

THE PHOTOSYNTHESIS OF SEMI-MUSTARD GAS, 2-CHLOROETHYL  
2-HYDROXYETHYL SULFIDE<sup>1</sup>WALTER H. C. RUEGGERBERG, WALTER A. COOK,<sup>2</sup> AND E. EMMET REID*Received August 22, 1947*

The compound 2-chloroethyl-2-hydroxyethyl sulfide, commonly referred to as semi-mustard gas, or simply as semi-H, is known to be an intermediate in the hydrolysis of mustard gas (1). Ogston (2), as well as Woodward and Owens (3) have isolated this compound after hydrolyzing mustard gas or one of its analogs.

At the time this work was done, a method for the synthesis of semi-H had not been reported in the published chemical literature (see footnote 1). Since then, Fuson and Ziegler (4) have reported the photochemical combination of ethanolmercaptan and vinyl chloride, while Grant and Kinsey (5) prepared semi-H by treating thiodiglycol with thionyl chloride in chloroform. Apparently, the work of Fuson and Ziegler (4) was performed while this work was in progress.

Prior to the appearances of the papers by Fuson and Ziegler and Grant and Kinsey, it appeared advisable to prepare semi-H by the novel reaction consisting in the photochemical addition of ethanolmercaptan to vinyl chloride:



The method used was an adaptation of that first developed by Vaughn and Rust (6) and later by Salzberg, Ellingboe and Lazier (7) and others (8).

Two methods were worked out for effecting the photochemical condensation of ethanolmercaptan to vinyl chloride. In the first method, vinyl chloride was absorbed at atmospheric pressure in a mixture consisting of the mercaptan and an inert solvent such as methanol or benzene under constant irradiation from a 100-watt CH<sub>4</sub> mercury vapor lamp as supplied by the General Electric Company. The solvents employed in this particular process should be capable of dissolving both reagents and product, and in addition should transmit the ultraviolet radiation down to about 3000 Å. This reaction is carried out at about 20–25°.

In the second, the preferred method, the photo-condensation was carried out using liquid vinyl chloride and ethanol mercaptan in sealed tubes. The mixtures so prepared were irradiated under water by means of an S-4 mercury vapor lamp. Since no inert solvent is used in this process, it is only necessary to open the tubes and allow excess vinyl chloride to escape. This procedure is superior insofar as that the reaction rate is faster and purification by distillation of the solvent is unnecessary.

<sup>1</sup> The work here reported was completed early in 1944; however, due to security reasons, publication was delayed. In the interim, Fuson and Ziegler (see reference 4) have published their results of the photosynthesis of semi-mustard gas from mercaptoethanol and vinyl chloride. Although these authors employed essentially the same reaction, the work described in this paper deals with the same synthesis under different conditions, indicating at the same time the rate of the reaction. The permission of the Chief, Chemical Corps has been granted for the publication of this article.

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TABLE I  
FORMATION OF SEMI-H IN BENZENE AT ATMOSPHERIC PRESSURE<sup>a</sup>

EXPT NO.	AMYL DISULFIDE CATALYST, G.	IRRADIATION TIME, MIN.	MAXIMUM REACTOR TEMPERATURE, °C.	WEIGHT OF PRODUCT, G.	UNREACTED MERCAPTAN, %	CONVERSION OF ETHANOLMERCAPTAN TO SEMI-H, %
1	0.0	60	19.5	312.9	11.77	55.0
2	.84	60	22.0	338.5	3.96	88.6
3	.84	60	23.0	333.9	4.25	82.7
4 <sup>b</sup>	.84	60	22.0	227.1	4.81	86.7

<sup>a</sup> Quantity of reagents indicated in text. Ethanolmercaptan purity 98%.

<sup>b</sup> Only 100 ml. benzene used in this run. Product was cloudy.

TABLE II  
FORMATION OF SEMI-H IN METHANOL AT ATMOSPHERIC PRESSURE<sup>a</sup>

EXPT. NO.	CATALYST, G.	IRRADIATION TIME, MIN.	MAXIMUM REACTOR TEMP., °C.	WT. OF PRODUCT, G.	UNREACTED MERCAPTAN, %	CONVERSION OF ETHANOLMERCAPTAN TO SEMI-H, %
1	0.85 g. amyl disulfide	15	16.0	265.1	24.26	21.1
2	.85 g. amyl disulfide	30	18.5	280.0	14.14	50.6
3	.85 g. amyl disulfide	45	20.0	305.8	4.17	84.4
4	.85 g. amyl disulfide	60	22.0	318.3	0.10	99.6
5	.85 g. amyl disulfide	75	20.5	320.9	0.07	99.7 <sup>b</sup>
6	.85 g. amyl disulfide	90	21.0	316.5	0.01	99.9 <sup>c</sup>
7	.0	45	19.5	294.7	10.13	63.5
8	.0	60	19.0	300.4	3.23	88.5

<sup>a</sup> Quantity of reagents indicated in text. Ethanolmercaptan purity 98.0%.

