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The reaction of liquid hydrogen sulfide and hydrogen persulfide on organic compounds

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THE REACTION OF LIQUID HYDROGEN SULFIDE AND HYDROGEN

PERSULFIDE ON ORGANIC COMPOUNDS

BY

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A Thesis submitted to the Graduate Faculty
for the Degree of

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THE REACTION OF LIQUID HYDROGEN SULFIDE

WITH THE GRIGNARD REAGENT

THE REACTION OF LIQUID HYDROGEN SULFIDE AND HYDROGEN PERSULFIDE ON ORGANIC COMPOUNDS

INTRODUCTION

It is known that the Grignard reagent reacts vigoriously with water regenerating the hydrocarbon and supposedly the basic magnesium halide $Mg\overset{-X}{\underset{-OH}{}}$. The exact idenity of the basic magnesium halide has not been determined. By analogy one would predict that liquid hydrogen sulfide[1] when treated with the Grignard reagent would give the hydrocarbon and a thio-basic magnesium halide.

It was thought also that the sulfur analogue of $Mg\overset{-OH}{\underset{-Br}{}}$ namely $Mg\overset{-SH}{\underset{-Br}{}}$ might lend itself to more exact identification. If this prediction could be verified then we could be more certain of the composition of the oxygen analogue. This phase of the work was undertaken with this analytical problem in mind together with the desire to learn more concerning the chemistry of liquid hydrogen sulfide.

(1) For reactions in liquid hydrogen sulfide see papers by,

Quam, J. Am. Chem. Soc., 47, 103 (1925)

Ralston and Wilkinson, ibid., 50, 258 (1928)

Meints and Wilkinson, ibid., 51, 803 (1929)

Borgeson and Wilkinson, ibid., 51, 1453 (1929)

EXPERIMENTAL

A. Reaction of Naphthyl Magnesium Bromide with Liquid Hydeogen Sulfide.

To about 10 cc. of liquid hydrogen sulfide contained in a 75 cc. hard glass test tube immersed in an ether-carbon dioxide bath, was added drop by drop 25 cc. of a solution of naphthyl magnesium bromide in ether. Vigorous reaction immediately took place with the formation of a yellowish-white precipitate which settled to the bottom of the test tube. At the end of the addition the solution gave no evidence of the Grignard reagent[2] showing that the reaction was immediate and that hydrogen sulfide was in excess. A calcium chloride tube was then inserted in the test tube and the reaction mixture allowed to come to room temperature. Since there was no Grignard reagent present, it was permissible to treat the mixture with dilute hydrochloric acid to dissolve the basic magnesium compound and extract any product soluble in ether. This was done and from the ether extract 2.5 grams of naphthalene was recovered. A mixed melting point proved the identity of the naphthalene.

(2) Gilman and Schulze, J. Am. Chem. Soc., 47,2002-5 (1925)

The same reaction was carried out except a tube was used which was sealed up for a week at room temperature then treated with acid and extracted with ether. Before adding the acid negative test for the Grignard reagent was obtained. Identical results were obtained in both experiments showing that it was needless to carry the reaction out in sealed tubes. The basic precipitate of magensium bromide was not studied as the purity of the product was questionable i. e., the complete removal of naphthalene by ether. A similar reaction which should give an identical precipitate was studied however using a Grignard reagent which gave a gaseous hydrocarbon when thio-hydrolyzed with liquid hydrogen sulfide. Several similar precipitated. were also studied. (See "B" below.)

B. The Reaction of p-bromophenyl Magnesium Bromide with Liquid Hydrogen Sulfide.

Using the same procedure as outlined in "A" 25 cc. of p-bromophenyl magnesium bromide was added to an excess of liquid hydrogen sulfide. It was made certain that no unchanged Grignard reagent was present. About 4 grams of a liquid boiling at 154-155° C were recovered. The liquid was bromobenzene as was proven by preparing the nitro derivative which melted at 124.5-125° C.

The basic magnesium precipitate was washed

several times with dry ether by decantation,put in a vacuum desiccator and all liquid removed from it. A white powder remained which had a strong odor of hydrogen sulfide. A weighed sample of this was put in a 250 cc. conical flask in which was fitted a two hole stopper carrying a 125 cc. dropping funnel and a tube bent at right angles to the flask. This exit tube extended to the bottom of a 75 cc. test tube containing 50 cc. of cadmium chloride solution in strong ammonia. Dilute hydrochloric acid was added from the dropping funnel. A vigorous evolution of hydrogen sulfide took place immediately which was absorbed by the cadmium chloride forming the characteristic yellow cadmium sulfide. The solution in the flask was boiled for a few minutes to drive over completely the hydrogen sulfide. The cadmium sulfide precipitate and solution were acidified with hydrochloric acid and an excess of standard iodine solution added. The excess iodine was titrated with standard thiosulfate solution. The per cent of sulfur was 12.21%.

A series of such determinations was run using samples obtained from different Grignard reagents. Also determinations were made on the same sample immediately after it was prepared and a few days after its preparation and again six weeks after its preparation. The following table gives the history of the sample with

the percents of sulfur and magnesium found.

