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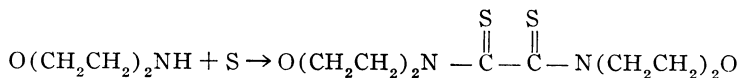
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The Formation of Morpholine Thiosulfate From Morpholine and Sulfur

By EDWARD M. PETERS AND WALTER T. SMITH, JR.

In recent years the use of morpholine and sulfur in the Willgerodt reaction has received considerable attention. There have been several mechanisms proposed for the Willgerodt reaction, but the most generally accepted mechanism today is that outlined by King and McMillan¹. These authors have attempted to show that an independent reaction between sulfur and the amine is essential to this reaction. They have postulated an amine sulfide intermediate similar to the already known amine oxides. These sulfides have not been isolated as by-products of the reaction nor have they been prepared in any other way.

The only previous evidence of a reaction between sulfur and morpholine is the formation of dithiooxalodi-morpholide reported by Horton and Van den Berghe²



This reaction apparently takes place only at elevated temperatures. It gives little or no clue as to the way in which sulfur attacks the morpholine molecule. In the course of our investigations of the reaction between morpholine and sulfur we have found that a definite reaction takes place at room temperature. This reaction may give more direct evidence concerning the morpholine-sulfur modification of the Willgerodt reaction.

When morpholine and sulfur are mixed and allowed to stand for several hours a deep red solution is formed. Upon standing for prolonged periods of time crystals form along the edge of the reaction vessel and across the surface of the liquid. This product can be isolated by washing the mixture first with ether, and then with acetone to remove the oily products which are also formed. The solid which remains is recrystallized from methanol. The product is a white crystalline material which decomposes at 152-3°. It is quite soluble in water and hot methanol but is only slightly soluble in other organic solvents. When this compound is treated with dilute mineral acids it decomposes to yield free sulfur and sulfur dioxide. This is a reaction characteristic of thiosulfate compounds.

¹ King and McMillan, *J. Am. Chem. Soc.* **70**, 4143 (1948).

² Horton and Van den Berghe, *J. Am. Chem. Soc.* **70**, 2425 (1949).

Positive tests with Ag^+ , Fe^{+++} , KI and I_2 , and KMnO_4 are further evidence for the presence of thiosulfate radical.³

When the compound is dissolved in alkali and treated with benzene sulfonyl chloride a derivative corresponding to that described in the literature for morpholine is obtained. These data, together with results of carbon-hydrogen, nitrogen, and sulfur analyses indicate that the compound formed from the reaction of morpholine and sulfur is morpholine thiosulfate.

Since this compound has not previously been reported it was necessary to devise an independent synthesis. An attempt to prepare morpholine thiosulfate from calcium thiosulfate and morpholine was unsuccessful, but it was found that morpholine thiosulfate could be prepared by a reaction analogous to that used for the preparation of ammonium thiosulfate. When sulfur dioxide is passed into a mixture of morpholine and sulfur a vigorous reaction takes place and the product obtained is identical with that formed when morpholine and sulfur are allowed to stand for long periods of time at room temperature.

The sulfur dioxide reaction gives a 47% yield and appears to be the best method for preparing morpholine thiosulfate.

EXPERIMENTAL

Morpholine thiosulfate from morpholine and sulfur. — In a 600 ml. beaker is placed 64 g. (2 moles) of sulfur and 200 ml. (2.3 moles) of morpholine. The beaker is covered with several layers of cheese cloth to exclude dust and still allow contact with air. The mixture is allowed to stand for three weeks at room temperature. It is then leached with 5-100 ml. portions of ether to remove the unreacted morpholine. The remaining organic material is removed from the desired product by means of eight extractions with 50 ml. portions of hot acetone. The solid material which is left behind is dissolved in hot methanol, filtered to remove free sulfur and then cooled to induce crystallization. Sixteen grams (5% yield based on morpholine) of compound melting at $150\text{-}3^\circ$ with decomposition is obtained in this manner. Recrystallization changes the melting point to $152\text{-}3^\circ$.

Morpholine thiosulfate from morpholine, sulfur and sulfur dioxide. — In a 250 ml. three-necked flask fitted with a mechanical stirrer, a thermometer, and a glass tube leading to the bottom of the flask is placed 16 g. (0.5 mole) of sulfur and 50 ml. (.57 mole) of morpholine. A current of sulfur dioxide gas is passed into the

³ Treadwell and Hall, Analytical Chemistry, Volume I, John Wiley and Sons, Inc., New York, 1937, pp. 412-13.

flask until the reaction mixture turns faint yellow in color. This requires about thirty minutes. The flask is immersed in an ice bath to prevent the temperature of the reaction from exceeding 100°C. To separate the crude morpholine thiosulfate from other possible products, the mixture is dissolved in 150 ml. of methanol. This solution is then filtered and concentrated to about one-half its volume. After allowing this solution to stand in the refrigerator overnight 38.5 g. (47% yield based on morpholine) of product melting at 139-40° with decomposition is obtained. In order to further purify the crude product the material is dissolved in methanol, filtered, cooled. There is thus obtained 20 g. (24%) of material melting at 146-51°C. Further recrystallization from methanol raises the melting point to 152-3°.

Identification of morpholine thiosulfate. — The material obtained from the reaction between morpholine and sulfur at room temperature reacted with either hydrochloric or sulfuric acid and also gave positive tests for thiosulfate ion when treated with Fe^{+++} , Ag^+ , KI and I_2 , and KMnO_4 . The benzene sulfonamide prepared from an alkaline solution of the compound ⁴ melted at 117-18° and showed no depression of the melting point when mixed with the benzene sulfonamide prepared from an authentic sample of morpholine.

The material prepared from morpholine and sulfur alone showed no depression of the melting point when mixed with morpholine thiosulfate prepared by the sulfur dioxide reaction.

Analyses:

Calculated for $[\text{O}(\text{CH}_2\text{CH}_2)_2\text{NH}]_2\text{S}_2\text{O}_3$ C 33.56%, H 6.29%,
N 9.79%, S 22.4%, Found C 33.57%, H 6.92%,
N 9.45%, S 22.6%

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⁴ Shriner and Fuson, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, 1948.