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Reactions of organic compounds with liquid hydrogen sulfide

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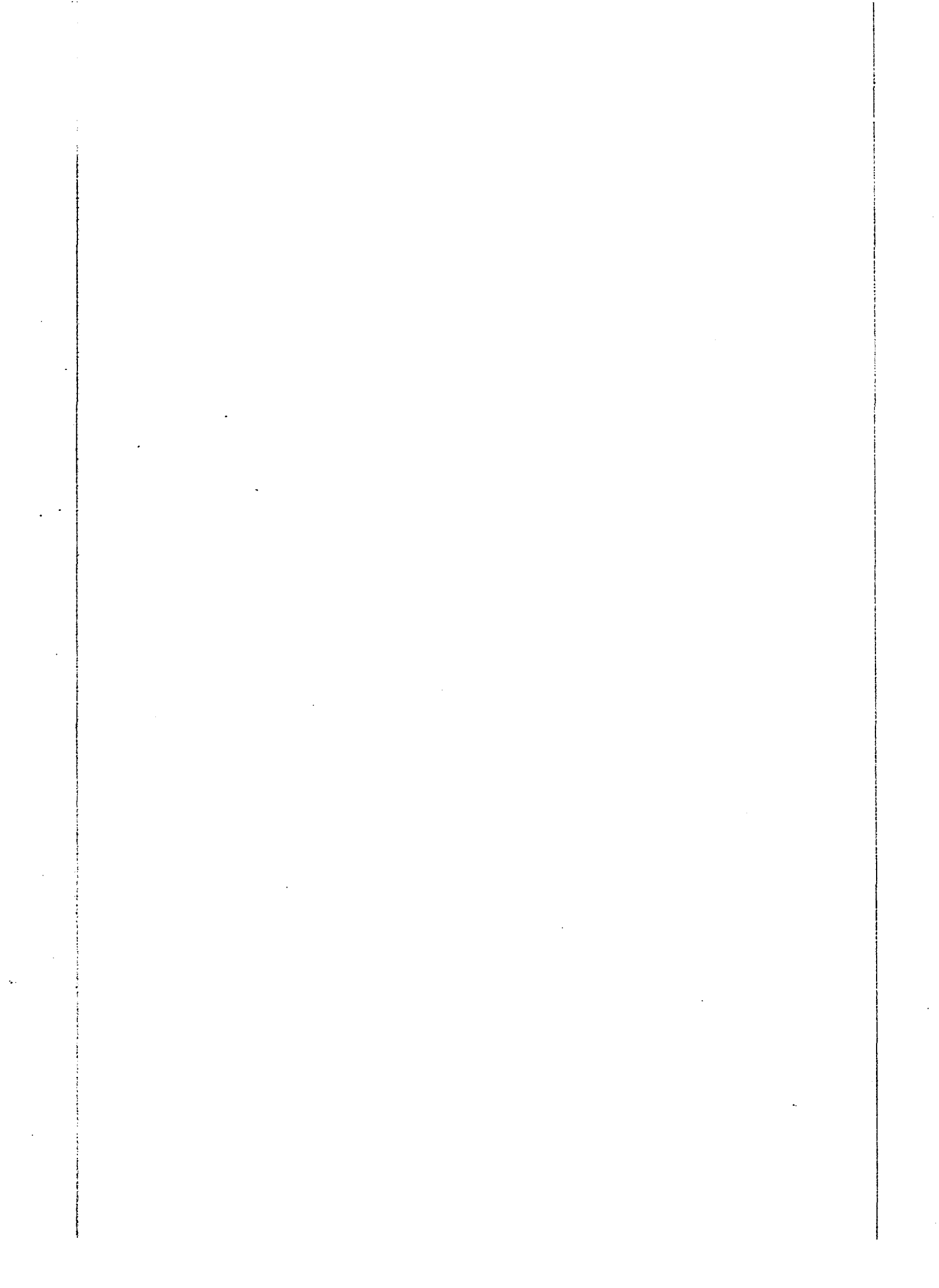
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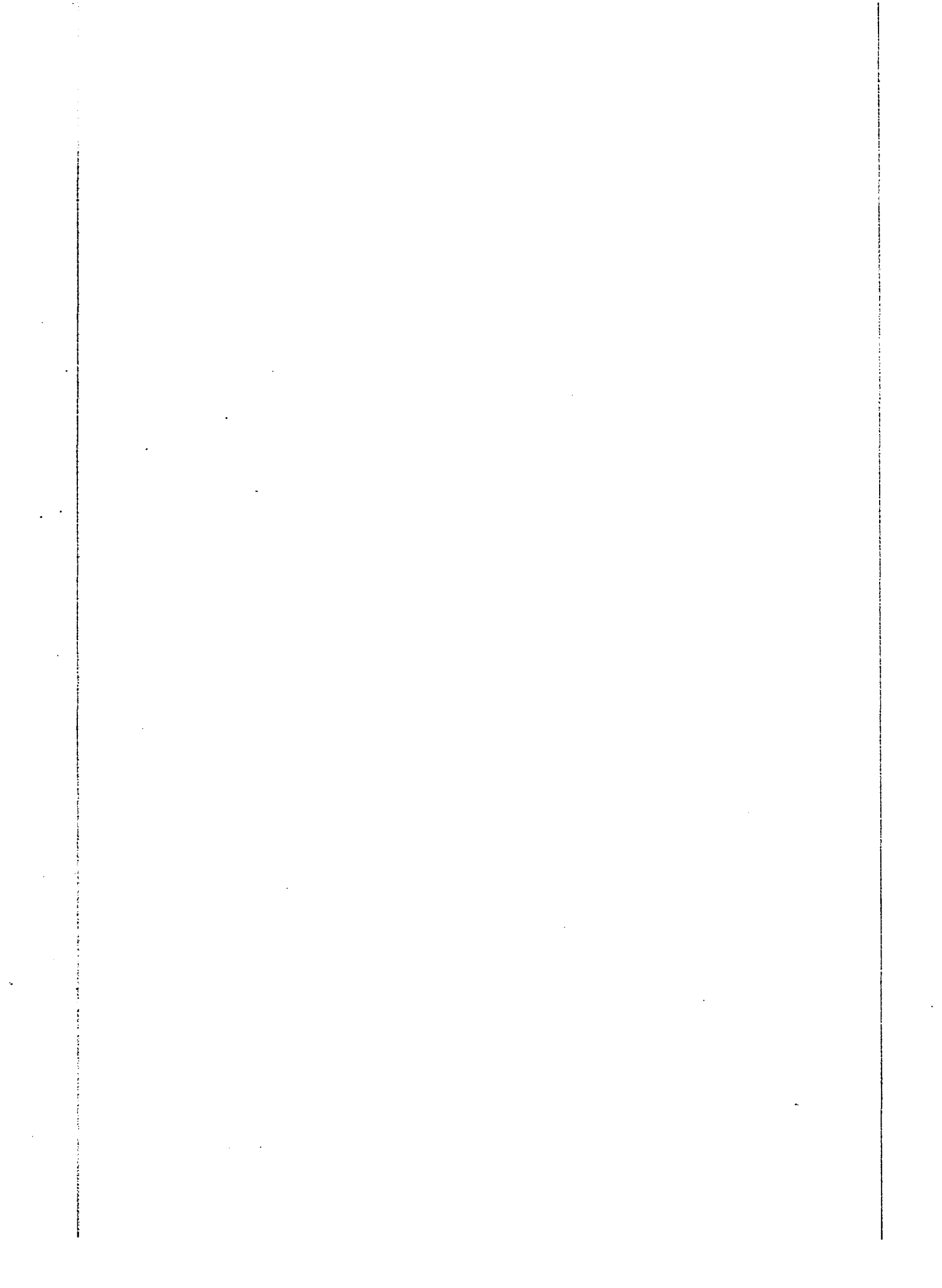
REACTIONS OF ORGANIC COMPOUNDS

