

1930

Reactions of inorganic compounds with liquid hydrogen sulfide

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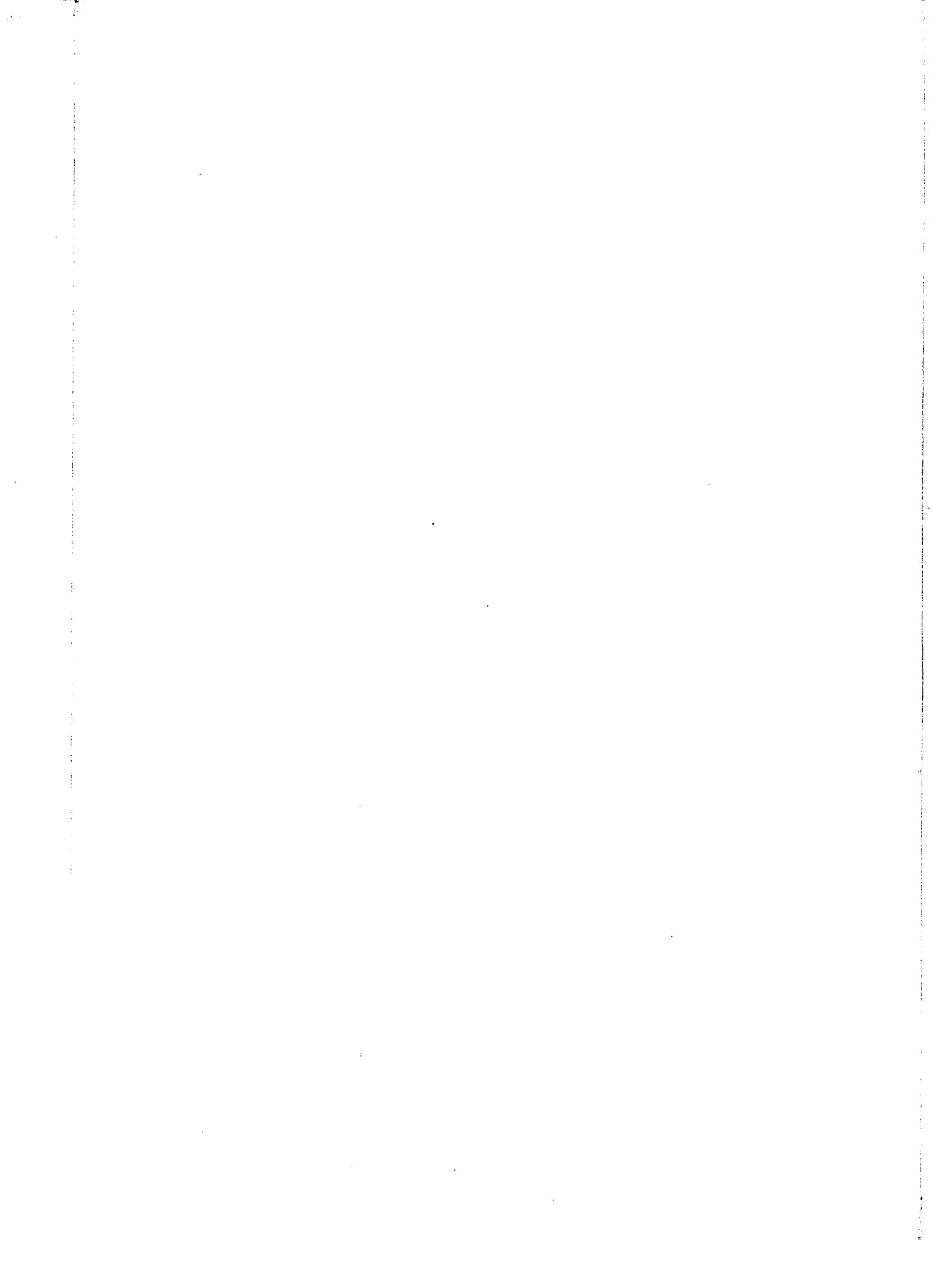
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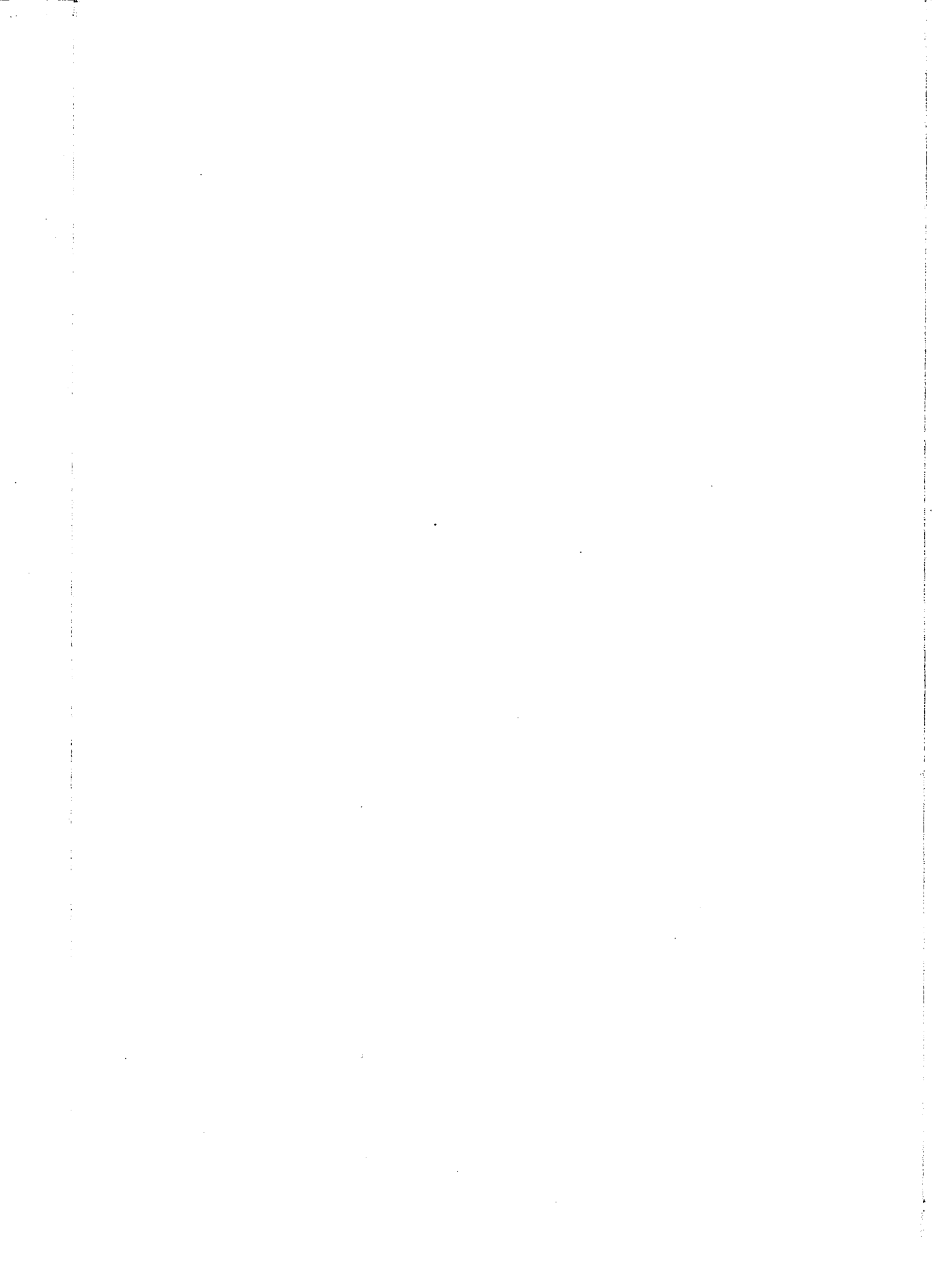
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REACTIONS OF INORGANIC COMPOUNDS
WITH LIQUID HYDROGEN SULFIDE