TABLE I. Analysis of the thio-basic magnesium halides.

sample	weight of sample	per cent sulfur	per cent magnesium	age of sample before analysis
p-bromophenyl magnesium bromide + H_2S	0.5369	12.21	not run	few days standing
phenyl magnesium bromide + H_2S	0.6331	9.22	17.63	
	0.5793	11.74	17.53	" " "
" " " " " "	0.2876	6.5	19.80	several days standing
" " " " " "	0.5928	no H_2S evolved	not run	sample dried on filter paper.
" " " " " " excess ether used	0.5732	10. 23	" "	no standing
" " " " " " conc. Grignard used	0.5266	6.92		
	0.5654	6.90	" "	" " "
dil. Grignard and dil. H_2S used.	0.4455	11.39	17.26	
	0.5798	11.14	17.00	" " "
10cc. C_2H_5MgBr 5cc. H_2S	0.4853	5.67	15.95	
	0.7996	5.65	15.65	six weeks standing
10cc. Grignard 10cc. ether 5cc. H_2S	0.7152		16.17	
	0.5838	7.92	16.49	" " " " "
10cc. Grignard 30cc. ether 5cc. H_2S	0.5210	7.70	18.19	
	0.8632		17.50	" " " " "
10cc. Grignard 50cc. ether 5cc. H_2S	0.3387	6.71	18.17	
	0.7268		18.27	" " " " "
5cc. Grignard 50cc. ether 5cc. H_2S	0.3206		17.24	" " " " "
	0.3209	trace		
theory for Br-Mg-S-Mg-Br		13.32	18.66	

The results of these analysis are interpreted in this way.

(a) The thiobasic magnesium halide $Mg\underset{X}{\overset{-SH}{}}$* is first formed which immediately loses a molecule of hydrogen sulfide giving the condensed product.

(b) This condensed product is relatively unstable and steadily loses hydrogen sulfide.

(c) If the thiobasic magnesium halide is prepared from concentrated reagents a material low in sulfur is obtained.

Other methods were used for analyzing this substance such as (1) decomposition with sodium peroxide (dangerous) (2) hydrogen peroxide in sodium hydroxide followed by precipitation with barium chloride. Consistent results however were not obtained. The magnesium was determined by diluting, boiling, and filtering the solution obtained after the hydrogen sulfide had been diven off and then precipitating as magnesium ammonium phosphate and weighing as the pyrophosphate. No satisfactory method for analyzing bromine in this residue was found. The following schemes were tried somewhat thoroughly but consistent results were not obtained.

Method A. The weighed sample was treated with cold dilute

(*) The product $MgBr_2.MgS$ is not at all improbable.

sulfuric acid to remove all hydrogen sulfide. Ammonium per-
sulfate was then added and the bromine given off collected
in potassium iodide and the liberated iodine titrated with
standard thiosulfate solution.

Method B. The weighed sample was treated with sulfuric
acid as in method "A" and then manganese dioxide added to
liberate free bromine which was then passed into potassium
iodide and the iodine liberated titrated with thiosulfate.

Method "A" was not reliable since it was found
that ammonium persulfate gave off some oxygen in the form
of ozone which would liberate free iodine from potassium
iodide.

Great care was used in preparing this basic
magnesium halide and the product should be quite pure. The
Grignard reagent was not exposed to the air, being trans-
ferred from the flask in which it was prepared directly to
the cooled tube containing the liquid hydrogen sulfide.
The delivery tube had filtering cloth on both ends to pre-
vent any finely divided magnesium which had not reacted
with the halide from passing over into the liquid hydrogen
sulfide.

SUMMARY

1. An attempt was made to analyze the thio-basic magnesium halide formed when a Grignard reagent is treated with liquid hydrogen sulfide.

2. An interpretation of the analysis is given.

PART II

REACTION OF HYDROGEN PERSULFIDE ON
ORGANIC COMPOUNDS

INTRODUCTION

Bloch and Hohn[3] in a series of articles pertaining to the chemistry of the persulfides of hydrogen called attention to the fact that all of the literature on the subject in texts or reference books is either incomplete or incorrect. With others[4] they cleared up several faulty ideas which were prevalent at that time and gave the first insight as to the structure of these bodies. Even now the chemistry of these compounds is far from being complete.

It occurred that these persulfides might give several reactions analogous to hydrogen peroxide since they, particularly the disulfide, are believed to be the analogue of hydrogen peroxide. Baeyer and Villiger[5] have prepared numerous peroxides by means of hydrogen peroxide in the presence of potassium hydroxide. Fenton[6] and others have made use of hydrogen peroxide in the presence of ferrous salts to bring about these reactions:

(3) Bloch and Hohn, Ber., 41, 1961-71 (1908)

(4) R.Schenck and V.Falcke, Ber., 41, 2600-3 (1908), (See. also Brunner and V. Vuilleumier. Abst. in C.A., 2, 3347 (1908); original not examined.)

(5) Baeyer and Villiger, Ber. 34, 738, (1901)

(6) Fenton, J. Chem. Soc., 47, 1899, (1894), 48, 774, (1895)

Glycollic acid, (OHCH$_2$COOH) = Glyoxylic acid (CHOCOOH)

Lactic acid (CH$_3$CHOHCOOH) = Pyruvic acid (CH$_3$COCOOH)

Tartaric acid (CO$_2$HCHOHCHOHCOOH) = Dihydroxy maleic acid
$$\text{(COOHCOH:COHCOOH)}$$

Primary amines (C$_6$H$_5$CH$_2$NH$_2$) = Aldehydes (C$_6$H$_5$CHO)

Walton and Jones[7] have shown that in general those substances that act as catalyzers to hydrogen peroxide in aqueous solutions act similarly when the peroxide is dissolved in nonaqueous solvents.

