

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

**THE SULFUR DERIVATIVES OF THE SIMPLE AMINES. I.
AMINE HYDROSULFIDES¹**BY MARVIN ACHTERHOF,² ROLLIN F. CONAWAY² AND CECIL E. BOORD

RECEIVED APRIL 15, 1931

PUBLISHED JULY 8, 1931

During the preparation of the polysulfides of certain organic bases it was noted that a white crystalline deposit was formed in the upper part of the reaction chamber and in the inner tube of the condenser. Since, under the conditions of the experiment, the principal constituents of the vapor phase were free amine and hydrogen sulfide, it seemed probable this deposit was the amine hydrosulfide. An examination of the literature revealed the fact that the hydrosulfides of the simple amines have not been definitely described.

As some of our more prominent theories on the mechanism of the activation of sulfur³ assume the formation of amine hydrosulfides and polysulfides, it has seemed altogether worth while to examine more carefully into the nature of these products.

Very early in the history of amines Wurtz⁴ observed a reaction between ethylamine and hydrogen sulfide when the two gases were brought together in a reaction chamber immersed in an ice-bath. The product was a white crystalline compound which soon turned yellow but no analysis or other descriptive details were given. Isambert⁵ in his vapor pressure studies measured the vapor pressure of ethylamine and diethylamine sulphydrates but did not separate the free compounds. Kindler⁶ has assumed the formation of dimethylamine hydrosulfide and attributed to it the function of a catalyst in the addition of hydrogen sulfide to benzonitrile. Peters,⁷ on the other hand, has studied the action of hydrogen sulfide upon several simple amines at the temperature of the carbon dioxide-ether bath. He concluded that under these conditions the normal sulfides were formed. The products were obtained as white crystalline powders all decomposing below 0°.

Bineau⁸ more than ninety years ago studied the interaction of ammonia and hydrogen sulfide by volume. He came to the conclusion that the

¹ Presented, in part, before the Division of Organic Chemistry of the American Chemical Society, at the meeting in Detroit, September 8, 1927.

² This paper is abstracted from a part of the dissertation of Marvin Achterhof as presented in partial fulfilment of the requirements of the degree of Doctor of Philosophy to the Faculty of the Graduate School of the Ohio State University, August, 1926 and from the Master's Thesis of Rollin F. Conaway at the same institution, in June, 1927.

³ Scott and Bedford, *J. Ind. Eng. Chem.*, **13**, 126 (1921).

⁴ Wurtz, *Ann.*, **76**, 331 (1850).

⁵ Isambert, *Jahresb.*, 81 (1883).

⁶ Kindler, *Ann.*, **431**, 201 (1923).

⁷ Peters, *Ber.*, **40**, 1479, 1481 (1907).

⁸ Bineau, *Ann. chim. phys.*, **67**, 230 (1838); **68**, 435 (1838); **70**, 261 (1839).

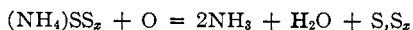
normal sulfide is stable only at very low temperatures, the usual form of the salt being the hydrosulfide. The work of Bloxam⁹ on ammonium hydrosulfides, sulfides and polysulfides is almost the only detailed study in the field. Although Bloxam obtained many of the sulfides of ammonium in the solid state, his reactions and analyses were almost wholly made on aqueous solutions. Ammonium hydrosulfide was obtained in colorless needles and scales but chiefly as a porcelain-like deposit by leading ammonia and hydrogen sulfide simultaneously into a bottle cooled with ice. The preparation of the pure hydrosulfide was found to depend upon having the hydrogen sulfide always in excess.

Using a procedure somewhat analogous to that of Wurtz, Peters and Bloxam, the hydrosulfides of twelve of the simple amines have been prepared. The successful preparation of these products may be accomplished by bringing together the dry, free amine and an excess of dry hydrogen sulfide at a temperature below 0°, and in the complete absence of air. The formation, filtering, washing and drying must be done in an atmosphere of hydrogen sulfide.

The solid amine hydrosulfides are rapidly decomposed on exposure to air. Those of low molecular weight show an appreciable vapor pressure of free amine and hydrogen sulfide, but the chief cause of their instability arises from a rapid decomposition by oxidation. The hydrosulfides of the more volatile amines are spontaneously oxidized with an almost quantitative deposition of free sulfur. Those of the less volatile amines are oxidized under the same conditions to give large yields of the corresponding thio-sulfate. All of these changes occur without the product taking on a color deeper than the tinge of yellow characteristic of free sulfur.

In the light of the above facts it would seem necessary to adopt a mechanism for the oxidation of these solid hydrosulfides different from that used by Bloxam in explaining the transformations characteristic of ammonium hydrosulfide in aqueous solution. He says: "These changes may be explained as follows. In the first stage, polysulfide alone is formed. . . . At the surface of the liquid some of the aqueous solution of ammonium hydrosulfide is resolved into ammonia, water and hydrogen sulfide, the latter undergoing oxidation and yielding water and sulfur. This sulfur then acts on ammonium hydrosulfide forming polysulfide. . . . There is not the slightest ground for supposing ammonium disulfide to be formed.