BY

Harlan Preston Guest

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject - Inorganic Chemistry

Approved

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TABLE OF CONTENTS

	<u>Page</u>
I. REACTIONS WITH LIQUID HYDROGEN SULFIDE	5
A. Introduction.....	5
B. Purpose of the Investigation.....	8
C. Preparation of Liquid Hydrogen Sulfide ...	8
1. Phosphorus Pentoxide as a Drying Agent for Hydrogen Sulfide.....	10
II. REACTION OF LIQUID HYDROGEN SULFIDE ON CALCIUM OXIDE AND CARBIDE	14
A. Experimental	14
1. Materials	14
2. Procedure and Observations	14
3. Analysis of Products	15
B. Discussion	19
III. PREPARATION OF THIO-CARBONATES	21
A. Experimental	21
1. Materials	21
2. Procedure and Observations	21
3. Analysis of Product	24
B. Discussion	24
IV. REACTION OF LIQUID HYDROGEN SULFIDE WITH LIQUID SULFUR DIOXIDE	26
A. Experimental	26
1. Materials	26

2. Procedure and Observations	26
B. Discussion	29
V. REACTIONS OF LIQUID HYDROGEN SULFIDE WITH OXYCHLORIDES	31
A. Experimental	31
1. Materials	31
2. Procedure and Observations	31
B. Discussion	36
VI. GENERAL SUMMARY AND CONCLUSIONS	38
VII. BIBLIOGRAPHY	41

I. REACTIONS WITH LIQUID HYDROGEN SULFIDE

Introduction

It has been found that liquid hydrogen sulfide is a rather poor solvent for inorganic substances altho it is an excellent one for organic. In the work from this laboratory Quam (1) determined the solubility and reactivity of over one-hundred and fifty elements, salts and organic materials. In the field of inorganic substances this work has been extended by Ralston (2) to cover a large number of chlorides which he found to fall into three general classes according to their reactivity, those that form addition products which may or may not be soluble, those that undergo thiohydrolysis, and those in which reduction of the halide occurs. Satwalekar (3) carried out an extensive study of the reaction of metals and oxides. His results show that the majority of the metallic elements slowly react at room temperature to form a hydrosulfide or a sulfide while the oxides are more reactive, some of them reacting rapidly at -77°C and most of them at room temperature to form sulfides; altho neither

1. Quam, J. Am. Chem. Soc., 47, 103-8 (1925)
2. Ralston and Wilkinson, *ibid*, 50, 258-64 (1928)
3. Satwalekar, Doctoral Thesis, Iowa State College (1928)

the metals, oxides nor their sulfide products were soluble in the solvent.