Also such reactions as the following have been effected by other workers.

Piperidine when oxidized with three percent peroxide solution, yields glutaric acid owing to the rupture of the ring. Benzene, with the peroxide, yields a certain amount of phenol while benzonitrile yields benzamide. Azo-compounds are converted into corresponding azoxy-derivatives, and phenol into dihydric phenols or quinones. The question arises can not the sulfides of hydrogen bring about similar changes.

Any reaction of the peroxide which occurs in alkaline solution is ruled out immediately since the persulfides are decomposed readily by alkalies. The use of

(7) Walton and Jones, J. Am. Chem. Soc., 38, 1956-61 (1916)

catalytic agents such as ferrous compounds of course is out
of the question since the catalyst itself would soon be
acted upon. Other inorganic catalysts are practically use-
less as is shown by the work of Walton and Parsons[8] who re-
port the following behavior of hydrogen trisulfide on in-
organic salt solutions when ether solutions of both the tri-
sulfide and the inorganic salts were used. Copper oleate
gave a red-brown colloidal precipitate; ferric chloride a
white precipitate, which redissolved; stannic iodide a
buff precipitate; silver nitrate no change, mercuric bro-
mide a yellow precipitate. As a check on the experiment
similar solutions of the salts were treated with a satur-
ated ether solution of hydrogen sulfide and in every case
a similar result was obtained. They concluded that the
behavior of the trisulfide in ether solution is essential-
ly the same as that of hydrogen sulfide. Because of the
extreme ease of decomposition of the disulfide the trisul-
fide alone was used in their experimental work.

In the case of organic compounds however we
found in this laboratory that the behavior of hydrogen
trisulfide is not the same as liquid hydrogen sulfide.
(See experimental part.)

(8) Walton and Parsons, J. Am. Chem. Soc., 43, 2546-7, (1921)

These same authors found that metallic oxides such as silver oxide, copper oxide, lead peroxide, stannic oxide, and magnetite brought about violent decomposition of the trisulfide. The effect was brought about by pouring small amounts of the sulfide on the oxide placed on a carefully cleaned watch glass.

The behavior of inorganic salts with the trisulfide was also studied. Most of them decomposed the trisulfide rapidly particularly copper and lead salts, the whole mixture turning dark.

Massive metals did not decompose the persulfide rapidly. They became coated with the sulfide of the metal and then the reaction ceased. Powdered arsenic, antimony, zinc and iron, however, brought about rapid decomposition.

It was found however that finely ground quartz, boric oxide and phosphorus pentoxide did not bring about decomposition. This last behavior suggests at once that quartz vessels are the ideal ones to use to handle these persulfides and that phosphorus pentoxide is the preferred drying agent.

The difficulty in preparing and purifying these compounds and the ease at which they decompose accounts no doubt for the reason that the chemistry of these bodies is not advanced as far as it might be.

CONSTITUTION

Bloch[9] has shown that Reb's[10] statement which claims that any polysulfide, irrespective of the amount of sulfur, yields the same product H_2S_2, is inaccurate. At low temperatures these substances are more stable and the tendency is to form chain compounds. At higher temperatures, being unstable, the compounds on the left side of the following equilibria are obtained; for H_2S_2:

$$-S=S{}^{-H}_{-H} \rightleftharpoons \quad HS\equiv SH \qquad \text{and for } H_2S_3$$

$$-S=S=S{}^{-H}_{-H} \rightleftharpoons \quad S=S-S{}^{H\ H} \rightleftharpoons HS-S-S-H$$
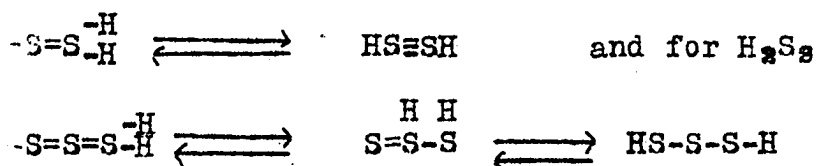
Hydrogen trisulfide is a persulfide of definite sulfur content, chemically bound, for if the sulfur is merely physically dissolved in H_2S_2 it would separate out when put in benzene. The change of colors with change in temperature is perhaps explicable by an intra-molecular change analogous to keto-enol tautomerism.

The yellow oily liquid that separates when an

(9) Bloch, Ber. 41, 1980-5 (1908)

(10) Reb, Ann., 246, 356-382 (1888)

excess of hydrochloric acid is added to a solution of a

polysulfide of an alkali is a complex mixture of sulfide

of hydrogen with dissolved sulfur. That sulfides higher

than the trisulfide do exist is evidenced by the existence

of addition compounds. Hoffman[11] prepared the strychnine

compound $(C_{21}H_{22}N_2O_2)$: H_2S_6 and Schmidt[12] prepared the

brucine compound, $(C_{23}H_{26}N_2O_4)_3 \cdot (H_2S_6)_2$. Both of these

were obtained by treating an alcoholic solution of stry-

chnine or brucine with an alcohol solution of ammonium

polysulfide. Brunner and Vuilleumier[13] were able to ob-

tain and characterize the following addition compounds:

$(C_6H_5CHO) \cdot H_2S_6$ from benzaldehyde; $(C_6H_4OCH_3CHO) \cdot H_2S_3$ from

anisic aldehyde; $(C_9H_8O) \cdot H_2S_4$ from cinnamic aldehyde and

$(C_6H_4O_2)_4 \cdot H_2S_5$ from benzoquinone.