WITH LIQUID HYDROGEN SULFIDE

By

Reuben Waldemar Borgeson

A Thesis Submitted to the Graduate Faculty

for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject - Inorganic Chemistry

Approved:

In charge of Major Work.

Head of Major Department.

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REACTIONS OF ORGANIC COMPOUNDS WITH LIQUID HYDROGEN SULFIDE

I. INTRODUCTION

The physical constants of liquid hydrogen sulfide, its solvent action, dissociating power, and chemical activity in general have been studied and reported by several investigators (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19).

Most of the reactions so far reported have been those with the elements and inorganic compounds, while comparatively little work has been done in the organic field. Quam (13) has given the solubility and reactivity of several organic

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16. Fournier and Lang, Compt. rend., 184, 1174 (1927).
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18. Satwalekar, Doctorate Thesis, (1928) Iowa State College.
19. Meints, M.S. Thesis, (1928) Iowa State College.

substances with liquid hydrogen sulfide. Ralston (20) has shown that thiohydrolysis of esters takes place in liquid hydrogen sulfide.resulting in an increase of conductivity due to the dissociation of the ester. Heints (19) has studied the action of liquid hydrogen sulfide on nitriles and found that they are thiohydrolyzed to form the di-thio acids or thioamides depending upon the catalyst employed. He also noted the action of liquid hydrogen sulfide upon furfural and concluded that his product was thio-furfuraldehyde or some polymer of it.

Some investigations of the behavior of organic compounds with other non-aqueous inorganic liquids have been made. Franklin and Kraus (21) have reported on the solubility in liquid ammonia of many members of the several classes of organic compounds. Kraus and others (22, 23, 24, 25) have studied the reducing action of strongly electropositive metals with organic substances in liquid ammonia.

More recently de Carli (26) has determined the solvent properties of liquid sulfur dioxide and of liquid ammonia for some organic compounds, with a view to forming generalizations

20. Ralston, Doctorate Thesis, (1927) Iowa State College.
21. Franklin and Kraus, Am. Chem. Jour., 20, 820 (1898).
22. Kraus and White, J. Am. Chem. Soc., 45, 768 (1923).
23. White, J. Am. Chem. Soc., 45, 779 (1923).
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25. Kraus and Kawamura, J. Am. Chem. Soc., 45, 2756 (1923).
26. de Carli, Gazz. chim. ital., 57, 347 (1927).

on the solubility of different classes of organic compounds in liquid SO_2 and in liquid NH_3.

It is obviously apparent that a wide field is open for the systematic study of the behavior of organic compounds with liquid hydrogen sulfide.

II. PURPOSE OF INVESTIGATION

The purpose of the present investigation is to study the behavior of organic compounds with liquid hydrogen sulfide, and to determine the types of reactions resulting and the composition of the products formed. This will be done by observing the reactions of several typical members in each of the various classes of organic compounds.

III. EXPERIMENTAL

Preparation of Liquid Hydrogen Sulfide

The apparatus used in the preparation of liquid hydrogen sulfide is a modification of that employed by Quam (13). The simplified and improved apparatus, shown in Figure 1, has been fully described by Meints (19). He has also discussed the process of liquefaction and the storage of liquid hydrogen sulfide, as well as the details of manipulation in the subsequent handling of reaction tubes.

Materials

The organic chemicals used throughout this work were the C.P. brands of Eastman Kodak Company. A few were from Kahlbaum. The Grignard reagents were furnished by Mr. J. H. McGlumphy of the organic laboratory.

General Procedure

The qualitative tests on individual compounds with liquid hydrogen sulfide were carried out in the Franklin type reaction tube made of specially thick lime-magnesia glass-tubing. This permitted of a closed distillation of the hydrogen sulfide from one arm to the other by simply cooling the empty arm of the tube. In this way solubilities could readily be determined and reaction products noted.

FIGURE 1.