In the field of organic chemistry Ralston (1) studied the thiohydrolysis of nitriles and esters, Meints (2) the preparation of thio acids and thio aldehydes in liquid hydrogen sulfide, while Borgeson (3) carried out a more general study of the reactions of the various classes of organic compounds. The latter found that all classes of organic compounds, except the sugars and salts, were soluble in liquid hydrogen sulfide while several classes, namely, the unsaturated hydrocarbons and unsaturated groups in general, the aldehydes, ketones, nitriles, esters, acyl halides, amines and the Grignard reagent react with the solvent. A further study of the reaction of the Grignard reagent has been carried out by King (4) who interpreted the results of his analysis in the following manner: the thio basic magnesium halide is first formed which immediately loses a molecule of hydrogen sulfide giving the condensed product which is relatively unstable and steadily loses hydrogen sulfide.

1. Ralston, Doctoral Thesis, Iowa State College (1927)
2. Meints and Wilkinson, J. Am. Chem. Soc., 51, 803 (1929)
3. Borgeson and Wilkinson, *ibid*, 51, 1453-6 (1929)
4. King, Doctoral Thesis, Iowa State College (1930)

If the thio magnesium halide is prepared from concentrated reagents a material low in sulfur is obtained.

Purpose of the Investigation

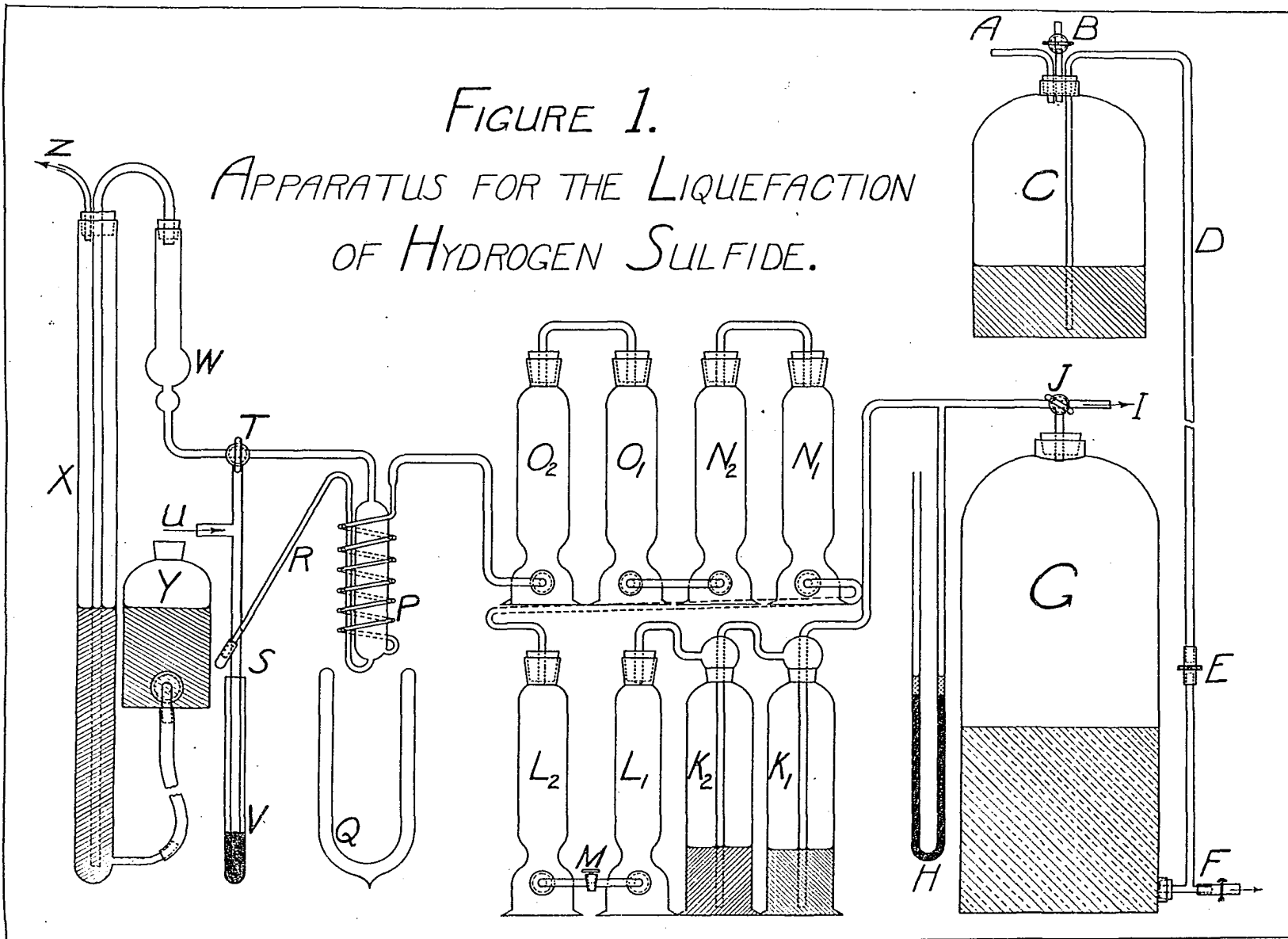
The purpose of this investigation is the preparation of inorganic thio compounds with liquid hydrogen sulfide.

Preparation of Liquid Hydrogen Sulfide

The apparatus used in the preparation of liquid hydrogen sulfide was a modification of that employed by Quam (1). The improved apparatus, shown in Fig. 1, the process of liquifaction, the details of manipulation and the subsequent handling of storage and reaction tubes has been fully described by Meints (2). Only a brief description of the apparatus will be given here. It can be divided into three sections, the generator for the preparation of gaseous hydrogen sulfide; the drying train to remove all moisture; and, the liquefaction coil and reservoir with the arrangement for the drawing off the liquid hydrogen sulfide. The drying train consists of two Drechsel wash bottles, (K_1) and (K_2), filled with water, and six drying towers, (L_1) and (L_2) filled with calcium chloride, (N_1) and (N_2) with aluminium sulfide,

1. Quam, J. Am. Chem. Soc., 47, 103-8 (1925)
2. Meints, Unpublished Masters Thesis, Iowa State College (1928)

FIGURE 1.
APPARATUS FOR THE LIQUEFACTION
OF HYDROGEN SULFIDE.