Walton and Whitford[14] by determining at

various temperatures the composition of the liquid phase

in the system in which solid sulfur existed in equili-

brium with the hydrogen sulfides, established the exis-

(11) Hoffman, Ber., 10, 1087 (1877).

(12) Schmidt, Ber., 10, 1289 (1877).

(13) Brunner and Vuilleumier, Schweiz. Wochschr.. 46. 456-
438 (1908) Abst. in C:A.,2, 3347 (1908) Original not examined.

(14) Walton and Whiteford, J. Am. Chem. Soc.,45,601-6
(1923)

tence of a compound having the composition H_2S_n. These authors prepared a solubility curve of sulfur in hydrogen trisulfide, and found a break in the curve at -1.45° C. At this temperature the liquid has the composition very close to H_2S_6. Above this temperature the hexasulfide seems to decompose very readily. Below and above -1.45° C the liquid phase of sulfur in persulfides consist of a equilibrium mixture of various persulfides, always with the possibility of the presence of dissolved sulfur. The instability of hydrogen hexasulfide above -1.45° C explains the necessity of keeping the reaction mixture cold when preparing the yellow oil.

Dodonov and Medox[15] treated H_2S_2 with PCl_3 and obtained P_2S_5, PCl_2S and HCl according to the following reaction: $3H_2S_2 + 3PCl_3 \longrightarrow P_2S_5 + PCl_3S + 6HCl$. They believe the mechanism of the reaction is as follows: $PCl_5 + H_2S_2 \longrightarrow PCl_3(SH)_2$. The $PCl_3(SH)_2$ then reacting in two ways to form $PS_2Cl + HCl$ and $PSCl_3 + H_2S$. The PS_2Cl reacting with H_2S to form $P_2S_5 + HCl$. The complete equations are:

(15) Dodonov and Medox, Ber. 61, 1767-70 (1928).

(1) $PCl_3 + H_2S_2$ ------- $PCl_3(SH)_2$

(2) a. $PCl_3(SH)_2$ ------ $PS_2Cl + 2HCl$

    b. $PCl_3(SH)_2$ ------ $PCl_3S + H_2S$

(3) $2PS_2Cl + H_2S$ ------ $P_2S_5 + 2HCl.$

From these reactions they conclude that H_2S_2 has a structure similar to H_2O_2.

Bruni and Borgo[16] have prepared a number of persulfides of hydrogen and find that the proportion of sulfur added to the alkali sulfide has no influence on the composition of the hydrogen persulfide obtained. Cryoscopic examination of the various products dissolved in bromoform, indicates the existence in solution of compounds varying from $H_2S_5 - H_2S$ Paterno[17] criticizes the conclusions drawn by Bruni and Borgo concerning the formula of H_2S_x, and states that the cryoscopic constant of bromoform is variable and that no values obtained for the molecular weight of sulfur correspond exactly with the molecule S_8. Borgo and Amadori[18] repeated the work of Bruni and Borgo and state again that sulfur in bromoform gives cryoscopic results corresponding very exactly with the formula S_8.

(16) Bruni and Borgo, Atti. R. Accad. Lincei., 16,(2) 745-754 (1907). Abst. in Brit. Abst.,94,(2) 102, (1908) Original not examined.

(17) Paterno, ibid., 17, (2) 627-633 (1908). Abst. in Brit. Abst., 96, (2) 118, (1909). Original not examined.

(18) Borgo and Amadori, ibid., 18, (1) 138-141 (1909) Abst. in Brit. Abst., 96 (2) 309, (1909). Original not examined.

The failure of Bruni and Borgo to prepare higher sulfides by leaving H_2S_2 and H_2S_3 in contact with sulfur for forty-eight hours at ordinary temperature, led them to believe that the successive decomposition of the various hydrogen persulfides $H_2S_7 \longrightarrow H_2S_6 \longrightarrow H_2S_3 \longrightarrow H_2S_2 \longrightarrow H_2S$ is not a reversible reaction. This belief has been shown to be incorrect by Walton and Whiteford[19]. (See page 21).

(19) Walton and Whiteford, J. Am. Chem. Soc., 45, 601-6 (1923)

GENERAL PROPERTIES

The yellow oil with a specific gravity of 1.7 has a pungent odor. When first prepared the vapors coming off attack the eyes, membranes in the nose and throat much more intensely than they do a few days after preparation. Tap water causes a rather rapid decomposition of the per- sulfides. The oil is stabilized by hydrochloric acid and by benzene and dissolved sulfur. Paraffins, carbon disul- fide and chloroform simply dissolve it. Its decomposition is brought about by basic material in general. Ammonia and alkalies decompose it immediately. Amines cause sulfur crystals to rain down. Amine salts are not nearly so des- tructible since their basic properties has been weakened. Alcohol, acetone, ether cause decomposition. Unsaturated compounds as ethylene, cyanide, benzonitrile, phenyliso- cyanate, acetophenone bring about its decomposition. Many substances which decompose the persulfide appear to form with it highly unstable addition compounds.