APPARATUS FOR THE LIQUEFACTION OF HYDROGEN SULFIDE.
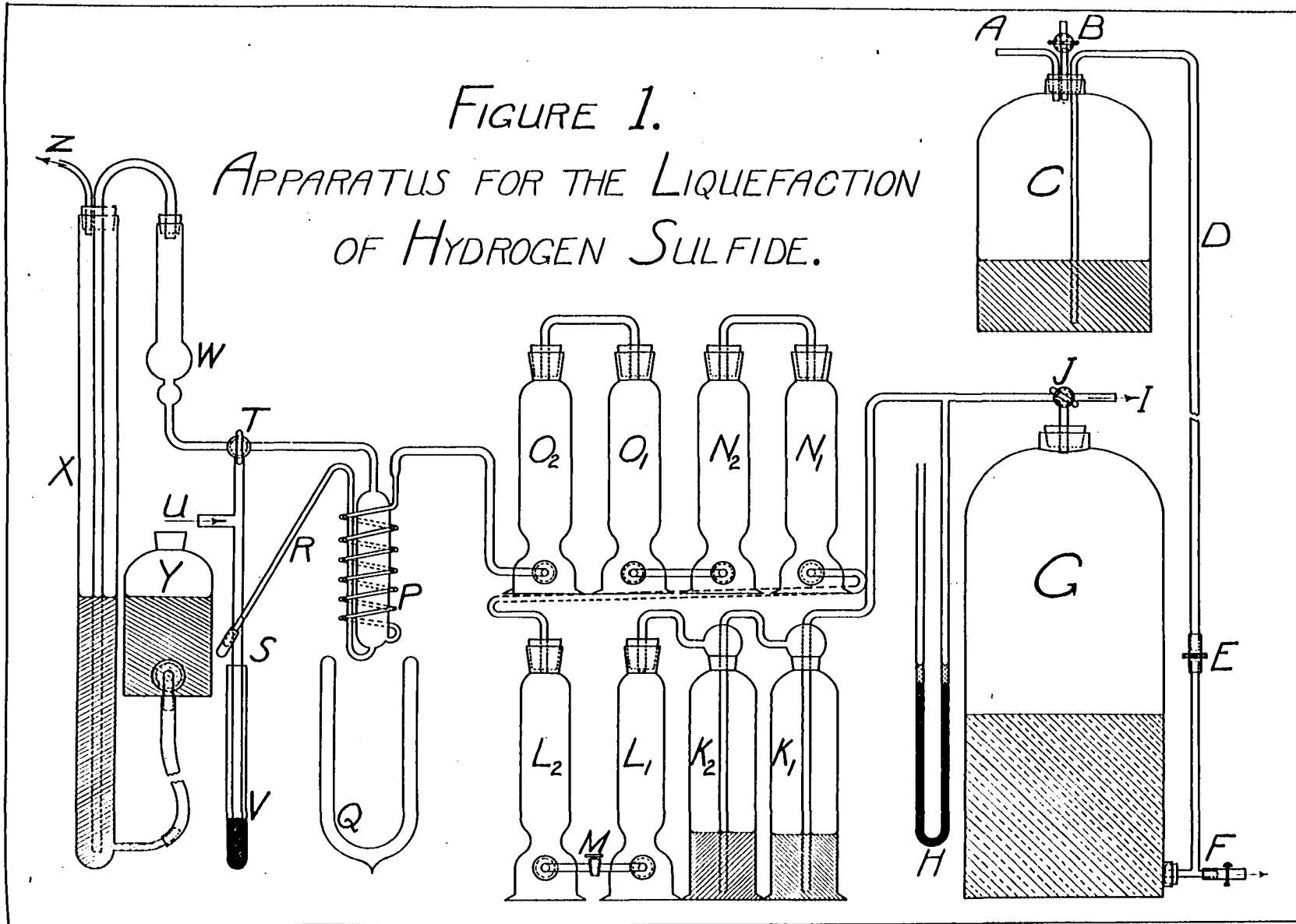
These reaction tubes were cleaned by means of a mixture of hot HNO_3 and H_2SO_4, rinsed several times with water and dried by alcohol and ether. The ether vapors in the tubes were removed by air dried over $CaCl_2$ or P_2O_5.

At the temperature of the cooling bath (-77°C.) about 2-3 cc. of liquid hydrogen sulfide was transferred to the tube from a storage tube. Then a cubic centimeter or less of substance, in the case of a liquid, or 0.3-0.5 gram in the case of a solid was added. Observations were made for solubility and indications of reaction at the low temperature for half an hour to two hours. The tube was then carefully sealed and annealed and placed in a special storage box. Observations were made daily for a week and then less often for a month, or until the reaction was apparently complete.

After a period of six weeks or two months the tube was carefully cooled down to -77°C. and opened. The hydrogen sulfide present was allowed to evaporate and the tube and its contents to come to room temperature gradually in order to prevent loss by spurting, which resulted when the temperature of the tube rose too rapidly.

Observations and tests were then made to determine whether or not a reaction had taken place between the compound and liquid hydrogen sulfide.

In those cases where a reaction was evident larger amounts

of material were sealed with liquid hydrogen sulfide in the larger storage tubes. The ratio of liquid hydrogen sulfide to material was generally two to one or even greater. After sufficient time for completion of the reaction, as determined in the previous qualitative tests, these tubes were opened. The physical properties of the reaction products were noted and various chemical tests made.

Where a definite compound was isolated, its solubility in all the common inorganic and organic solvents was determined as well as its other physical constants. Complete qualitative and quantitative analyses were also made.

Observations and Discussion

It should be noted here that hydrocarbons, ethers, esters, sulfides and mercaptans, nitriles and carbohydrates were not observed in this work. These classes have been treated by other investigators (13, 19, 20). Their observations and conclusions are included here in order to make the discussion complete.

Hydrocarbons.

Quam (13) has found that benzene, toluene, naphthalene, anthracene and also gasoline, kerosene and vaseline are soluble and nonreactive in liquid hydrogen sulfide. Related compounds such as pyridine, piperidine, quinoline and azo benzene

he reported as soluble and reactive. Walker, McIntosh and Archibald (5) found that pyridine, piperidine, nicotine and quinoline gave with liquid hydrogen sulfide solutions of considerable conducting power.

Unsaturated Hydrocarbons.

Amylene and tri-methyl ethylene were miscible with liquid hydrogen sulfide at $-77^\circ C$. but showed no reaction at this low temperature.

After contact with the liquid hydrogen sulfide for four days a reaction was evident in each case as shown by the fact that upon cooling each tube down to $-77^\circ C$. a white crystalline body separated. Neither amylene nor tri-methyl ethylene solidify at this temperature, and in each case upon first mixing with the hydrogen sulfide clear colorless solutions resulted.

Upon opening the tubes and allowing the hydrogen sulfide to evaporate and the contents to come up to room temperature the solids disappeared. A very distinct mercaptan odor was evident in both cases and the mixtures gave strong positive tests for sulfur.

Undoubtedly then an addition to the double bond had resulted with the probable formation of $CH_3 \cdot (CH_2)_2 \cdot CHSH \cdot CH_3$ in the case of amylene, and of $(CH_3)_2 \cdot CH \cdot CHSH \cdot CH_3$ in the case of tri-methyl ethylene.

Alcohols.

Methyl, ethyl and iso-amyl alcohol are miscible with liq-
uid hydrogen sulfide at $-77^{\circ}C$. Allyl and furyl alcohol are
soluble at room temperature. Upon cooling the tubes containing
methyl, ethyl and iso-amyl alcohol, after a period of two
months, beautiful white crystals separated. These were found
to be sulfur having a melting point of $118^{\circ}C$. This confirms
the finding of Antony and Magri (8).

These alcohols probably catalyze the decomposition of
liquid hydrogen sulfide inasmuch as sulfur is soluble in alco-
hol. It is doubtful that a thiohydrate is formed since this
would in all probability be unstable, while the crystals, which
were found to be sulfur, were stable at the boiling points of
the alcohols.

Allyl alcohol gave, upon evaporation of the excess hydro-
gen sulfide, a colorless rather viscous liquid with a slight
but distinct mercaptan odor. An addition to the double bond
probably occurs in this case.

Quam (13) found that iso-butyl alcohol and glycerol are
soluble in liquid hydrogen sulfide and non-reactive with it.

Phenols.