(O₁) and (O₂) with phosphorus pentoxide.

Phosphorus Pentoxide as a Drying Agent
for Hydrogen Sulfide

Lilienfeld and White (3), after performing the following experiment, conclude that phosphorus pentoxide is unfit to use as a dryer of hydrogen sulfide as it oxidizes this gas to sulfur dioxide. They passed a stream of hydrogen sulfide thru a drying tube containing phosphorus pentoxide for ten minutes. The gas from the drying tube was led into a sodium hydroxide solution. The phosphorus pentoxide was washed out with water and extracted with carbon disulfide. When the carbon disulfide was allowed to evaporate from an evaporating dish, yellow crystals of sulfur appeared. The sodium hydroxide solution was treated with dilute hydrochloric acid until neutral. The sulfide ions were precipitated with an excess of cadmium nitrate and the cadmium sulfide removed by filtration. The filtrate being tested with sodium nitroprusside to see if all sulfide ions were precipitated. The filtrate was found to decolorize malachite green solution (0.025 g. in 300 cc. of water),

3. Lilienfeld and White, J. Am. Chem. Soc., 52, 887 (1930)

and when barium nitrate was added a white precipitate formed. The precipitate dissolved in hydrochloric acid and the resulting solution decolorized iodine solution. They said that these tests indicated the presence of a sulfite.

This work was repeated in this laboratory along with a check run on hydrogen sulfide that had not been passed thru phosphorus pentoxide. The hydrogen sulfide was generated by the action of hydrochloric acid on iron sulfide in a Kipp generator and passed thru a Drechsel wash bottle half full of water to remove any hydrochloric acid carried over by the gas. The gas was divided into approximately equal parts, by means of a "T" tube and a pinch clamp, one part passed thru a drying tube containing phosphorus pentoxide into a sodium hydroxide solution while the other part passed directly into another sodium hydroxide solution. The phosphorus pentoxide was washed out with water and extracted with carbon disulfide. A fresh portion of phosphorus pentoxide, which had not been used, was dissolved in water and extracted with carbon disulfide. When the carbon disulfide was allowed to evaporate no difference could be noticed in the amount of residue left.

The two sodium hydroxide solutions were divided into equal parts and neutralized with dilute hydrochloric acid. The sulfide ions were precipitated from one of the parts of each solution with cadmium nitrate and from the others with cadmium chloride. The filtrates gave no test for sulfide ions with sodium nitroprusside and all decolorized malachite green solution. But the filtrates were now acid due to the formation of free nitric and hydrochloric acid in the respective solutions in the precipitation reaction. The solutions were again neutralized, this time with dilute sodium hydroxide, and upon testing with malachite green solution they did not decolorize it. It was further found that malachite green solution was decolorized by either dilute acid or base.

The above solutions were made alkaline with sodium hydroxide and concentrated. After being neutralized with hydrochloric acid, barium nitrate was added. The white granular precipitate formed was soluble in hydrochloric acid but would not decolorize a small drop of 0.01 normal iodine solution.

From these results it is apparent that the tests employed by Lilienfeld and White do not indicate

the presence of a sulfite and we may conclude that phosphorus pentoxide can be used as a drying agent for hydrogen sulfide.

II. REACTION OF LIQUID HYDROGEN SULFIDE ON CALCIUM OXIDE AND CARBIDE

Experimental

Materials:

CaO - prepared by dissolving precipitated calcium carbonate in hydrochloric acid, made slightly alkaline with ammonium hydroxide, filtered, the calcium precipitated as the oxalate with ammonium oxalate, filtered and ignited to the oxide at 900°C in a platinum dish.

CaC₂ - National Carbide Sales Corporation. By analysis 95 - 96% CaC₂.

Procedure and Observations:

The reactions were carried out in 20.5 x 2.5 cm. pyrex test tubes enclosed in heavy steel cylinders. Each cylinder had a needle valve in the cap. Five to ten grams of the solid was placed in the test tube which was then cooled to -77°C and about 20 cc. of liquid hydrogen sulfide added. The tube was transferred quickly to the steel cylinder and the cap screwed down. After two weeks or more the needle valve was opened allowing the excess hydrogen sulfide to escape, and the product removed.

The product from the hydrogen sulfide treatment of the calcium oxide was a light pink or flesh colored, fluffy substance which was analyzed immediately as it was rather unstable giving off hydrogen sulfide and on longer standing liberating sulfur. On treatment with hydrochloric acid a violent evolution of hydrogen sulfide took place.

The product from the calcium carbide was a light yellow powder with a mercaptan odor. Upon extraction with anhydrous ether the odor was removed and a white powder remained. The powder did not yield acetylene with water and gave off hydrogen sulfide on treatment with dilute acid. The ether extract was light yellow, after distilling off the ether a small quantity of yellow liquid remained which turned red on further heating. On standing in a tightly stoppered bottle, the unextracted product turned a reddish brown while the extracted material slowly changed from white to greenish yellow; in both cases sulfur was liberated.

Analysis of Products

The calcium was determined by precipitating it as the oxalate with ammonium oxalate from a slightly ammoniacal solution, dissolving in dilute sulfuric acid

and titrating with standard potassium permanganate solution.