"In the second stage, the polysulfides are acted on by oxygen, sulfur being liberated.



"In the third stage, the sulfur acts upon ammonia as follows



resulting in the production of ammonium sulfite and hydrosulfide.

⁹ Bloxam, *J. Chem. Soc.*, **67**, 277 (1895); **77**, 753 (1900).

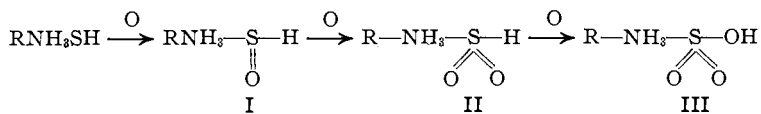
"In the fourth stage it will be observed that there are now two modes in which sulfur may combine, namely, by union with ammonium sulfite, thereby transforming it into thiosulfate or by acting on ammonium hydrosulfide whereby more polysulfide is formed."

It is true that stages (I) and (II) would account for the quantitative deposition of sulfur by the oxidation of the lower amine hydrosulfides except for the fact that the mechanism requires the intermediate formation of the polysulfide. This seems a doubtful explanation in view of the fact that the product during these changes never takes on a color deeper than a faint yellow.

The mechanism indicated is objectional also from another point of view. Bloxam assumes a dissociation of the hydrosulfide previous to any oxidation. In solution this assumption offers no difficulty. But for the solid hydrosulfide such an assumption would mean a dissociation into gaseous amine and hydrogen sulfide. It seems scarcely logical to believe gaseous hydrogen sulfide will oxidize leaving approximately a quantitative deposition of sulfur at the point of generation. Experiment has shown that dimethylamine hydrosulfide is spontaneously oxidized in air with a deposition of more than 97% of its total sulfur.

By the same reasoning the mechanism as given seems inadequate to explain the formation of thiosulfates. It is true the amine hydrosulfides when confined in a closed space, as in the bottom of a test-tube or in a loosely stoppered bottle, decompose slowly with partial liquefaction of the product. Under these conditions the mass takes on the blood-red color indicative of polysulfide formation. But if the solid hydrosulfide is exposed as a mass of loose crystals or spread out in a thin layer, thus insuring a free circulation of air, the oxidation proceeds to the formation of thiosulfate with no evidence of polysulfide formation.

Since the amine hydrosulfides pass through the initial stage of the oxidation previous to dissociation, and since the oxidation can continue to the formation of thiosulfate without the polysulfide stage as an essential step in the process, a mechanism quite analogous to that commonly used to explain the oxidation of mercaptans to sulfonic acids or of thio ethers to sulfones would seem to be applicable to the present case.



T. M. Lowry¹⁰ has shown that the oxygen acids of sulfur corresponding to I and II must be expected to show marked instability when considered from the standpoint of their electronic structure.

The quantitative deposition of sulfur by the spontaneous oxidation of

¹⁰ Lowry, *Trans. Faraday Soc.*, 18, 289 (1923).

to keep the latter always in excess of an equimolecular amount. The hydrosulfide was deposited as an encrusted mass upon the walls of the reaction tube and suspended as feathery crystals. After a suitable deposit had been formed, the passage of the amine vapor was discontinued and 50–60 cc. of anhydrous ether admitted from the funnel A. The feathery crystals were loosened by shaking the tube and the suspension filtered into

the crucible and dried as described above. The encrusted mass adhering to the walls of the reaction chamber was dried *in situ*.

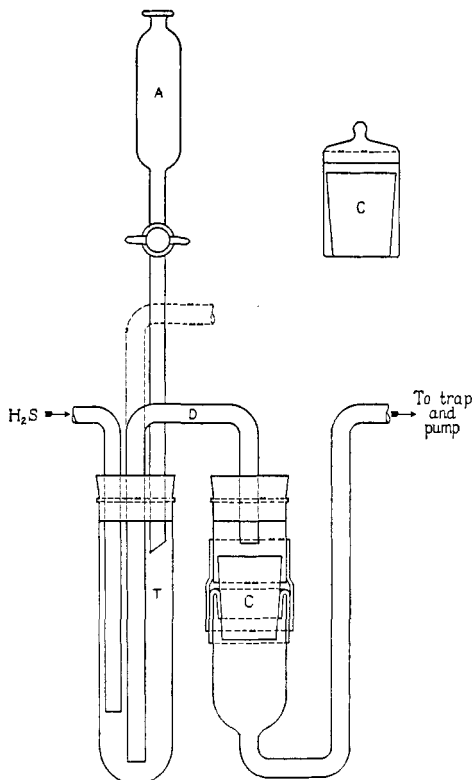


Fig. 1.—Apparatus for the preparation of amine hydrosulfides.