Phenol, meta-amino-phenol and cresol (m) were found to
be soluble in liquid hydrogen sulfide, although meta-amino-
phenol is only slightly so. None of these gave any indication

of reaction even after contact with the liquid hydrogen sulfide for more than two months.

Quam (13) has reported that resorcinol, pyrogallol, thiophenol and thiocresol are soluble in liquid hydrogen sulfide but do not react with it.

Ethers.

Quam (13) found that ether was soluble and non-reactive in liquid hydrogen sulfide. We have confirmed this, observing that it is miscible in all proportions but does not react.

Aldehydes.

Acetaldehyde was miscible with liquid hydrogen sulfide at -77°C. After one day a small amount of a heavier liquid appeared at the bottom of the tube. The amount of this heavier liquid gradually increased during several days. Upon cooling the tube and its contents to -77°C., after a period of three months, a white solid appeared. This is evidence of a reaction since the melting point of the original acetaldehyde is -123°C. and when it was first mixed with the hydrogen sulfide a clear colorless solution was obtained. Upon opening the tube and allowing its contents to come to room temperature two liquid layers were present. These liquids gave off an intensely foul odor of a sulfo or mercaptan nature, and showed strong positive test for sulfur.

Butaldehyde was found to be miscible with liquid hydrogen

sulfide. After two days two distinct liquid layers appeared.
A large amount of crystals appeared all over the tube, after
a period of several weeks. Upon cooling the tube the bottom
liquid layer froze immediately, much as water does. The
crystals appeared to be the same as those formed when pure
water and liquid hydrogen sulfide are sealed up together.
These have been shown by Quam (13) to be a hydrate, $H_2S \cdot 5.7H_2O$.
It is quite possible that in the reaction water is formed which
then reacts with the liquid hydrogen sulfide to yield the hy-
drate. Since butaldehyde melts at -99°C. the formation of a
white solid upon cooling to -77°C. is further evidence of re-
action. At room temperature, after opening the tube, two
liquid layers resulted. The contents of the tube had an ex-
ceedingly foul, musty odor, similar to that of old damp and
decaying wood. The odor was also mercaptan like and very per-
sistent. A very strong positive test for sulfur was obtained
upon the material.

Acryl-aldehyde reacted with liquid hydrogen sulfide at
-77°C. giving a white precipitate and a slight mercaptan odor
was evident. After four weeks a small amount of heavier liquid
appeared as in the case of the other aldehydes. When the tube
was cooled in the cooling bath its contents solidified, which
is another evidence of reaction since the original material

freezes at -88°C. At room temperature after opening the tube
a yellow liquid was obtained, having the same foul sulfo odor
referred to above. In addition to the reaction with the alde-
hyde group there is also the possibility in this case of ad-
dition to the double bond.

Benzaldehyde was soluble in liquid hydrogen sulfide and
in three weeks gave evidence of a reaction. Crystals similar
to those mentioned above appeared. Upon reaching room temper-
ature after opening of the tube a pink gelatinous mass remain-
ed. This gave off the same foul odor as observed with the
other aldehydes. A strong test for sulfur was obtained.

Meta-nitro-benzaldehyde and tri-nitro-benzaldehyde were
also found to be soluble in liquid hydrogen sulfide and re-
active with it. The products gave distinct mercaptan odor and
positive tests for sulfur. There was also evidence of deposi-
tion of sulfur in both these cases of nitro compounds.

Para-tolualdehyde was found to be soluble in liquid hydro-
gen sulfide and also reacted with it giving a pink solution.
The first tube sealed up burst after four weeks and a very
strong and distinct mercaptan odor was apparent. In the second
tube crystals appeared as with the other aldehydes, and a very
pink solution was obtained. Upon reaching room temperature af-
ter opening of the tube a beautiful pink gel, quite rigid, was

obtained. This had a mercaptan odor and gave a strong positive test for sulfur.

Cinnamaldehyde was soluble in liquid hydrogen sulfide and after three days large beautiful crystals appeared. These continued to grow for several days. In about a month the crystals disappeared and a heavy liquid formed, as occurred with some of the other aldehydes. Upon reaching room temperature after opening the tube a yellow gel which was quite rigid was formed. This material had a mercaptan or sulfo odor and gave positive test for sulfur.

Furfuraldehyde was found to be soluble in liquid hydrogen sulfide and reacted with it. Within a day needle-like crystals appeared and the amount of these increased rapidly. After one week the content of the tube was a very viscous crystalline mass. The large tube burst during the eighth week. The residue was recovered and contained needle-like glistening crystals. It gave a definite mercaptan odor and showed a strong positive test for sulfur.

That aldehydes as a class react with liquid hydrogen sulfide is certain. All the individuals observed gave definite evidence of reaction. The products formed had distinct mercaptan or sulfo odors and gave strong positive tests for sulfur.

Meints (19) obtained a compound from the reaction between

furfuraldehyde and liquid hydrogen sulfide which checked the formula C_5H_4OS according to the sulfur analysis. Molecular weight determinations indicated that it is polymerized about twenty times.

Baumann and Fromm (27) studied the action of gaseous hydrogen sulfide on a solution of furfural in benzene and chloroform at $-5^\circ C$. and isolated a product which analyzed C_5H_4OS.

The reaction is undoubtedly with the aldehyde group since we found that furfuraldehyde reacted with liquid hydrogen sulfide while furyl alcohol did not when treated in the same way for the same length of time. Meints (19) also found that furan, pyromucic acid and the ethyl ester of pyromucic acid gave no evidence of reacting with liquid hydrogen sulfide. Further evidence of the reaction of the aldehyde group comes from the fact that cinnamaldehyde reacted with liquid hydrogen sulfide while cinnamic acid showed no evidence of reaction except a very slight mercaptan odor which probably was due to some addition to the double bond.

The probability of the replacement of oxygen by sulfur in the aldehyde group, to give the thio aldehyde, is shown by the formation of the crystals referred to under several of the aldehyde discussions. In the reaction

$$R-C{\overset{H}{\underset{O}{\big\langle}}} + H_2S \longrightarrow R-C{\overset{H}{\underset{S}{\big\langle}}} + H_2O$$
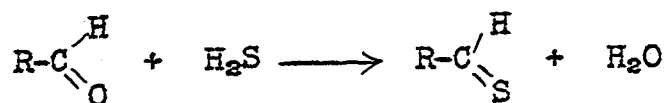
the water formed would react with the liquid hydrogen sulfide

27. Baumann and Fromm, Ber., 24, 3591 (1891).

to give the hydrate $H_2S \cdot 5.7H_2O$ described by Quam (13). The crystals formed in the tubes are similar to those formed when pure water reacts with liquid hydrogen sulfide. Both were examined under a microscope.

Ketones.