Sulfur was determined either by the evolution method or by oxidation to sulfate with liquid bromine in potassium hydroxide solution, precipitating and weighing as barium sulfate.

In the evolution method the weighed sample was placed in a 500 cc. conical flask fitted with a three hole rubber stopper carrying a 125 cc. dropping funnel, a tube with a stop-cock and another tube bent at right angles to the flask. The tube with the stop-cock extended almost to the bottom of the flask and was connected with a cylinder of nitrogen which was used to sweep the liberated hydrogen sulfide from the flask. The exit tube was connected to a tall 300 cc. Drechsel wash bottle containing 100 cc. of ammoniacal cadmium chloride solution. Dilute hydrochloric acid was added from the dropping funnel causing a vigorous evolution of hydrogen sulfide which was absorbed by the cadmium chloride solution forming cadmium sulfide. The solution in the flask was boiled for a few minutes and nitrogen was allowed to pass slowly thru the system to insure the removal of any residual hydrogen

sulfide that might remain in the flask. The excess ammonia in the Drechsel wash bottle was neutralized with hydrochloric acid, an excess of standard iodine solution added, followed by additional hydrochloric acid to decompose completely the sulfide. The excess of iodine was titrated with standard sodium thio-sulfate solution.

Consistent results were not obtained in the analysis of the product from the reaction between liquid hydrogen sulfide and calcium oxide, as is shown by the following table:

	% sulfur	% calcium
Tube #1.	40.48	46.62
	48.71	45.86
	38.01	42.67
Tube #2.	43.68	39.93
	42.50	41.55
Tube #3.	43.30	42.97
Tube #4.	48.76	40.90
Tube #5. *	41.58	48.89
	42.94	49.20
	43.85	47.60
Tube #6. **	43.33	
Theory for CaS	44.44	55.55
$\text{Ca}(\text{SH})_2$	60.35	37.73

* the analysis was run on this tube after it had stood in a desiccator over sulfuric acid for two weeks.

** this result was obtained by the Carius method.

An attempt was made to determine the ratio between calcium and sulfur by placing an unweighed sample immediately into potassium hydroxide solution and analyzing aliquot parts. From the results obtained on three different samples the ratio of sulfur to calcium was calculated to be 1 to 1.149; 1 to 1.136; 1 to 1.123. The sulfur in the first ratio was determined by the evolution method while the last two were by oxidation with liquid bromine and weighing as barium sulfate.

The results from the analysis of the product from the calcium carbide are shown in the following table:

	% sulfur	% calcium
Tube #1. *	47.73	52.77
	49.52	50.64
	50.83	50.30
Tube #2. **	49.47	50.75
	50.63	51.30
Tube #3. ***	36.82	51.84
	36.89	51.70
	36.60	
Tube #4. ***	38.00	51.45
	38.07	51.43
	37.73	
Tube #5.		50.90

	§ sulfur	§ calcium
Theory for CaS	44.44	55.55
Ca (SH) ₂	60.35	37.73

* this is an analysis on the unextracted sample, sulfur determined by the evolution method.

** this sample was extracted once with ether, sulfur by the evolution method.

*** samples extracted three or four times with ether, sulfur determined by the potassium hydroxide - liquid bromine method.

Discussion

The product from the reaction between liquid hydrogen sulfide and calcium oxide was unstable giving off hydrogen sulfide on standing and therefore was not dried. Water was probably the other product from the reaction and could easily have interfered with the analysis. It is also possible that the water formed in the reaction slowly hydrolyzed the product, causing it to give off hydrogen sulfide. In order to test this assumption the work on calcium carbide was taken up in which it was hoped that the other product of the reaction would not interfere with the compound being analyzed.

Considering the fact that the calcium carbide used was not over 95 - 96% pure, (the purity was determined from the percentage calcium and the amount of residue insoluble in dilute acid) it is probable that calcium sulfide is the solid formed in this reaction. Quam (1), who did not separate the reaction products, states that his observations indicate the possibility of the formation of a thioacetaldehyde as described in Richtex's Organic Chemistry I, 202. This would apply to the yellow liquid with the mercaptan odor formed in the reaction.

1. Quam, Doctoral Thesis, Iowa State College (1924)

III. PREPARATION OF THIO-CARBONATES

Experimental

Materials

$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ - C P crystals

K_2S - fused lump

CaS - prepared in part II

NH_3 - commercial cylinder

CS_2 - C P Mallinckrodt Chemical Works

Procedure and Observations

The reactions were carried out in large size storage tubes. About 10 cc. of liquid hydrogen sulfide were transferred to the tubes, an equal amount of carbon disulfide added and then three or four grams of the solid sulfide. In the case of ammonium sulfide about 10 cc. of liquid ammonia were added. The tubes were sealed and observed over a period of several months.

Potassium and calcium sulfides do not form thiocarbonates under these conditions.

Hydrated sodium sulfide formed two layers in the tube, the top layer being clear while the small bottom layer was orange red. Both layers were liquids.

On cooling the bottom layer solidified and was found to be sodium thio-carbonate dissolved in the water of crystallization of the sodium sulfide. The top layer was the hydrogen sulfide and excess carbon disulfide.

In order to determine if either solid potassium hydroxide or hydrogen chloride gas would catalyze the reaction other tubes were sealed containing them in small amounts. The same results were obtained as above.