<sup>b</sup> Product turbid at end of reaction.

<sup>c</sup> Insoluble solid separated. Analysis showed this material to contain 53.12% chlorine approximating the theoretical chlorine content of 65.71% for polyvinyl chloride.

TABLE III  
FORMATION OF SEMI-H IN METHANOL AT ATMOSPHERIC PRESSURE  
USING PURIFIED ETHANOLMERCAPTAN<sup>a</sup>

EXPT. NO.	AMYL DISULFIDE CATALYST G.	IRRADIATION TIME, MIN.	MAXIMUM REACTOR TEMP., °C.	WT. OF PRODUCT, G.	UNREACTED MERCAPTAN, %	CONVERSION OF ETHANOLMERCAPTAN TO SEMI-H, %
1	0.0	45	19.0	289.8	5.76	80.0
2	.0	60	22.0	310.1	1.15	95.7
3	.85	30	19.5	276.6	15.00	50.3
4	.85	45	22.0	307.8	2.20	91.9
5	.85	60	22.0	307.0	0.08	99.7

<sup>a</sup> Quantity of reagents indicated in text. Ethanolmercaptan purity 99.8%.

It has been shown previously (8), that a trace of amyl disulfide is a catalyst or perhaps better, a reaction promoter, for the photo-addition of mercaptans to vinyl chloride. As seen from the results in Tables I to V, amyl disulfide acts catalytically in the initial reaction period. Although disulfides boost the reac-

tion rate, they are not essential unless reaction inhibitors such as sulfur or copper are present. These facts, together with other evidence (9), led to the formulation

TABLE IV  
FORMATION OF SEMI-H IN SEALED TUBES USING 98.0% PURE ETHANOLMERCAPTAN<sup>a</sup>

EXPT. NO.	AMYL DISULFIDE CATALYST, G.	IRRADIATION TIME, MIN.	WT. OF PRODUCT, <sup>b</sup> G.	UNREACTED MERCAPTAN, %	CONVERSION OF ETHANOLMERCAPTAN TO SEMI-H, %
1	0.0	2	5.116	48.03	33.9
2	.0	5	6.519	14.33	71.1
3	.0	10	7.262	5.30	87.6
4	.0	15	7.428	3.67	91.2
5	.0	20	7.783	1.51	97.6
6	.0	25	8.019	0.45	101.7 <sup>c</sup>
7	.045	2	6.060	21.55	60.6
8	.046	5	6.969	8.46	80.7
9	.046	10	7.919	1.08	99.2
10	.046	20	7.930	0.83	99.5

<sup>a</sup> Quantity of reagents indicated in text.

<sup>b</sup> After degassing and evacuating.

<sup>c</sup> *Anal.* calc'd for C<sub>4</sub>H<sub>9</sub>ClOS: Cl, 25.22; S, 22.81.  
Found: Cl, 24.66, 25.09; S, 22.20, 22.26.

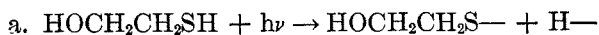
TABLE V  
FORMATION OF SEMI-H IN SEALED TUBES USING 99.8% PURE ETHANOLMERCAPTAN<sup>a</sup>

EXPT. NO.	AMYL DISULFIDE CATALYST, G.	IRRADIATION TIME, MIN.	WT. OF PRODUCT, G.	UNREACTED MERCAPTAN, %	CONVERSION OF ETHANOLMERCAPTAN TO SEMI-H, %
1	0.0	2	5.684	43.66	40.0
2	.0	5	6.648	21.25	65.4
3	.0	10	7.466	6.61	87.1
4	.0	15	7.387	10.20	82.9
5	.0	20	7.685	4.66	91.5
6	.053	2	6.119	32.23	51.2
7	.046	5	7.153	12.60	77.5
8	.045	10	7.707	5.21	92.0
9	.046	15	8.007	1.44	98.0
10	.046	25	8.241	0.20	102.2 <sup>b</sup>

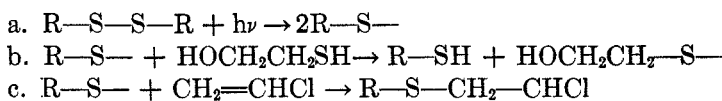
<sup>a</sup> Quantity of reagents indicated in text.