Acetone, di-ethyl ketone, acetyl acetone, acetophenone and benzophenone were sealed up with liquid hydrogen sulfide and observed. All were found to be soluble in the hydrogen sulfide. The aryl ketones, acetophenone and benzophenone, gave no evidence of reaction.

Acetyl acetone apparently reacts, for the colorless solution first formed became yellow after two weeks. Upon opening the tube a red brown liquid remained after evaporation of the hydrogen sulfide. This gave indication of a slight mercaptan odor.

Acetone and di-ethyl ketone evidently reacted for both yielded products having distinct mercaptan odor, and di-ethyl ketone produced with liquid hydrogen sulfide a pink solution.

Hock and Stuhlmann (28) have studied the action of liquid ammonia upon acetone and isolated a compound of the composition $Me_2CO_2 \cdot NH_3$. They have given $Me_2C(OH)NH_2$ as its most probable structure. An analogous structure $Me_2C(OH)SH$ might be hypothe-

28. Hock and Stuhlmann, Ber., 61B, 470 (1928).

cated for the reaction product between acetone and liquid hydrogen sulfide.

Since both aldehydes and ketones have been found to give evidence of reaction with liquid hydrogen sulfide it may safely be assumed that the seat of reaction lies in the carbonyl group. This reaction of the carbonyl group with liquid hydrogen sulfide merits further careful investigation.

Alkyl and Aryl Halides.

Ethyl chloride, ethyl bromide, n-butyl bromide, allyl bromide, methyl iodide, ethyl iodide, n-propyl iodide, allyl iodide, n-butyl iodide, benzyl chloride and benzyl bromide were found to be soluble in liquid hydrogen sulfide.

Allyl bromide and allyl iodide gave definite evidence of reacting with liquid hydrogen sulfide. Allyl bromide with liquid hydrogen sulfide gave off a mercaptan odor at the low temperature of the cooling bath. A solid body separated upon cooling the solution of allyl bromide and liquid hydrogen sulfide, which is further evidence of reaction since the freezing point of allyl bromide is -119°C.

In the case of allyl iodide an iodine-brown solution was observed the second day after sealing the tube. Upon opening it, and at room temperature, two liquid layers were present, a dark red one and a heavier black red liquid.

The products from both of the allyl halides gave very
strong distinct mercaptan odors. The reaction in these two
cases probably occurred at the double bond.

Reactions in the cases of the other halides were doubt-
ful, though some gave very slight indication of mercaptan
odor and a few solutions became turbid upon cooling to $-77^{\circ}C$.,
whereas the freezing points of these individual halides is
much lower than that temperature.

Quam (13) reported $CHCl_3$, $CHBr_3$, CHI_3, CCl_4 and n-amyl
bromide as soluble in liquid hydrogen sulfide and non-reactive.

Acids.

Acetic, propionic, benzoic and cinnamic acids were found
to be soluble in liquid hydrogen sulfide. None of these gave
evidence of reaction except cinnamic acid, whose solution af-
ter opening of tube and evaporation of hydrogen sulfide gave
a very slight mercaptan odor. This probably was due to a
small amount of reaction at the double bond. A deposit of
sulfur was observed in each reaction tube.

Quam (13) has reported that trichloro-acetic, stearic,
salicylic and phthalic acids are soluble in liquid hydrogen
sulfide and non-reactive. He also found that tartaric, cit-
ric and amino acetic acids are insoluble and non-reactive.

Thioacetic acid was found by Quam (29) to be soluble

29. Quam, Doctorate Thesis, (1924) Iowa State College.

and reactive. He obtained a compound $CH_3COSH \cdot H_2S$ which he assumed to have the structure $CH_3 \cdot C(OH)(SH)_2$.

Quam and Wilkinson (14) have reported on the equivalent conductivities of acetic acid derivatives in liquid hydrogen sulfide, and Ralston (20) has determined the conductivities of thio acids in this solvent.

Acid Anhydrides.

Acetic, benzoic, succinic and maleic anhydrides were found to be soluble in liquid hydrogen sulfide, although maleic anhydride only slightly so. None of them gave evidence of reacting with the solvent. In the cases of acetic and maleic anhydrides some decomposition of hydrogen sulfide was evident from the presence of free sulfur in the tubes.

Esters.

Ralston (20) has found that esters of thio acids are soluble in liquid hydrogen sulfide. He has also determined that thio hydrolysis of esters takes place in liquid hydrogen sulfide, and that the hydrolysis values become greater as the molecular weight of the "R" group increases.

Salts.

Silver acetate was insoluble in liquid hydrogen sulfide but quickly turned black indicating the rapid formation of silver sulfide. Sodium acetate, hydrazine hydrochloride and

ethyl amine hydrochloride were found to be insoluble in liquid hydrogen sulfide and did not react with it.

Quam (13, 29) has reported that ammonium acetate and ammonium cyanate are insoluble and non-reactive. He found however that hydroxylamine hydrochloride and phenylhydrazine hydrochloride were soluble.

It is evident then that the metallic salts of organic acids and most of the addition compound salts of basic organic compounds are insoluble in liquid hydrogen sulfide and do not react with it.

Sulfides and Mercaptans.

Quam (29) found that ethyl disulfide, n-butyl sulfide and n-butyl mercaptan are soluble and non-reactive in liquid hydrogen sulfide. He also reported that saturated solutions of these exhibited no specific conductivity.
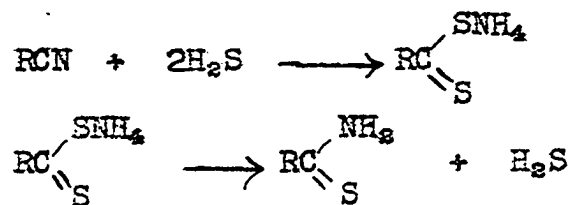
Nitriles.

Benzo-nitrile was found to be soluble and non-reactive in liquid hydrogen sulfide.

Ralston (20) found that in the presence of hydrogen chloride nitriles do react with liquid hydrogen sulfide, forming the corresponding dithiocarboxylic acids, thio amides and ammonium sulfide.

Meints (19) has studied further the action of nitriles

with liquid hydrogen sulfide. He has found that it is possible by the choice of suitable catalysts to hydrolyze nitriles in liquid hydrogen sulfide to dithio acids, but that ordinary methods of separation are not applicable. The best catalysts found were HCl and HBr although alkali bases are effective. Phosphorus pentoxide and alcoholic KOH catalyze the reaction to the formation of the thio amide.

