[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF IOWA STATE COLLEGE]

THE FORMATION OF ETHYL MERCAPTAN FROM ETHYL IODIDE IN AQUEOUS HYDROGEN SULFIDE SOLUTIONS AND ITS BEARING ON THE MECHANISM OF THE PRECIPITATION OF METALS BY HYDROGEN SULFIDE

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A recent paper on "The Mechanism of the Precipitation of Metals by Hydrogen Sulfide"[1] closes with the statement, "After a careful consideration of the evidence including that offered in the experimental part, the writers do not hesitate to draw the conclusion. . . .that the precipitation of the heavy metals with hydrogen sulfide, both in acid and in alkaline solutions, will eventually be regarded in the light of the coördination theory of Werner, as are already so many of the subjects of chemistry."

The evidence presented includes several lines of experiment and citation. Among others Smith and Semon describe the following experiments.

> "Into each of six numbered test-tubes, almost filled with freshly saturated hydrogen sulfide water, about 1 cc. of ethyl iodide or bromide was introduced. Nothing further was added to Mixture No. 1; to Nos. 2, 3 and 4, respectively, freshly precipitated ferrous sulfide, cadmium sulfide and mercuric sulfide were added; to No. 5 was added a slightly acidified solution of ferrous chloride; and to No. 6, dried and heated mercuric sulfide, either black or red. The tubes were then tightly stoppered and allowed to stand. In Nos. 2, 3 and 4, the odor of mercaptan was detected within two or three hours, and in No. 4, in case ethyl iodide was used, crystals of mercuric iodide appeared within a week. In No. 6, the odor of mercaptan was noted in about a week; but in Mixtures 1 and 5 the odor of mercaptan could not be detected at any time during a month."

From this group of experiments the following conclusions were drawn.

> "The formation of mercaptan as noted in these experiments cannot be ascribed to a direct reaction between hydrogen sulfide and ethyl halide, because, in the absence of metallic sulfide, these substances yield no mercaptan. Nor can the formation of the mercaptan be ascribed to a catalytic action of the metallic ion because, in the absence of metallic sulfide, no mercaptan is formed in the mixture containing ferrous chloride. We are forced to the conclusion that in the tubes containing the sulfide precipitates, in which alone mercaptan formation takes place, *both hydrosulfide and sulfide are present, in equilibrium, and that the formation of mercaptan is due to an exchange of halogen for hydrosulfide radical.* The formation of the mercaptan may therefore be represented by the following equations: $MS + H_2S \rightleftharpoons M(SH)_2$; and $M(SH)_2 + 2C_2H_5I \rightleftharpoons MI_2 + 2C_2H_5SH$."

As small an amount of ethyl mercaptan as 2×10^{-9} mg. is said to be detectable by odor.[2] If mercaptan forms by the reaction between ethyl iodide and precipitated sulfides, it might form from ethyl iodide and a saturated solution of hydrogen sulfide in which the concentration of SH ions[3] is 0.95×10^{-4} at 25°.

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[1] Smith and Semon, THIS JOURNAL, **46**, 1325 (1924).

[2] Norris, "Organic Chemistry," second ed., McGraw-Hill Book Co., **1922**, p. 362.

[3] Stieglitz, "Qualitative Chemical Analysis," The Century Co., **1921**, Vol. I, Part II, p. 200.

If this concentration is insufficient, however, there should be an HS-ion concentration obtainable by adding ammonium hydroxide to the hydrogen sulfide solution which would be sufficient to form mercaptan. The concentration of the hydrogen ion should be more important than the presence of precipitated sulfides unless adsorption plays an important part in the reaction. The effect of concentration of hydrogen ion on the formation of mercaptan from ethyl iodide in a saturated solution of hydrogen sulfide was determined by varying the acidity of the solution.

Experimental Part

Effect of Acidity on Formation of Mercaptan.—Five cc. of freshly saturated hydrogen sulfide water was placed in each of twenty numbered test-tubes. No acid or base was added to No. 1; to Nos. 2 to 10 were added increasing amounts of ammonium hydroxide; and to Nos. 11 to 20 were added increasing amounts of hydrochloric acid.