<sup>b</sup> *Anal.* Calc'd for C<sub>4</sub>H<sub>9</sub>ClOS: Cl, 25.22; S, 22.81.  
Found: Cl, 25.09; S, 22.96.

of an over-all reaction mechanism in the case of the disulfide-free reaction, which is postulated to be of a free radical chain nature:

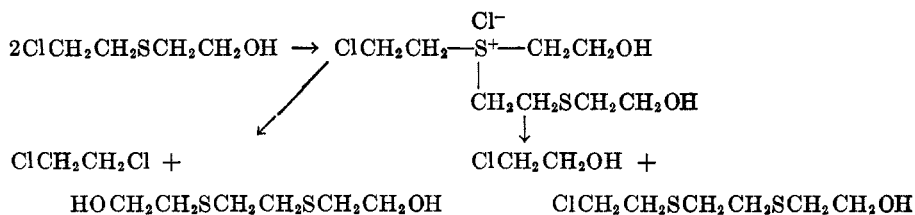


It has been shown that disulfides dissociate into thioalkyl radicals when irradiated with light of wavelengths longer than those required to rupture or excite the S—H bond (10). This fact suggests that disulfides, such as amyl disulfide used in this work, will initiate a chain more readily by breaking into two alkylthio radicals which, from the above mechanism, are recognized to be the chain carriers. The initial phases of the disulfide catalyzed chain are represented as follows:

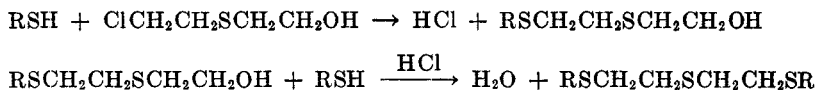


Although isolation of the semi-H produced either by the solvent method at atmospheric pressure or by the liquid vinyl chloride-sealed tube method is quite simple, the distillation of the product even at one mm. Hg pressure was accompanied by deterioration. It has already been pointed out that semi-H hydrolyzes very much more rapidly than mustard gas itself (1), thus indicating the greater reactivity of the residual chlorine atom in semi-H as compared with mustard. Ogston (2) attributes much of the instability of semi-H to the formation of sulfonium complexes with subsequent decomposition. Similar beliefs are presently held by Fuson and Ziegler (4) and Bell, Bennett, and Hock (11). As a result of the present investigation, it is believed that the decomposition of semi-H follows two courses, namely, the formation of sulfonium complexes, as pointed out by Ogston, and the reaction of semi-H with unreacted mercaptan to form hydrogen chloride, which in turn, partially at least, can form water and the chloride by reacting with the resulting glycol. These reactions are represented by the following equations:

*Sulfonium formation:*



*Elimination of hydrogen chloride:*



These two types of decomposition manifest themselves readily in the distillation of the product. Above 1 mm. Hg pressure, the distillations are accompanied by large residues which are free of sulfhydryl groups, and in which the increasing sulfur and decreasing chlorine content approximate that obtained from a polythio ether of higher molecular weight. This indicates the removal of lower molecular weight volatile decomposition products which contain chlorine.

## EXPERIMENTAL

*Synthesis of 2-chloroethyl 2-hydroxy ethyl sulfide.* a. *Runs at atmospheric pressure.* The apparatus used in this phase of the work consisted of a one-liter, three-necked Pyrex flask equipped with a mercury seal stirrer, thermometer, vinyl chloride inlet and outlet tubes, and a cold-finger type reflux condenser charged with a Dry Ice-acetone mixture. The flask was surrounded by a metal 4-liter bath into the side of which was installed a 6" x 6" Vycor window to allow the radiation from a CH<sub>4</sub> Hg-vapor lamp to impinge upon the reactants. Water at a temperature of 9 to 10° was circulated through the bath during a run. The flask was charged with 83.6 g. (1.05 moles) of ethanolmercaptan (obtained from the Carbide and Carbon Chemicals Corporation; purity 98.0% by iodimetric titration in absolute methanol) and 175.9 g. (2.25 moles) of benzene (Baker's C.P. grade). The entire system was swept out with dry nitrogen gas and gaseous vinyl chloride (E. I. duPont de Nemours & Co., cylinder grade) was passed into the reaction mixture under constant irradiation from the ultraviolet light. The amount of vinyl chloride absorbed was calculated from two dry-test gas meters which were inserted in the vinyl chloride inlet and outlet lines. In those runs where a catalyst was employed, the latter was added prior to the vinyl chloride passage. At the end of each run an aliquot sample was removed and titrated for unreacted mercaptan with iodine, using anhydrous methanol as solvent. The results of these runs are tabulated in Table I.