PREPARATION

Scheele in 1777 found that if the yellow solution of calcium polysulfide is poured slowly into cold concentrated hydrochloric acid, a yellow oil separates which later was shown to be a mixture of persulfides.

Thenard's method consists in the decomposition of calcium persulfide by hydrochloric acid.

Brunner and Vuilleumier[20] also used a similar method during their study of hydrogen persulfide.

Bloch and Hohn[21] improved the method by observing certain precautions which are essential, especially the control of temperature, methods of preparing the alkali polysulfide and removal of any alkalinity in the glass by treating with dry hydrogen chloride gas. These authors by heating sodium sulfide with varying amounts of sulfur in an atmosphere of hydrogen for three hours on a water bath and dissolving the products in water obtained solutes of the composition Na_2S_2, Na_2S_3, Na_2S_4, Na_2S_5.

(20) Brunner and Vuilleumier, Schweiz. Wochschr., 46, 436-438 (1908)
    Original not examined. Abst. in C.A., 2, 3347 (1908)

(21) Bloch and Hohn, Ber., 41, 1961-1985 (1908).

These solutions when allowed to flow into a mixture of equal parts of ice and concentrated hydrochloric acid were decomposed yielding crude hydrogen persulfide.

Little work was done on these compounds until Walton and Parsons[22] greatly improved the method of preparation and purification. Their method consists in heating a mixture of C. P. sodium sulfide crystals, flowers of sulfur and water, on a water bath for three to four hours with occasional shaking. The flask containing the contents is closed with a Bunsen valve which obviates the necessity of passing hydrogen through the solution. The polysulfide solution thus obtained is allowed to run into cold concentrated hydrochloric acid kept at a temperature of -4° C to -10° C. The solution of the polysulfide is added below the surface of the acid at a rate of about three liters per hour. Fresh acid is substituted as soon as a brown scum appears floating on top of the acid, indicating decomposition of the persulfides. The polysulfides form first largely as emulsion which settles in about two hours. This liquid is separated by a separatory funnel and washed with distilled water and

(22) Walton and Parsons, J. Am. Chem. Soc., 43, 2539-48
(1921)

and dried over P_2O_5. To aid us in determining how rapidly

the persulfide was being added and also to obtain a more

even flow of persulfide into the acid, the apparatus as

described by Walton and Parsons was slightly modified. A

funnel was placed beneath the delivery tube from the sup-

ply jar which permits the operator to see just how rapid-

ly the solution is being added. The tube, fitted to the

end of the funnel which dips 'beneath the surface of the

acid, is bent into the form of a U. This prevents any

splattering back of liquid caused by pressure of hydrogen

sulfide. The distillation was carried out as described by

Walton and Parsons.

EXPERIMENTAL

Reaction of Crude Hydrogen Persulfide With Azobenzene.

6.0 grams of azo-benzene was dissolved in 50
cc. of dry benzene and placed in a 200 cc. three-necked
round-bottomed flask fitted with a stirrer, upright con-
denser and dropping funnel. To this was added slowly and
with stirring 5 cc. of crude hydrogen persulfide dissolved
in 30 cc. of dry benzene. There was no apparent reaction
at the start but after one hour a light yellow solid se-
parated out. The red color, however, of azo-benzene was
still present. 5 cc. more of persulfide dissolved in ben-
zene was then added. After three hours the mixture was
refluxed at the boiling point of benzene. After twenty
minutes of refluxing the red color of azo-benzene changed
to a pale yellow color showing destruction or change in
the azo-benzene. 10 cc. of the hot solution was removed
by means of a pipette and immediately on cooling a heavy
needlelike precipitate of sulfur came down. The liquid
above it, on decantation and cooling, gave up more of these
needlelike crystals. The entire solution was then cooled
down to 20° C when a large amount of yellow crystals came
out. These were filtered off and proved to be sulfur.
The benzene layer which was light yellow in color was

distilled to remove the excess solvent. On filtering, the
liquid which remained after removal of the benzene changed
almost entirely to a solid, having the appearance of hydrazo-
benzene with a melting point of 112° C. The solid was dis-
solved in ether which removed most of the sulfur, and then
recrystallized three times from 95% alcohol. A melting
point was then taken immediately which was found to be
122-124° C. This product of almost white leaflets was
placed in a vacuum desiccator to remove traces of alcohol.
After all the alcohol had been removed the leaflets melted
at 126° C. A mixed melting point was then taken which
showed no depression, showing the product to be hydrazo-
benzene. Reduction of the azo-benzene had been effected
by the persulfide in hot benzene solution.

Reaction of Crude Hydrogen Persulfide With Styrene.

In a 500 cc. round-bottomed flask fitted with
an upright condenser, were placed 20 grams of persulfide
dissolved in 180 cc. of pure dry benzene. To this was
added 40 grams of styrene. The solution, on adding the sty-
rene, became warm and at first had a clear yellow color.
Within a few minutes a distinct greenish tinge was noticed
and this was followed by a milky appearance. After a few
hours the mixture was refluxed at the boiling point of

benzene for six hours. Upon cooling sulfur crystals came out leaving a solution light yellow in color. Ammonia gas was passed through this benzene solution for five minutes. A heavy precipitate, orange red in color, came down. This solution was filtered and the benzene removed by a vacuum pump. The product which amounted to 42 grams was then taken up in ether and ammonia gas again passed through. The solution became red in color and some sulfur was deposited. This was filtered off, leaving a wine colored solution. The ether was then removed and a clear light yellow liquid remained. This liquid was then placed in boiling water under a vacuum of 30 mm. to remove any unchanged styrene. It was then taken up in ether and ammonia gas again passed through the solution. The wine color reappeared, but no deposition of sulfur. Upon passing air or illuminating gas through it and warming, the red faded out and the light yellow color returned. This change could be brought about apparently any number of times with no deposition of sulfur.