The amine hydrosulfides were usually obtained as white needle-shaped crystals, less frequently as clear colorless plates. Melting points taken in an open tube were quite indefinite since the products melted with decomposition over wide ranges of temperature. The molten hydrosulfides decomposed rapidly, with marked ebullition, as the hydrogen sulfide was expelled. Melting points taken in a sealed tube were higher and more clearly defined, but still were not sharp. The crystalline products in sealed tubes frequently sublimed below their melting points. Methylamine hydrosulfide melts at 90–92° in a sealed tube. The melting points of the higher members decrease with increasing carbon content. The hydrosulfide of

n-butylamine was obtained as a colorless, viscous liquid, which only partially solidified on cooling in a bath of ice and salt. Tri-*n*-butylamine hydrosulfide could not be induced to crystallize but on the other hand the isoamyl derivative melted at 62–67°.

The rapid decomposition of the amine hydrosulfides upon exposure to air necessitated that for analysis the samples be freshly prepared for each determination. The experimental conditions were set so as to provide a sample of from 0.2–0.5 g. in the crucible C. When the sample was thoroughly dried it was quickly transferred to the weighing bottle, W, and rapidly weighed.

The sulfur determinations were made by oxidizing the hydrosulfides in

sodium peroxide solution, acidifying and precipitating as barium sulfate. The nitrogen determinations were for the most part made by the Kjeldahl method but in a few cases it was determined as the amine hydrochloride by adding an excess of hydrochloric acid and evaporating to dryness.

The physical characteristics and analyses of twelve amine hydrosulfides, prepared as described above, are shown in Table I.

TABLE I
THE AMINE HYDROSULFIDES

| Formula | Crystal form | Melting point, °C. | | Analysis, S, % | | | Analysis, N, % | | |
|---|--------------------|--------------------|-------------|----------------|-------|-------|----------------|-------|-------|
| | | Open tube | Closed tube | Calcd. | Found | | Calcd. | Found | |
| $\text{CH}_3\text{NH}_2\text{SH}$ | Needles | 40-44 | 90-92 | 49.15 | 49.19 | 49.08 | 21.51 | 21.51 | 21.54 |
| $(\text{CH}_3)_2\text{NH}_2\text{SH}$ | Needles and leaves | 34-40 | ... | 40.51 | 39.85 | 40.58 | 17.69 | 17.62 | 17.72 |
| $(\text{CH}_3)_3\text{NHSH}$ | Leaves and plates | 15-20 | 28-30 | 34.37 | 33.90 | 33.81 | 15.04 | 14.94 | 14.92 |
| $\text{C}_2\text{H}_5\text{NH}_2\text{SH}$ | Needles | 50-55 | 55-57 | 40.51 | 41.01 | 40.92 | 17.69 | 17.76 | 17.94 |
| $(\text{C}_2\text{H}_5)_2\text{NH}_2\text{SH}$ | Needles | ... | 55-62 | 29.91 | 29.90 | 29.91 | 13.07 | 13.02 | 13.00 |
| $(\text{C}_2\text{H}_5)_3\text{NHS}$ | Needles | 25-27 | ... | 23.64 | 23.54 | 23.58 | 10.36 | 13.37 | 10.32 |
| $n\text{-C}_3\text{H}_7\text{NH}_2\text{SH}$ | Needles | 38-42 | 40-42 | 34.37 | 34.45 | 34.44 | 15.04 | 15.09 | 15.02 |
| $(n\text{-C}_3\text{H}_7)_2\text{NH}_2\text{SH}$ | Needles | 58-62 | 76-78 | 23.64 | 23.30 | 23.44 | 10.36 | 10.42 | 10.29 |
| $n\text{-C}_4\text{H}_9\text{NH}_2\text{SH}$ | (Oil) | 18-20 | ... | 29.91 | 28.52 | 28.65 | 13.07 | 13.51 | 13.30 |
| $(n\text{-C}_4\text{H}_9)_2\text{NH}_2\text{SH}$ | | 25-30 | 28-32 | 19.52 | 19.08 | 19.07 | 8.59 | 8.63 | 8.70 |
| $i\text{-C}_6\text{H}_{11}\text{NH}_2\text{SH}$ | Plates | 62-67 | ... | 26.42 | 27.00 | 26.62 | 11.56 | 11.53 | 11.52 |
| | | 80-85 | | | | | | | |
| $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{NH}_2\text{SH}$ | | 32-34 | ... | 13.84 | 13.85 | 13.83 | 6.06 | 6.15 | 6.14 |

The amine hydrosulfides are readily soluble in water and alcohol but only slightly soluble in ether and benzene. The solubility in water decreases and the stability increases with increasing molecular weight. The freshly prepared water solutions precipitate yellow cadmium sulfide and black lead sulfide from solutions of the respective acetates. The aqueous solutions soon become yellow on standing and will dissolve free sulfur, taking on a blood-red color indicative of the formation of polysulfides.