This reaction was carried out in absolute alcohol solution. The hydrogen sulfide was dissolved in alcohol, carbon disulfide in alcohol added, the resulting solution was clear. One tube of this solution was sealed and was unchanged after standing for a month. When liquid ammonia was added a rather vigorous reaction took place with the formation of a yellow solid. The tubes were sealed and placed in the storage tank. In two days the solid and liquid had changed to an orange red color. On cooling to -77°C the solid became lighter in color and a yellow solid separated out of the liquid. The tube was opened and washed out with ether. The orange solid decomposed fairly rapidly in air giving off hydrogen sulfide and

ammonia. It was soluble in water and gave the following reactions: dilute silver nitrate - reddish brown precipitate turning dark on standing; dilute lead acetate - red precipitate turning black on standing; dilute ferric hydroxide - an intense red color giving a greenish black precipitate on standing; dilute cupric acetate - a red color and some reddish brown precipitate; dilute acetic acid - decomposed giving off hydrogen sulfide and the solution was yellow finally going to colorless. On standing for several days under a mixture of alcohol and ether, in a bottle with a one hole stopper carrying a drying tube containing anhydrous calcium chloride, the orange solid gave off hydrogen sulfide forming a more stable crystalline body.

This new product did not further decompose when kept under ether. It was soluble in water and gave the following reactions: dilute lead acetate - yellow precipitate; dilute silver nitrate - yellow precipitate turning dark; dilute cupric acetate - yellow precipitate turning dark; dilute ferric hydroxide - intense red color giving a greenish black precipitate on standing. It is soluble in alcohol and can be recrystallized from it by ether, giving a white

flocculent solid which gave the same reactions as the yellow solid. It gradually decomposes in contact with air giving off hydrogen sulfide, ammonia and carbon disulfide.

Analysis of Product

The compound gave the following analysis:

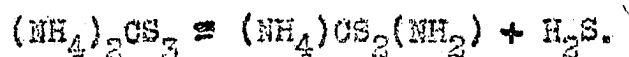
% nitrogen	% sulfur
25.21	58.19
25.46	57.85
25.41	58.15
25.72	58.85

which agrees very closely with ammonium dithio carbonate, $(\text{NH}_4)_2\text{CS}_2(\text{NH}_2)$, which has 25.47% nitrogen and 58.19% sulfur.

Nitrogen was determined by the Kjeldahl method and sulfur by that of Carius.

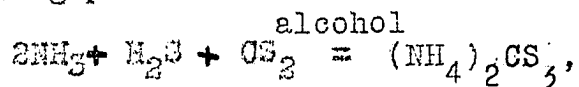
Discussion

According to Mellor (1) Zeise (2) found that ammonium thiocarbonate when left with alcohol in a closed vessel decomposed according to the following equation,



1. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry VI, 122 (1925 Ed.).
2. Zeise, Ann. chim. phys., (2) 26, 66 (1824)

From this it is apparent that the orange colored compound formed is ammonium thiocarbonate and the reaction taking place in the sealed tube is probably



which on standing under a mixture of alcohol and ether breaks down into ammonium dithio carbamate and hydrogen sulfide.

IV. REACTION OF LIQUID HYDROGEN SULFIDE WITH LIQUID SULFUR DIOXIDE

Experimental

Materials

SO₂ - a cylinder of liquid from Wilkens-Anderson Company.

Procedure and Observations

The reaction was carried out in large storage tubes. These tubes were cleaned with chromic acid solution, washed with distilled water and dried with alcohol and ether. The ether fumes were driven out by passing a stream of air, dried by phosphorus pentoxide, thru them. They were then placed in the cooling bath of ether and solid carbon dioxide.

The sulfur dioxide was dried by passing it thru a drying tower containing phosphorus pentoxide and liquified in a large test tube placed in a cooling bath of ether and solid carbon dioxide.

About 5 cc. of the liquid sulfur dioxide were transferred from the test tube to each of the two reaction tubes in the cooling bath and about 10 cc. of

liquid hydrogen sulfide added. The sulfur dioxide soon solidified and two layers were formed in the tube. Two hours later the tubes were carefully sealed and annealed. At this time there was a little sulfur on the surface of the solid sulfur dioxide where the hydrogen sulfide came in contact with it. The tubes were wrapped in towels and placed in the storage tank. A few minutes later the first tube placed in the tank was shattered by the excessive pressure in the tube and then the second. The interval between the explosions very nearly corresponded to the time required to take the tube from the cooling bath, wrap it in a towel and place it in the storage tank.

In order to watch the reaction another tube was cleaned and dried in the same manner except that it was placed in an electric oven for two hours at 140°C while the stream of dry air was passing thru it to insure the removal of all the ether vapors. It was then allowed to cool to room temperature with the dry air still passing thru and placed in the cooling bath. About 5 cc. of sulfur dioxide was liquified directly in the tube and twice as much liquid hydrogen sulfide added. The tube was carefully sealed and annealed.

Again there was a slight deposit of sulfur at the interface of the solid sulfur dioxide and liquid hydrogen sulfide which did not appear to increase on standing in the cooling bath for twelve hours.

In order that the tube could be observed from this point it was not placed in the storage tank but in a tall liter beaker filled with kerosene. This was placed behind a heavy glass screen to protect the observer from flying glass. The purpose of the kerosene was to prevent moisture from condensing and freezing on the surface of the tube and thus make it impossible to further observe the contents of the tube. About four minutes after the tube was placed in the bath more yellow solid began to form, then in the next five seconds the contents appeared to boil with a large amount of yellow solid forming in the body of the liquid and the tube exploded.