The reactions are shown by these equations:

$$RCN + 2H_2S \longrightarrow RC\begin{smallmatrix} \nearrow SNH_4 \\ \searrow S \end{smallmatrix}$$

$$RC\begin{smallmatrix} \nearrow SNH_4 \\ \searrow S \end{smallmatrix} \longrightarrow RC\begin{smallmatrix} \nearrow NH_2 \\ \searrow S \end{smallmatrix} + H_2S$$

The difficulty of isolating the dithio acid arises from the fact that its ammonium salt undergoes decomposition to the thio amide according to the second equation above.

Meints (19) prepared and isolated thioacetamide, thiopropionamide and thiobenzamide, obtaining a yield of over eighty per cent in the case of thiobenzamide. He concluded however that unless the change from the ammonium salt of the dithio acid can be prevented by some means, the method is not applicable to the preparation of dithio acids.

Kindler (30, 31, 32), in a study of firmness of union of

30. Kindler, Ann., 431, 187 (1923).
31. Kindler, Ann., 450, 1 (1927).
32. Kindler, Ann., 450, 90 (1927).

organic radicals and reaction velocity, has prepared several thio amides by the reaction of the corresponding nitriles with alcoholic solutions of hydrogen sulfide, employing both acids and bases as catalysts. He has determined the velocity constant for each reaction and found that benzonitrile reacts about four times as rapidly as propionitrile. Meints (19) found this to be the case also in the reactions of these nitriles with liquid hydrogen sulfide.

Walker, McIntosh and Archibald (5) have reported that solutions of acetonitrile in liquid hydrogen sulfide exhibit fair conductivity.

Sugars.

Quam (13) found that sucrose, glucose, maltose, lactose, mannose, arabinose and raffinose are insoluble in liquid hydrogen sulfide and show no evidence of reacting with it.

It is of interest on the other hand to note that Franklin and Kraus (21) found these sugars very soluble in liquid ammonia.

As a class, sugars are insoluble or only slightly soluble in most organic solvents. This points further to the similarity between liquid hydrogen sulfide and the ordinary organic solvents.

Nitro Compounds.

The nitro derivatives observed were nitrobenzene, dini-

trobenzene, nitrobenzaldehyde, trinitrophenol (picric acid)
and picramide. All were soluble in liquid hydrogen sulfide
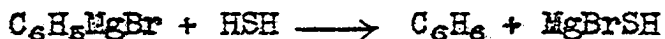and caused the separation of a considerable amount of free
sulfur.

This confirms the results of Quam (29) who found that
the organic nitro compounds oxidize liquid hydrogen sulfide
and suffer reduction.

Grignard Reagent.

Ethylmagnesium bromide, phenylmagnesium bromide and ben-
zylmagnesium chloride reacted vigorously with liquid hydrogen
sulfide at $-77^{\circ}C.$, yielding in each case a white solid in the
solution.

After evaporation of the hydrogen sulfide upon opening
the tubes the white residue in the case of phenylmagnesium
bromide gave off a definite odor of benzene and in the case of
benzylmagnesium chloride a distinct odor of toluene was very
apparent.

The reactions which are analogous to those with water may
be represented by the following equations:

$$C_2H_5MgBr + HSH \longrightarrow C_2H_6 + MgBrSH$$

$$C_6H_5MgBr + HSH \longrightarrow C_6H_6 + MgBrSH$$

$$C_6H_5CH_2MgCl + HSH \longrightarrow C_6H_5CH_3 + MgClSH.$$

The white residues after being stoppered in tubes for
some time gave off hydrogen sulfide. This indicates the in-

stability of the compound whether it be MgClSH or the more probable mixture of Mg(SH)$_2$ + MgCl$_2$. Upon exposure to the atmosphere of the laboratory the residue took up water very rapidly indicating the presence of the very hygroscopic MgCl$_2$.

It is apparent then that the action of liquid hydrogen sulfide upon the various Grignard reagents is exactly analogous to that of water upon them.

Amides.

Acetamide, n-butyramide, acetanilide and benzanilide were soluble in liquid hydrogen sulfide but gave no evidence of reacting with it.

Picramide was soluble and caused the separation of some free sulfur, which may be accounted for by the presence of the nitro groups.

Phthalimide was soluble in liquid hydrogen sulfide but gave no evidence of any reaction.

Amines.

Aniline, dimethylaniline, diethylaniline, diphenylamine, ∝-naphthylamine, β-naphthylamine and benzidine were soluble in liquid hydrogen sulfide. Of these aryl amines only aniline reacted with the liquid hydrogen sulfide, forming an addition product which appeared as a white flocculent precipitate.

Walker, McIntosh and Archibald (5) found that solutions

of dimethylaniline and diethylaniline in liquid hydrogen sulfide showed very slight conductivity.

All the alkyl amines observed were soluble in liquid hydrogen sulfide and reacted with it, forming addition compounds.

Diethylamine reacted at the low temperature of the cooling bath. After one day the solution was quite yellow and contained long needle-like crystals. Upon opening the tube after a period of six weeks a solid mass of yellowish white crystals was obtained. These had a strong odor of hydrogen sulfide. After washing with ether beautiful orange-yellow crystals were obtained which gave off much hydrogen sulfide and decomposed rapidly giving an orange viscous liquid in a few minutes. They do not decompose so readily when kept under ether but even then break down after several days. The product is undoubtedly an amine hydrosulfide, an addition compound of the formula $(C_2H_5)_2NH \cdot H_2S$. An analysis was not obtained because of the great instability of the compound under atmospheric conditions.

Sec.-butylamine gave a yellow very viscous liquid which gradually decomposed giving off hydrogen sulfide.

Iso-butylamine gave an orange colored, rather viscous liquid containing a large amount of crystals. Evidence of decomposition was had by the strong odor of hydrogen sulfide coming off as well as a test for it using lead acetate paper.

Di-n-butylamine reacted with liquid hydrogen sulfide at
-77°C. A yellow fairly viscous solution was apparent in a few
days. A closed distillation revealed the presence of a yellow
crystalline solid. These crystals are unstable however, for
upon evaporation of the hydrogen sulfide after opening the
tube a red-brown viscous liquid containing some crystals was
obtained. The resulting liquid crystalline product decomposed
rapidly with evolution of hydrogen sulfide.

Benzylamine reacted with liquid hydrogen sulfide yielding
a yellow solution within a few hours. In the course of two
days needle-like crystals appeared. The tube was opened after
a period of three weeks. Upon evaporation of the hydrogen sul-
fide a yellow-white crystalline solid remained. This was wash-
ed with ether and beautiful yellow crystals were obtained.
These decomposed rapidly in air to give a brownish liquid of
amine odor. The decomposition was attended by a strong evolu-
tion of hydrogen sulfide, indicating the probable formula of the
compound as $C_6H_5CH_2NH_2 \cdot H_2S$.

Benzalmethylamine gave a dark red liquid containing a mass
of yellow crystals. In this case also there is the possibility
of addition to the double bond as well as the formation of the
hydrosulfide addition compound.