The same product was obtained by treating styrene and the persulfide with no solvent and keeping the temperature below 40° C. The analysis for sulfur using the Carius method follows:

wt. of sample	0.4520	0.3543
wt. of BaSO$_4$	1.2319	0.9645
% sulfur	37.44	37.40
Theory for sulfur in C$_6$H$_5$CH-CH$_2$		38.78%

$$C_6H_5CH-CH_2$$
$$\mid \quad \mid$$
$$S - S$$

The molecular weight determination gave 252.

All attempts to distill this product under a high vacuum proved futile. The material decomposed, giving off styrene and turning dark red with deposition of sulfur. It no longer added bromine, and was stable toward various reagents which included hypochlorites and hot dilute alkalies. It was not exposed to prolonged treatment with any reagent except nitric acid which converts it to water, carbon dioxide, and sulfuric acid. Its stability, in part, is doubtless due to its insolubility in aqueous media.

In all of the runs with styrene and the persulfide not a trace of ethyl benzene was found. An attempt to force the reaction of reduction was made by raising the temperature. 4.5 grams of freshly distilled styrene was mixed in 9.5 grams of persulfide in a 75 cc. hard glass tube, fitted with a delivery tube to catch any volatile material coming off. The persulfide was added until no heat was evolved. The mixture took on a green-

ish-yellow color. It was then treated on a water bath for two hours, but no apparent change took place. When it was heated on a glycerine bath for six hours at a temperature of 190-210° C, the material turned brownish-red color. No readily condensible product came off, however, hydrogen-sulfide was detected. The material was extracted with benzene four times, leaving a residue of sulfur. The benzene extract was cooled with ice water, filtered and distilled. After removal of all benzene a high boiling fraction remained which was deep red in color. Upon heating to 200° C about 1cc. of liquid, having the odor of styrene, came over. This liquid decolorized a bromine solution of CCl_4 immediately, indicating decomposition with the formation of styrene.

Reaction of Hydrogen Trisulfide on Amylene.

To 10 grams of freshly distilled hydrogen trisulfide 50 cc. of amylene were added. No reaction took place at once, but after a few hours a foul smelling compound similar to a mercaptan was very evident. Crystals of sulfur formed within a few days. After standing one week, the amylene was distilled off and the remaining product of greenish-yellow color was heated for five minutes in a bath of boiling water with a vacuum from a water pump,

but nothing came over. This solution was then treated with ether, causing sulfur to be deposited quite heavily. Dry ammonia was then passed through the solution immediately bringing down an orange semi-colloidal precipitate which would not settle. This mixture was stoppered up and set aside. At the end of two days all the precipitate had settled out and a clear liquid, smelling strongly of mer-captan, was obtained. The ether was removed and the li-quid, light yellow in color, failed to add bromine, showing that unsaturated properties had been removed. This sub-stance was stable toward hypochlorite, alkalies and acids, but concentrated nitric in the cold attacks it vigorously, liberating free sulfur along with a foul smelling liquid. A molecular weight determination gave 242 which shows that polmerization has taken place and no doubt accounts for the inactivity it shows with the reagents tried. The analy-sis for sulfur follows:

wt. sample	0.3158	0.2817
wt. BaSO$_4$	1.0430	0.9194
% sulfur	43.57	44.90
Theory for C$_5$H$_{10}$S	31.37	
Theory for C$_5$H$_{10}$S$_2$	47.76	

Unsymmetrical methylethylethylene was used.

Reaction of Crude Hydrogen Persulfide on Amylene.

To 95 grams of amylene (B. P. 31.5) dissolved in 100 cc. of benzene were added 50 grams of crude persulfide. This mixture was allowed to stand for a few days before separating the products formed. At the end of a week the excess amylene and most of the benzene were distilled off. Ammonia gas was bubbled through and some sulfur precipitated out. All of the benzene was now removed under a vacuum of 25 mm. and at a temperature of boiling water. The remaining yellow liquid began to distill at 122° C under 7 mm. Most of the material distilled at 142.5° - 144° C with slight decomposition. The distillate was redistilled and a fraction of fairly constant boiling came over at 132-135° C at 8 mm. This product was analyzed and the analysis follows:

wt. sample	0.3091	0.3944
wt. $BaSO_4$	0.9243	1.1680
% sulfur	40.43	41.08

Reaction of Liquid Hydrogen Sulfide on Styrene.

In a glass tube sufficiently strong to withstand the vapor pressure of liquid hydrogen sulfide at room temperature were placed 7.3 grams of freshly prepared and purified styrene. The tube and contents were then cool-

ed in an ether-carbon dioxide bath. Under these conditions
the styrene soon solidified. 4 cc. of liquid hydrogen sul-
fide was then added to the solidified styrene and the tube
sealed and put away for two weeks. At room temperature, the
two materials were completely miscible. The solution re-
sembled water with no deposit of sulfur. At the end of two
weeks apparently no change had taken place. The tube was
then opened and the hydrogen sulfide allowed to boil off.
The remaining liquid solidified on cooling in an ether-car-
bon dioxide bath as did pure styrene. The boiling point
also was the same. This experiment emphasizes the stability
of styrene toward reducing agents.