The acidity ranged from 3 *N* acid through neutral to 3 *N* base. Five drops of ethyl iodide were then added to each. The tubes were stoppered and allowed to stand for one day Upon opening the tubes, the odor of mercaptan was detectable in every tube, the intensity decreasing with the acidity. Contrary to Smith and Semon's results,[1] these experiments show that mercaptan *is* formed by the action of ethyl iodide on hydrogen sulfide in the absence of precipitated sulfide, and even in acid solutions.

Effect of Sulfides on Formation of Mercaptan in Hydrogen Sulfide Water.—Hydrogen sulfide alone, lead, antimonous, mercuric, silver, cupric, bismuth, cadmium and stannic sulfides were used in this experiment. Each metal sulfide was freshly precipitated, washed with distilled water, and then transferred to a test-tube containing freshly saturated hydrogen sulfide water. After the mixture had been shaken for an hour, 5 cc. was transferred to another tube. To the remainder, neutral salt was added if necessary to coagulate colloidal material, and the mixture was filtered. Five cc. of the clear filtrate was then transferred to another tube. A tube containing 5 cc. of hydrogen sulfide water alone was also prepared. Into each of the tubes thus prepared, five drops of ethyl iodide were introduced. The tubes were stoppered and allowed to stand. At intervals of 15 minutes each tube was opened, and the time noted until the first odor of mercaptan was detectable. The results are given in Table I.

TABLE I

SULFIDES IN HYDROGEN SULFIDE WATER

Sulfide	H_2S and all filtrates	PbS	Sb_2S_5	HgS	AgS	CuS	Bi_2S_3	CdS	SnS_2
Time in hrs. and min. before C_2H_5SH is detected	12	2:15	2:15	2	2:30	2:30	2:15	2	2:15

These results show that precipitated sulfides greatly accelerate the formation of mercaptan in hydrogen sulfide solutions. This may, however, be due in whole or in part to the adsorption of hydrogen sulfide and ethyl iodide by the precipitated sulfides.

To determine whether other adsorbents have an accelerating effect similar to that of the precipitated sulfides, the following experiments were made.

Effect of Adsorbing Agents on the Formation of Mercaptan in Hydrogen Sulfide Water.—The adsorbing agents used in this experiment were bone black, charcoal, aluminum hydroxide, gelatin, barium sulfate, cotton, potato starch and silicic acid.

Each of the above substances containing no added metal sulfide was washed and placed in a test-tube containing 5 cc. of freshly saturated hydrogen sulfide water. Five drops of ethyl iodide were added to each. The tubes were stoppered and the time elapsing before the formation of mercaptan was determined as before. The results are given in Table II.

Table II

Adsorbing Agents in Hydrogen Sulfide Water

Substance	H_2S alone	Bone black	Charcoal	$Al(OH)_3$	Gelatin	$BaSO_4$	Cotton	Potato starch	Silicic acid
Time in hrs. and min. before C_2H_5SH is detected	12	1:45	12	1	6	3	10	8	12

These results show that some adsorbing agents greatly accelerate the formation of mercaptan. It is quite conceivable that the metal sulfides act in a similar manner.

Conclusions

1. The formation of ethyl mercaptan from ethyl iodide and hydrogen sulfide in the absence of solids and the retarding effect of the increase in the concentration of hydrogen ions indicate that the HS-ion is one of the reactants.

2. The fact that adsorbing agents other than freshly precipitated metal sulfides also increase the rate of reaction between ethyl iodide and hydrogen sulfide would indicate that adsorption instead of the formation of complexes of the Werner type causes the increase in rate of formation of ethyl mercaptan, when these solids are present.

Summary

1. Ethyl mercaptan forms when ethyl iodide is introduced into aqueous solutions of hydrogen sulfide. The rate of its formation decreases as the acidity increases.

2. The presence of freshly precipitated metal sulfides or of some adsorbing agents increases the rate of formation of ethyl mercaptan from ethyl iodide in saturated hydrogen sulfide solutions.

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