Phenylhydrazine was found to be soluble in liquid hydrogen

sulfide. Within a week the solution was yellow and a small amount of yellow or yellow-white crystals was apparent. Three weeks after sealing the tube a large amount of these crystals, which were needle-like in form, had appeared. This product is undoubtedly an addition compound corresponding to the formula $C_6H_5NHNH_2 \cdot H_2S$.

Upon evaporation of the hydrogen sulfide after opening the tube a dark red liquid was obtained at room temperature, the crystals disappearing. After being stoppered for two or three days a myriad of small bubbles arose throughout the liquid. This gas proved to be ammonia as evidenced by the smell and tests with moist red litmus and gaseous HCl. The amount of ammonia formed and its odor increased upon standing a few days more.

Upon boiling a portion of the red liquid until no odor of ammonia was perceptible a yellow liquid resulted having the odor of aniline and being slightly turbid due to the presence of free sulfur.

After standing about ten days an appreciable amount of free sulfur had separated from the main portion of the red liquid. This red liquid is undoubtedly an intermediate sulfur product which gradually decomposes.

The red liquid was distilled and the major fraction which came over between 180°C. and 185°C. was collected. The boil-

ing point did not rise above 185°C. The boiling point of aniline is 184°C. The odor and boiling point therefore indicated that the end-product of the reaction is aniline.

A derivative with acetic anhydride was prepared. It melted at 113°-114°C., and a mixed melting point determination with pure acetanilide gave the same result. The melting point of acetanilide is 114°C. It is therefore certain that aniline is the end-product of the reaction.

This reaction is one of reduction and may be represented by the equation:

$$C_6H_5NHNH_2 + HSH \longrightarrow C_6H_5NH_2 + NH_3 + S$$

That intermediate complex bodies are formed is indicated by the deep red solution and deposition of sulfur, and the reaction therefore merits further investigation.

It is known (33) that phenylhydrazine is decomposed into aniline and ammonia by zinc dust and hydrochloric acid. Phenylhydrazine also is known (34) to be an oxidizing agent in the formation of phenylglucosazone from glucose.

Some phenylhydrazine was saturated with gaseous hydrogen sulfide and a red solution resulted. Upon standing the color deepened but no odor of ammonia was apparent until the fourth day. The intensity of the ammonia odor increased greatly in

33. Cohen, Theoretical Organic Chemistry, p.433, Macmillan and Co., London, 1922.
34. Cohen, Theoretical Organic Chemistry, p. 294, Macmillan and Co., London, 1922.

the course of a few days more.

The reaction with gaseous hydrogen sulfide is evidently the same as the one mentioned above although in the first case the hydrogen sulfide comes from the decomposition of the phenylhydrazine hydrosulfide formed in the reaction between phenylhydrazine and liquid hydrogen sulfide.

Acyl Halides.

The reaction of an acyl halide with water to form the corresponding organic acid and halogen hydride is well known. It was thought that a similar reaction might occur using liquid hydrogen sulfide to yield the thio or dithio acid.

All of the acyl halides observed were soluble in liquid hydrogen sulfide and all reacted with it, although in a few cases more than a month elapsed before evidence of reaction was apparent.

Benzoyl chloride gave indication of reacting only after four weeks of contact with the liquid hydrogen sulfide when the solution became light yellow. After two months a reddish orange solution had resulted. A closed distillation gave a deep reddish orange heavy liquid. Upon opening the tube and evaporating the excess hydrogen sulfide a red-violet liquid of pungent odor remained. After standing a few days the liquid became quite viscous and crystals were apparent in it. Dithiobenzoic acid has

been reported (35) as a reddish violet, pungent oil.

Benzoyl bromide reacted within two days giving a red solution. Within a week a deep blood red solution had resulted and this contained large beautiful hexagonal crystals. These crystals continued to grow for some time, some of them being as much as three millimeters in diameter and seven millimeters long, their cross-sections perfect hexagons. Upon opening the tube a reddish sticky mass containing the crystals was obtained. This product had a very pungent odor. Some of the crystals, free from the mother liquor, were recovered from a tube which exploded. These gave off a great deal of hydrogen sulfide after having been stoppered in a tube for some time. Upon pouring ether over the crystals decomposition was apparent with evolution of hydrogen sulfide, as was evident from its odor and a test with lead acetate paper. The crystals then lost their lustre and were readily crumbled to a powder.

They are evidently some compound with hydrogen sulfide of crystallization.

<u>∝-Bromopropionyl bromide</u> reacted with liquid hydrogen sulfide in three to four days forming two liquid layers, the heavier being orange-brown in color and the other yellow. Needle-like crystals appeared in a few days. When the tube was opened

35. Houben and Pohl, Ber., 39, 3219 (1906).

and the excess hydrogen sulfide evaporated a white solid, slightly colored yellow, remained. After standing in contact with ether for a few days a black red oily-like material was obtained. This probably is due to some decomposition.

Phthalyl chloride gave indication of reacting in about two weeks, the solution having a slight reddish color. In a period of four weeks the solution had become strong yellow-brown in color. Upon evaporation of the excess hydrogen sulfide salmon pink crystals remained.

Succinyl chloride and liquid hydrogen sulfide formed a solution which became light yellow in color after two weeks. After two months the solution was deep yellow in color. A closed distillation gave a dark red liquid in the warmer arm of the tube. Upon evaporation of the excess hydrogen sulfide after opening the tube a dark red liquid was obtained.

Benzenesulfonyl chloride apparently reacted in three or four days with the formation of a fine, yellow-white precipitate. This fine deposit was later found adhering to the sides of the tube, and proved to be sulfur.

Chloroacetyl chloride produced with liquid hydrogen sulfide, in four to five days, a yellow deposit adhering firmly to the sides of the tube. There also appeared at the bottom of the tube some of this yellow deposit which was sulfur. In

three weeks the solution took on an orange color which gradually deepened to a deep black red in two weeks more. In two months a heavier almost black liquid layer was also present. When the tube was opened and the excess hydrogen sulfide evaporated the dark red liquid still remained as such, and contained the flaky crystalline solid which was sulfur.

Phenylacetyl chloride reacted with liquid hydrogen sulfide in one week to give a slightly orange-yellow solution. In three weeks the solution was deep orange in color. When the tube was opened and the excess hydrogen sulfide evaporated a reddish yellow solution of very pungent odor was obtained. After standing a few days large thin plate-like crystals separated out. Houben and Kesselkaul (36) prepared dithiophenylacetic acid from benzylmagnesium chloride and described it as a reddish yellow oil of unpleasant odor.

Acetyl Chloride.