Reaction of Liquid Hydrogen Sulfide on Amylene.

The same procedure as described in the experi-
ment of liquid hydrogen sulfide and styrene was used here.
10 grams of amylene was placed in a strong glass tube and
cooled. 4 cc. of liquid hydrogen sulfide was added and the
tube sealed. After standing for two weeks at room tempera-
ture the mixture gave no evidence of reaction. After re-
moval of the hydrogen sulfide the remaining liquid was
identified as amylene. No odor of mercaptan was noticed.

Reaction of Benzenediazonium Chloride With Persulfide.

Pure benzenediazonium chloride was prepared according to the directions given in W. A. Noyes' Organic Laboratory Manual, and used immediately.

If the dry diazonium salt (caution: not over a few tenths of a gram of the salt alone should be placed together) is brought in contact with the persulfide at room temperature an explosion results immediately. Cooling modifies the reactions providing the diazonium salt is added slowly. When the persulfide is dissolved in carbon disulfide or benzene the reaction is rather mild. A strong evolution of hydrogen chloride was noticed. In carbon disulfide the mixture turns brown, and, when allowed to stand and then filtered, a red filtrate is obtained leaving a buff colored residue. This residue when heated explodes slightly, indicating some unchanged diazonium compound.

We are not certain just what the products formed are when the two substances are brought in contact. The odor of mercaptan was noticed.

The difficulty in this reaction lies in our ability to find a solvent for both the persulfide and the diazonium salt. There may be none when one realizes the constitution of these bodies, one soluble in organic solvents such as benzene, chloroform and carbon disulfide; while the other possessing the properties of a salt.

Isoamyl alcohol dissolves the diazonium salt to a limited extent, but too low temperatures must be used to prevent the alcohol from decomposing the persulfide.

In order to advance the chemistry of the persulfides to the degree where it might be, certain specifications must be attained. Just what these specifications are we now do not know, but can only mention reasonable possibilities. The finding of suitable catalysts would fill in a large gap. The chemistry of hydrogen peroxide would hardly be beyond the experimental stage were it not for the large and varied number of catalysts which are used with that substance. Lower temperatures will aid providing of course suitable catalysts are present. We already have a satisfactory solvent in benzene. As the situation now stands we have a substance with possibilities, but so far we have yet to meet the conditions that it demands, and until those conditions are met it will remain a substance that easily decomposes, raining down sulfur in spite of our present efforts to prevent it.

DISCUSSION

Azo-compounds are converted by oxidizing agent into azoxy, and by reducing agents, e.g., phenylhydrazine in the cold, into hydrazo or amino compounds.

Bloch and Hohn[23] report that hydrogen persulfide is both reducing and oxidizing or sulfurizing, on account of its relative stability as hydrogen trisulfide and its decomposition into hydrogen sulfide and sulfur. It occurred that the sulfur analogue of azoxy-benzene might readily be prepared by treating azo-benzene with hydrogen persulfide, and also by a change of conditions to prepare azo-benzene from hydrazo-benzene if this persulfide can function as an oxidizing agent. Under the conditions of experiment the persulfide acted only as a reducing agent. The change of azo-benzene into hydrazobenzene was affected, but no trace of the formation of the sulfur analogue of azoxy-benzene was found. The two negative phenyl groups joined by a double bond may have something to do with the failure of sulfur to add. Hydrazobenzene seems to undergo little if any change when treated with the persulfide in

(23) Bloch and Hohn, Ber., 41, 1971-5 (1908)

the cold. A faint red color was noticed when the two were allowed to stand in contact with each other for forty-eight hours, indicating some change into azo-benzene, but we are not justified in concluding that the persulfide brought about this color change, and acted as an oxidixing agent since hydrazo-compounds in contact with air are transformed into azo-compounds.

Bloch, Hohn, and Bugge[24] treated freshly distilled styrene with both the disulfide and trisulfide, and noticed that a large amount of heat was given off. Using the trisulfide, the temperature was not allowed to go above 35° C. After standing over night the excess persulfide was destroyed by bubbling ammonia gas through the solution. Then the residue which consisted chiefly of sulfur was extracted twice with boiling chloroform. After concentrating the solution, a yellow oil remained behind and in order to free this from any sulfur it was dissolved in methyl alcohol and then digested with alcoholic ammonium sulfide for twenty-four hours. It was then diluted with water and extracted with ether. On driving off the ether there remained a characteristic unpleasant and strong odorous, viscous
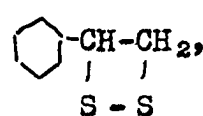
(24) Bloch, Hohn, and Bugge, J. Prakt. Chem., 82, 473-85
(1908)