Oxidation of Dimethylamine Hydrosulfide.—A sample of 0.3418 g. of dimethylamine hydrosulfide was placed on a watch glass and exposed to the air for two days. The residue was dried and weighed. The weight of the residual deposit was 0.1344 g. and an examination showed it to be entirely free sulfur. This yield corresponds to 97.1% of the total sulfur content of the original sample.

Oxidation of Isoamylamine Hydrosulfide. Preparation of Isoamylamine Thiosulfate.—A quantity of the isoamylamine hydrosulfide was exposed to the air for several days. The product took on a slightly yellowish tinge. At no time did the product assume the blood-red color indicative of polysulfide formation. The major product was purified from the small quantity of free sulfur by recrystallization from water. The purified product was crystalline, stable and free from water of crystallization.

Analysis for nitrogen by the Kjeldahl method and titration by standard iodine solution gave the following results. Subs., 0.3000, 0.3000: 10.06, 10.03 cc. of 0.20845 *N* HCl. Found: N, 9.79, 9.76. Calcd. for $(\text{C}_5\text{H}_{11}\text{NH}_2)_2\text{S}_2\text{O}_3$: N, 9.78. Subs., 0.1000, 0.1000, 0.1000: 34.80, 34.60, 34.62 cc. of *N*/100 iodine. Calcd. for $(\text{C}_5\text{H}_{11}\text{NH}_2)_2\text{S}_2\text{O}_3$: 34.73 cc.

Isoamylamine thiosulfate partially sublimes when heated to 176° and melts with decomposition at 192-196°. Its aqueous solution decolorizes permanganate, precipitates sulfur when acidified with hydrochloric acid and gives a white precipitate, which slowly changes through brown to black, when treated with silver nitrate solution. These reactions are characteristic of the thiosulfate ion.

Several residues, formed by the spontaneous oxidation of a number of amine hydrosulfides, had been standing in open tubes for eight months. The residue from *n*-butylamine hydrosulfide was large in comparison with the others at hand. Recrystallization of this product from water yielded a white crystalline compound which began to sublime at 175° and melted with decomposition and charring at 180–193°.

Analysis for nitrogen and titration with standard iodine gave the following results. Subs., 0.3000, 0.3000: 11.23, 11.20 cc. of 0.2485 *N* HCl. Found: N, 10.93, 10.90. Calcd. for $(C_4H_9NH_2)_2S_2O_3$: N, 10.85. Subs., 0.1000: 38.86 cc. of *N*/100 iodine. Calcd. for $(C_4N_9NH_2)_2S_2O_3$: 38.90 cc.

The residues from *n*-propyl and methylamine hydrosulfides were extracted with water and the solutions evaporated to dryness. The amount of product in each case was too small to be analyzed quantitatively, but qualitative tests were positive for the thiosulfate ion. The residues from trimethyl and trimethylamine hydrosulfides proved to be entirely free sulfur.

Summary

The hydrosulfides of twelve of the simple amines have been described. These include the hydrosulfides of methyl-, ethyl-, *n*-propyl-, *n*-butyl-, *i*-amyl-, dimethyl-, diethyl-, di-*n*-propyl-, di-*n*-butyl-, dibenzyl-, trimethyl- and triethylamines.

The amine hydrosulfides undergo rapid oxidation upon exposure to air. Those derived from the more volatile amines leave an almost quantitative deposition of sulfur. Those derived from the less volatile amines are oxidized to the corresponding thiosulfates. These oxidation reactions take place without evidence of polysulfide formation. A mechanism is suggested for the oxidation reactions which fully accounts for all the facts observed.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS
WELLCOME AND COMPANY]

RHODANINES. I. DERIVATIVES OF β -PHENYLETHYLAMINES

BY JOHANNES S. BUCK AND CLIFFORD S. LEONARD

RECEIVED APRIL 15, 1931

PUBLISHED JULY 8, 1931

Apparently no rhodanine derivatives of β -phenylethylamines have been described previously in the literature. The pharmacological properties of such compounds may prove interesting on account of their relation to compounds such as adrenaline, epinine, etc. On the other hand, they also contain the rhodanine (keto-thioketo-thiazolidine) ring, which, when alkylated in the methylene carbon, has been shown by Leonard¹ to possess pharmacological properties of the same type as the barbituric acid derivatives. The compounds described in the present paper contain an unsubstituted or an ether-substituted benzene ring and a non-alkylated

¹ Leonard, *Medd. Vetenskapsakad. Nobelinst.*, Bd. 4, No. 14 (1921).