons in the outer shell of the sulfur atom, may unite with the hydroxylamine molecule by accepting the free pair of electrons on the nitrogen atom (g). As in Whitmore's electronic mechanism for rearrangements of the Beckmann type,⁶ the hydroxyl group may form an ionic bond leaving the nitrogen with a positive charge (h). However, since the nitrogen atom has a much greater affinity for the electron pair than does the sulfur atom, the free pair of electrons on the sulfur atom shifts immediately to the nitrogen atom (i). The negatively charged hydroxyl group can then unite with the positively charged sulfur atom, forming the sulfamic acid molecule (j).

It is probable that steps (h), (i), and (j) take place almost simultaneously. That is certainly the case with steps (h) and (i) due to the greater mobility of the electron pair than of the hydroxyl group. The fact that step (i) can take place probably makes possible step (h). The removal of the electron pair by the oxygen from the nitrogen

atom in step (h) does not necessarily mean that the hydroxyl group ever exists as a free ion, but merely that it forms an ionic bond. In fact, it is likely that the hydroxyl group is never out of the sphere of influence of the rest of the molecule during the rearrangement.

This mechanism satisfactorily accounts for the fact that the reaction is inhibited by a large hydronium ion concentration, for the excess of hydronium ions should drive the equilibrium in (f) far to the left so that the free pair of electrons furnished by the nitrogen on the hydroxylamine molecule would be covered up by protons. It also explains why, in the presence of enough alkali to change all the sulfur dioxide, sulfurous acid, and bisulfite to normal sulfite, and to neutralize the acid attached to the hydroxylamine, no reaction takes place, for, as shown in (d), two moles of hydroxide ion would completely convert all the sulfur dioxide to normal sulfite, leaving no free sulfur dioxide to react with the hydroxylamine. Thus, an excess of acid renders the hydroxylamine incapable of coordination, while an excess of alkali makes the existence of sulfur dioxide or of sulfurous acid impossible.

Summary

1. The procedure for the preparation of sulfamic acid by the interaction of hydroxylamine salts and hydroxylamine-yielding compounds with sulfur dioxide has been improved by operation under pressure.

2. A mechanism for the reaction has been proposed involving coordination between the hydroxylamine molecule and sulfur dioxide with subsequent rearrangement to sulfamic acid.

(6) Whitmore, *THIS JOURNAL*, **54**, 3274 (1932).