To arrive at an approximate value for the temperature at which the reaction took place, tubes of ether and alcohol were cooled to the temperature of the cooling bath (-77°C). These were placed in a kerosene bath at room temperature and the time noted for the rise to 0°C . The average determined by several runs

was three and one-half minutes.

Discussion

Anhydrous liquid hydrogen sulfide and liquid sulfur dioxide react vigorously with the formation of free sulfur in a sealed tube, which is in agreement with the work of Quam (1). The exact temperature at which the reaction took place was not determined but by a comparative method it was found to be above 0°C.

Pressure, which depends upon the temperature, must have a marked influence on the reaction as Mathews (2) found that there was no reaction at the temperature of solid carbon dioxide and that in an open vessel the liquids boiled away completely without action when the temperature was raised.

Antony and Magri (3) state that there must be an ionizing liquid present to bring about the reaction between the liquids. Mathews (2) carried out experiments with hydrogen sulfide and sulfur dioxide in both the liquid and gaseous state in the presence of a third substance. He found that substances that brought about the reaction of the gases at ordinary temperature,

1. Quam. J. Am. Chem. Soc., 47, 103-8 (1925)
2. Mathews, J. Chem. Soc., 129, 2270-3 (1926)
3. Antony and Magri, Gazz. chim. ital., 35, 206-26 (1905)

as liquids, had no effect on the liquid mixture if they were solids at the temperature of solid carbon dioxide. For example: ice, aniline, benzaldehyde, allyl alcohol and glycerol which are solids at this temperature bring about no reaction, altho at ordinary temperatures, when liquid, they cause immediate reaction; while ether, alcohol, acetone and substances that are liquids at both temperatures cause immediate reaction.

Biltz and Keuneche (1) did not get sulfur dioxide and liquid hydrogen sulfide to react as stated by Quam (2) and say that this might be due to the degree of dryness or that they worked at lower temperatures or their observations were over a shorter period of time.

In their investigation Lang and Carson (3) found that a reaction took place forming free sulfur and water. Their reaction was carried out in a sealed tube but they do not state the temperature and say that the drying of the gases probably was not thorough enough.

In this laboratory precautions were taken to insure the dryness of the gases and all alcohol and ether vapors were driven out of the reaction tubes.

1. Biltz and Keuneche, Z. anorg. allgem. chem., 147, 171-87 (1925).
2. Quam, J. Am. Chem. Soc., 47, 103-8 (1925).
3. Lang and Carson, Proc. Chem. Soc., 21, 158-60 (1905).

V. REACTION OF LIQUID HYDROGEN SULFIDE
WITH OXYCHLORIDES

Experimental

Materials

SOCl_2 - two samples used, one prepared by Mr. Gittens in this laboratory, the other from Eastman Kodak Company.

SO_2Cl_2 - Eastman Kodak Company.

NOCl - prepared in this laboratory.

POCl_3 - prepared in this laboratory.

SeOCl_2 -

VOCl_3 - Dr. F. M. Brown and Mr. Griffiths.

Procedure and Observations

When the thionyl chloride prepared in this laboratory was used, the reaction with liquid hydrogen sulfide was rapid and the contents of the tubes solidified in the form of a white solid. The reaction tubes were sealed and placed in the storage tank. In two days three layers had formed in the tubes, the top layer was a clear liquid, the middle a white suspension and in the bottom a heavy yellow liquid had started to form. A week after the tubes had been seal-

ed only two liquid layers were present. The clear layer had disappeared while the bottom layer had increased and some free sulfur had been formed. On cooling to -77°C both layers solidified.

Using the thionyl chloride from Eastman Kodak Company there was no reaction at -77°C and the liquids were miscible. On raising the temperature to the boiling point of the liquid hydrogen sulfide and shaking the reaction started forming a white suspension. The tubes were cooled, sealed and placed in the storage tank. Several tubes were shattered due to the high pressure caused by the heat of the reaction and the hydrogen chloride formed. On standing several months more free sulfur separated out at the expense of the yellow liquid layer.

The tubes were cooled and opened. The excess pressure in the tubes was due to the presence of hydrogen chloride gas. After allowing the excess hydrogen sulfide to evaporate the two layers were separated. The top layer consisted of hydrogen chloride in water which on standing became clear with a small amount of sulfur settling out. The bottom layer consisted of free sulfur and a yellow oily liquid. The mixture was

filtered thru a Gooch to remove the crystals of sulfur. The liquid decomposed on heating. An attempt was made to distill it at 4 mm. pressure but it decomposed giving off hydrogen sulfide from the outlet valve of the oil pump and leaving a residue of sulfur in the distilling flask. It was soluble in carbon disulfide, chloroform, and benzene and insoluble in alcohol and ether. Alcohol rapidly decomposed it while ether hastened the decomposition. The specific gravity of the impure product was found to be 1.80. The odor was similar to that of hydrogen persulfide.

Sulfuryl chloride was miscible with liquid hydrogen sulfide and the reaction did not start while standing in the cooling bath for three hours with the temperature being raised to the boiling point of liquid hydrogen sulfide several times and shaking. The tubes were sealed and placed in the storage tank. About six hours later one of the tubes was shattered by the pressure generated in the reaction. Some of the yellow oil formed in the reaction, which was similar to that formed in the reaction with thionyl chloride, was found on the towel that the tube was wrapped in and on the surface of the water in the storage tank.

The next day two layers had formed in the other tubes, the top being a white suspension and the bottom being a heavy yellow oil. The products were identified as free sulfur, water, hydrogen chloride and hydrogen persulfide.