almost colorless liquid. An analysis gave

C	59.35	Theory	C	57.07
H	4.85		H	4.79
S	29.8		S	38.13*

They conclude that the product is probably a mixture of

$\bigcirc$-CH-CH$_2$, metastyrene and oxidation products.
  | |
  S -S
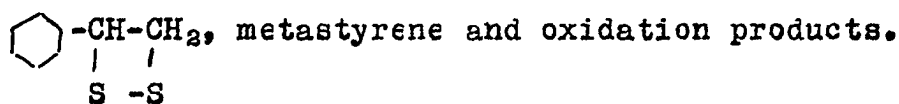
The method used by these workers in purifying the product seems questionable. Ammonium sulfide has a great tendency to add sulfur, and it seems quite likely that the reason their percent of sulfur ran so low was due to this great attraction. An appreciable amount of chemically combined sulfur may have been removed from the compound $\bigcirc$-CH-CH$_2$, by this digestion with ammonium sulfide
  | |
  S - S

for so many hours. Our analysis of the product prepared, and purified by a method not nearly so drastic, seems to substantiate our criticism of their method. Also when ammonia gas is passed through an ether solution of this product a reddish color is imparted. On passing air or illuminating gas through the solution, there by removing the am-

* This value is in error. It should be 38.78.

monia, the reddish tint disappears. What causes this color change is not known. A somewhat loose molecular addition product is probable. If ammonia gas when in contact with the product for only a few seconds can form a complex, loose to be sure, it seems reasonable that digestion for twenty-four hours would cause permanent removal of chemically combined sulfur.

Our method of purification which consists in passing ammonia gas through an ether solution two or three times, or until no more sulfur is precipitated, seems quite adequate considering the low solubility of sulfur in ether.

It is interesting to note that no ethyl benzene was formed from styrene when treated with the persulfide. Styrene is reduced by heating with hydriodic acid which, to be sure, is a potent reducing agent. The failure of the persulfide to reduce styrene is not due to any lack of intimate contact as the two are completely immiscible in each other. Rubber is strongly vulcanized by the persulfide which shows that the sulfur is not so tightly bound in the molecule. Azo-benzene is reduced by the persulfide only in boiling benzene which shows that the so-called active hydrogens of the persulfide are not as reactive toward double linkages as are the sulfur atoms, i.e., the speed of formation of the sulfurized compound far surpasses the

speed of formation of the hydrogenated product which would account for the lack of any appreciable amount of ethyl benzene. This argument may at first appear contrary to sound reason when we recall that azobenzene was reduced and not sulfurized. However, two negative phenyl groups joined by a double union will exert quite a repelling force on relatively heavy negative atoms such as sulfur. Azoxy-benzene, to be sure, is formed by the careful reduction of nitro-benzene, but azoxy-benzene is very readily reduced to azo-benzene. Also when hydrazo-benzene is exposed to the air, or treated with ferric chloride, azo-benzene is formed and not azoxy-benzene, which again shows the unstable property possessed by azoxy-compounds.

This sulfurized styrene body behaves quite differently when heated than does vulcanized rubber. Very recently Wolesensky[25] has shown that the rubber-sulfur compound in vulcanized rubber splits off hydrogen sulfide at all times and at all temperatures between 20° and the temperature of complete thermal decomposition. The reaction affords a new explanation of the formation of hydrogen sulfide during vulcanization, and possibly also, in part at

(25) Wolesensky, Bureau of Standards Jour.of Research 4, 501-513 (1930).

least, of the excess of combined sulfur over that required

by the formula C_5H_8S. No hydrogen sulfide was detected when

the sulfurized styrene was heated. The grouping $\begin{matrix} H & H \\ -C-C- \\ | & | \\ S-S \end{matrix}$

or a polymer apparently is very stable. A molecular weight

determination gave 252, which shows that polymerization has

taken place.

From the results obtained from styrene and the

persulfide, one would predict closely agreeing results when

amylene is substituted for styrene. Such results are veri-

fied from the analyses and the marked similarity in being

inert toward the same reagents. The amylenes polymerize

readily which probably accounts for the percent of sulfur

running low. The molecular weight of the sulfurized amy-

lene body was found to be 242, which shows that the degree

of polymerization is practically the same for this compound

as was found for the styrene body.

It seems to matter little whether the crude

persulfide is used or the pure trisulfide or disulfide in

regard to the final product formed, especially where the

reaction is heated or allowed to stand for a few days. As

previously mentioned, Bloch and Hohn[26] obtained the same

(26) Bloch and Hohn, J. Prakt. Chem., 82, 473-85 (1908).

dithio acids regardless of the persulfide used. The tri-
sulfide addition product loses a sulfur atom most easily.
Also in the distillation of the pure trisulfide about 15%
of the disulfide is always formed. Another point is the
effect of dissolved sulfur on the composition of the re-
sulting persulfide solution. The same product results
when either the disulfide and the trisulfide is saturated
with sulfur; and, due to the instability of these com-
pounds, free sulfur will be present. This will alter the
composition of the original persulfide, making it appear
that in many reactions little is to be gained by using the
pure di- or trisulfide. On account of this behavior the
crude persulfide was used in place of the individual com-
pounds in most of our work.

SUMMARY

1. A comparison of the reaction of hydrogen sulfide and hydrogen persulfide on unsaturated hydrocarbons has been made.

2. The oxidizing properties of hydrogen persulfide are wholly sulfurizing. Its reducing property is comparable to hydrogen sulfide.

3. The behavior of hydrogen persulfide with a number of reagents is mentioned.

4. Lower temperatures with suitable catalysts are named as possible specifications which must be met in order to advance the chemistry of the persulfides of hydrogen.