The reaction between acetyl chloride and liquid hydrogen sulfide gave in one day a deep yellow solution and in two or three days the solutions were deep orange in color. This indicates the formation of dithioacetic acid because of the characteristic color.

Upon opening the tubes and evaporating the excess hydro-

36. Houben and Kesselkaul, Ber., 35, 3695 (1902).

gen sulfide a large mass of fine white crystalline meal was obtained. In some cases these crystals appeared even before the hydrogen sulfide had evaporated, and immediately after the hydrogen sulfide pressure within the tube was released by cooling or by cooling and opening the tube. In each case there was always present after opening the tube an orange-red or yellow liquid of pungent odor, generally intermixed with the crystalline mass.

By washing the crystalline meal with ether the adhering orange-yellow liquid was dissolved and pure white crystals obtained. Since these are sparingly soluble in ether they were purified by recrystallization from this solvent. Beautiful white clear crystals of varying size can be obtained depending upon the rate of crystallization. They belong to the monoclinic system.

A definite sharp melting point indicated that a pure compound had been obtained. An elementary analysis showed the presence of carbon and of much sulfur. A complete quantitative analysis, given below, proved the compound to be the anhydride of dithioacetic acid.

The mechanism of the reaction may be shown by the following equations:

$$CH_3COCl + 2HSH \longrightarrow CH_3CSSH + HCl + H_2O$$

$$2CH_3CSSH \longrightarrow (CH_3CS)_2S + H_2S$$
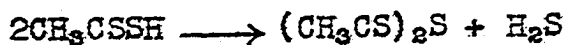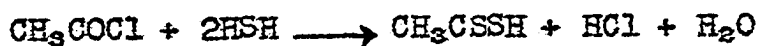
The water formed undoubtedly reacted with a molecule of CH_3COCl to form CH_3COOH which has been shown above to be soluble and non-reactive in liquid hydrogen sulfide.

A search of the literature has failed to reveal the preparation of this compound up to the present time. Delépine (37) in an article on the physical properties of organic sulfur compounds has described the anhydride of thiolacetic acid, $(CH_3CO)_2S$, as a colorless liquid boiling at 121°C. Houben and Pohl (38) have prepared thioacetyl disulfide, $(CH_3CS)_2S_2$, a yellow solid, by treating dithioacetic acid with iodine in KI solution. But the anhydride of dithioacetic acid is nowhere described or reported as having been prepared.

This same compound was prepared by the action of acetyl bromide on liquid hydrogen sulfide, as described below.

Properties of Dithioacetic Anhydride.

Dithioacetic anhydride is a clear, white crystalline body, of the monoclinic system, having a slight sulfo odor. It is readily ignited and burns freely and completely giving off the odor of a burning sulfur compound. It melts at 225°C.

The common organic solvents, acetone, benzene, carbon disulfide, chloroform, ethyl acetate and carbon tetrachloride dissolve it readily. It is fairly soluble in cold ether and

37. Delépine, Ann. chim. phys., 25, 533 (1912).
38. Houben and Pohl, Ber., 40, 1303 (1907).

petrolic ether, and is soluble in hot alcohol. Aniline and amines in general dissolve it in the cold.

It is insoluble in water, dilute acid, dilute alkali and the inorganic solvents in general.

The compound is very stable. Boiling concentrated KOH does not affect it. Attempts to prepare a derivative with ammonia, aniline and p-toluidine have failed. In each case upon neutralizing the reaction mixture with acid the original anhydride was obtained.

Concentrated HNO_3 reacts in the cold with it rapidly, oxidizing it almost completely. Sulfur analyses, using only HNO_3 in an open beaker for the oxidation, gave results within 0.5% of the theoretical which is 64.01%.

Molecular weight determinations by the freezing point method using benzene as a solvent gave values of 269, 270, and 273, from which we see that this compound is associated to a considerable extent in benzene inasmuch as its molecular weight calculated from the empirical formula is 150.

Analysis of Dithioacetic Anhydride.

The analysis for sulfur, carbon and hydrogen were made according to the methods recommended by Gatterman (39).

39. Gattermann, Practical Methods of Organic Chemistry, pp. 86, 111, Macmillan Co., New York, 1925.

:% calculated for $(CH_3CS)_2S$	:	% found :
:Sulfur 64.01	:	63.98 :
:	:	63.84 :
:	:	63.68 :
:Carbon 31.97	:	32.60 :
:	:	32.27 :
:Hydrogen 4.02	:	4.14 :
:	:	4.12 :

Acetyl Bromide.

Acetyl bromide reacted with liquid hydrogen sulfide within a day yielding two liquid layers in the tube, both of which were dark yellow or orange in color. Upon opening the tube a granular solid was obtained as in the case of acetyl chloride. A heavy red liquid of strong pungent odor was also present. By washing with ether and then recrystallizing from the same solvent crystals identical with those from the acetyl chloride reaction were obtained. Melting point determinations proved it to be the same compound.

From the observations and results recorded above we see that the acyl halides do react with liquid hydrogen sulfide to form the dithio acids and in some cases yielding the anhydrides of these acids. The time for completion of reaction varies considerably in the different cases observed. The evidence of intermediate products and by-products formed and the possibility of isolating other new compounds merits the further investigation of this interesting reaction.

IV. GENERAL SUMMARY AND CONCLUSIONS

We have found that all classes of organic compounds, except the sugars and salts, are soluble in liquid hydrogen sulfide. In this respect liquid hydrogen sulfide is very much like the ordinary organic solvents. It is a much better solvent for organic compounds than liquid sulfur dioxide or liquid ammonia.

Several classes, namely, the unsaturated hydrocarbons and unsaturated groups in general, the aldehydes, ketones, nitriles, esters, acyl halides, amines and Grignard reagent react with liquid hydrogen sulfide. The time necessary for completion of reaction varies from a few minutes in some cases to several weeks in others.

Different types of reactions of organic compounds with liquid hydrogen sulfide have been found.

1. Addition to the double bond, with the formation of mercaptan bodies, takes place in the case of unsaturated hydrocarbons and unsaturated groups in general.

2. Replacement reactions are evident with aldehydes, ketones and acyl halides. Here the seat of reaction is in the carbonyl group.

3. Reducing action takes place in the case of phenyl hydrazine, and nitro bodies oxidize liquid hydrogen sulfide with apparent ease.

4. Thiohydrolysis occurs with nitriles and esters.

5. Another analogy to the chemistry of water is shown in the rapid reaction of the Grignard reagent with liquid hydrogen sulfide.

6. Hydrogen sulfide of crystallization is apparent with some acyl halides and the amines form unstable crystalline salts, amine hydrosulfides, which may be considered bodies with hydrogen sulfide of crystallization.

The use of various catalysts may be found to facilitate some of the reactions and also promote reactions with some classes where none has so far been evident.