Nitrosyl chloride reacts vigorously with liquid hydrogen sulfide at -77°C , giving off white fumes of hydrogen chloride and forming a greenish yellow solid. The tube was sealed and placed in the storage tank. On standing the solid changed to a yellow color and a small amount of yellow oily liquid separated out. After the tube was opened and the excess hydrogen sulfide evaporated, the yellow solid was found to be sulfur while the yellow oil was similar to that formed in the preceding reactions.

With selenium oxychloride a very vigorous reaction took place giving off white fumes. A yellow solid was formed and the liquid was dark red. On standing the liquid became colorless and the solid a burnt orange. The products of the reaction were similar to those above and in addition free selenium separated out.

Phosphorus oxychloride is miscible with liquid hydrogen sulfide at room temperature but

separates out as white crystals on cooling to -77°C . The reaction was very slow with the formation of a little yellow solid.

With vanadyl trichloride a vigorous reaction took place forming a wine colored solid. On standing the solid changed to a brown color. Excessive pressure in the tube was due to the pressure of hydrogen chloride. Crystals of sulfur could be separated from the solid. On exposure to air the solid turned dark. This reaction was also carried out by dissolving the vanadyl trichloride in anhydrous benzene before adding it to the liquid hydrogen sulfide. The reaction was not as vigorous and free sulfur was not detected in the product. The product was washed with benzene, dried for five minutes at $90 - 95^{\circ}\text{C}$ and by analysis was shown to contain vanadium, sulfur and chlorine. The analysis for these elements did not total 100% and the difference was too great to be due to oxygen. The following results were obtained in the analysis:

% vanadium	% sulfur	% chlorine
27.85	19.79	33.03
27.80	20.41	33.13
27.58	19.60	
	20.76	

	% vanadium	% sulfur	% chlorine
average	27.78	20.14	33.08

total = 81.00%

The vanadium was determined by dissolving the sample with nitric acid, taking it down to white fumes with sulfuric acid, oxidation with permanganate, reduction with sulfur dioxide and titration with standard potassium permanganate. The sulfur was determined by oxidation with liquid bromine in potassium hydroxide solution, precipitating and weighing as barium sulfate. The chlorine was determined by dissolving in potassium hydroxide solution, neutralizing with nitric acid, boiling to decompose any possible sulfide and precipitating and weighing as silver chloride.

Discussion

The reactions between liquid hydrogen sulfide and the oxychlorides of phosphorus, sulfur and selenium have been previously studied by Quam (1). He states that the product of the reaction with phosphorus oxychloride is a sulfide of phosphorus. As only a small amount of yellow solid was formed in the present work it was not analyzed. With thionyl chloride he gives

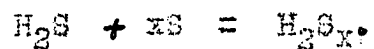
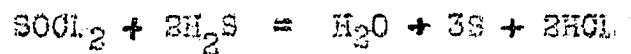
L. Quam, Doctoral Thesis, Iowa State College (1924)

the products as hydrogen chloride and sulfur chloride. With sulfuryl chloride, free sulfur, sulfur dioxide in water, hydrogen chloride and sulfur monochloride. In the present study, the yellow oil formed was not soluble in alcohol or ether as is sulfur monochloride but is decomposed by them. It had the solubility, odor, color and specific gravity of hydrogen persulfide as found by King (1) and was compared with some that he prepared. In the case of sulfuryl chloride, sulfur dioxide in water could not have been one of the products if an excess of liquid hydrogen sulfide was present as it has been shown to react (2), forming free sulfur and water, especially in the presence of water (3), (4).

Selenium oxychloride and nitrosyl chloride gave similar reactions with the formation of free selenium and probably free nitrogen respectively in addition to the above products. No test was run on the gases formed in the reaction with nitrosyl chloride for nitrogen.

1. King, Doctoral Thesis, Iowa State College (1930)
2. Quam, J. Am. Chem. Soc., 47, 103-8 (1925)
3. Antony and Magri, Gazz. chim. ital., 35, 206-26 (1905)
4. Mathews, J. Chem. Soc., 129, 2270-3 (1926)

A possible mechanism for these reactions, using thionyl chloride as an example, may be:



It is possible that the hydrochloric acid formed and the pressure developed may catalyze the second reaction.

The only product identified from the reaction with vanadyl trichloride was hydrogen chloride.

VI. GENERAL SUMMARY AND CONCLUSIONS

The foregoing pages contain an account of the results of the present investigation. It has been shown:

(a) that the tests employed by Lilienfeld and White (1) do not indicate the presence of sulfur dioxide in hydrogen sulfide dried with phosphorus pentoxide.

(b) that calcium sulfide is the product formed in the reaction between liquid hydrogen sulfide and calcium carbide.

(c) that thiocarbonates are not formed in liquid hydrogen sulfide from the sulfide and carbon disulfide. In alcohol solution ammonium thiocarbonate is formed which decomposes when kept under alcohol and ether into ammonium dithio carbamate and hydrogen sulfide.

(d) that liquid hydrogen sulfide and sulfur dioxide react vigorously in the liquid state in a sealed tube at about 0°C or above

1. Lilienfeld and White, J. Am. Chem. Soc., 52, 887 (1930)

with the formation of free sulfur and water. The pressure exerted by the liquids at this temperature plays an important part in the reaction.

(e) that the oxychlorides of nitrogen, sulfur and selenium react vigorously with liquid hydrogen sulfide with the formation of hydrogen persulfide, water, hydrogen chloride and the free elements. A mechanism is suggested for the reaction.

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