In Table II similar data are presented for the reaction of 1.05 moles of ethanolmercaptan in 4.94 moles of methanol as solvent in place of 2.25 moles of benzene.

In order to determine the effect of purity of ethanolmercaptan on the progress of the condensation, the crude mercaptan (purity 97.8% by iodimetric titration) was distilled in an all glass column and a fraction boiling at 44.5° at 6 mm. was collected. The purity of the distilled ethanolmercaptan was found to be 99.8%. As seen from Table III, this purified mercaptan gave better results than the undistilled material.

b. *Distillation of product.* The products of all runs, conducted in methanol at atmospheric pressure, in which the conversions of ethanolmercaptan to semi-H were greater than 90%, were combined for the purpose of isolating the product by stripping off methanol and subsequent fractionation. These operations were performed in a simple Fenske-type column approximately two feet in length and  $\frac{3}{4}$ -inch diameter, packed with  $\frac{1}{8}$ -inch helices. The initial pressure was 180 mm. which was slowly reduced to 4 mm. The stripped residue was analyzed for sulfur, chlorine, and free sulfhydryl groups.

*Anal.* Calc'd for C<sub>4</sub>H<sub>6</sub>ClOS: Cl, 25.22; S, 22.81.

Found: Cl, 19.83; S, 21.43; free SH groups (calculated as ethanolmercaptan), 0.05.

The stripped material was fractionated in the same column at 0.5–0.75 mm. A constant boiling fraction was isolated at 87°:  $n_D^{20}$  1.5205.

*Anal.* Calc'd for C<sub>4</sub>H<sub>6</sub>ClOS: Cl, 25.22; S, 22.81.

Found: Cl, 23.53; S, 21.63.

The kettle residue, which underwent visible decomposition, was also analyzed for chlorine and sulfur.

*Anal.* Found: Cl, 13.76; S, 26.08; free SH groups (calculated as ethanolmercaptan), nil.

c. *Runs in sealed tubes.* Pyrex tubes of approximately one-inch diameter and 60 ml. capacity were charged with 4.457 g. (0.057 mole) of ethanolmercaptan and 6.90 g. (0.11 mole) of freshly condensed vinyl chloride free of stabilizer and with a catalyst, if used. The tubes were cooled in a Dry Ice-acetone bath and sealed. They were suspended vertically on the periphery of a circular circulating water-bath. The tubes were consequently under water, as was the 100 Watt S-4 mercury vapor lamp at the center of the bath, at a distance of 11 cm. from each tube. By this radial distribution, an equal amount of radiant energy impinged upon each tube. After the desired exposure time, each tube was again chilled, opened, evacuated to constant weight at 50° and subjected to a residual mercaptan analysis. Table IV

contains the data obtained from ethanolmercaptan of 98.0% purity while in Table V reaction data obtained from the use of 99.8% pure ethanolmercaptan are presented.

d. *Preparation of amyl disulfide* ( $C_5H_{11}S$ )<sub>2</sub>. An aqueous solution consisting of 45.0 g. of potassium iodide, 34.1 g. of iodine, and 250 ml. of water was added slowly with stirring to 25.0 g. of amyl mercaptan until the iodine color persisted. The mercaptan used was obtained from Sharples Chemicals, Inc., and probably is a mixture of  $C_5$  mercaptans. After the reaction was complete, the small excess of iodine was reduced with sodium thiosulfate solution. The oily upper layer was separated and extracted with diethyl ether. Before distilling, the ether extract was dried over activated silica gel. The fraction boiling at 105–107° at 2.5 mm. (or 74–75° at 1 mm.) was collected:  $n_D^{25}$  1.4867.

*Anal.* Calc'd for  $C_{10}H_{22}S_2$ : S, 31.07. Found: S, 31.10.

#### SUMMARY

Two methods for the photosynthesis of 2-chloroethyl-2-hydroxyethyl sulfide from ethanolmercaptan and vinyl chloride are described. The effect of amyl disulfide as reaction accelerator, as well as the effect of the purity of ethanolmercaptan on the reaction, are presented.

The reaction mechanism is postulated to be of the free radical nature.

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