

1927

# Thiohydrolysis in solutions in liquid hydrogen sulfide

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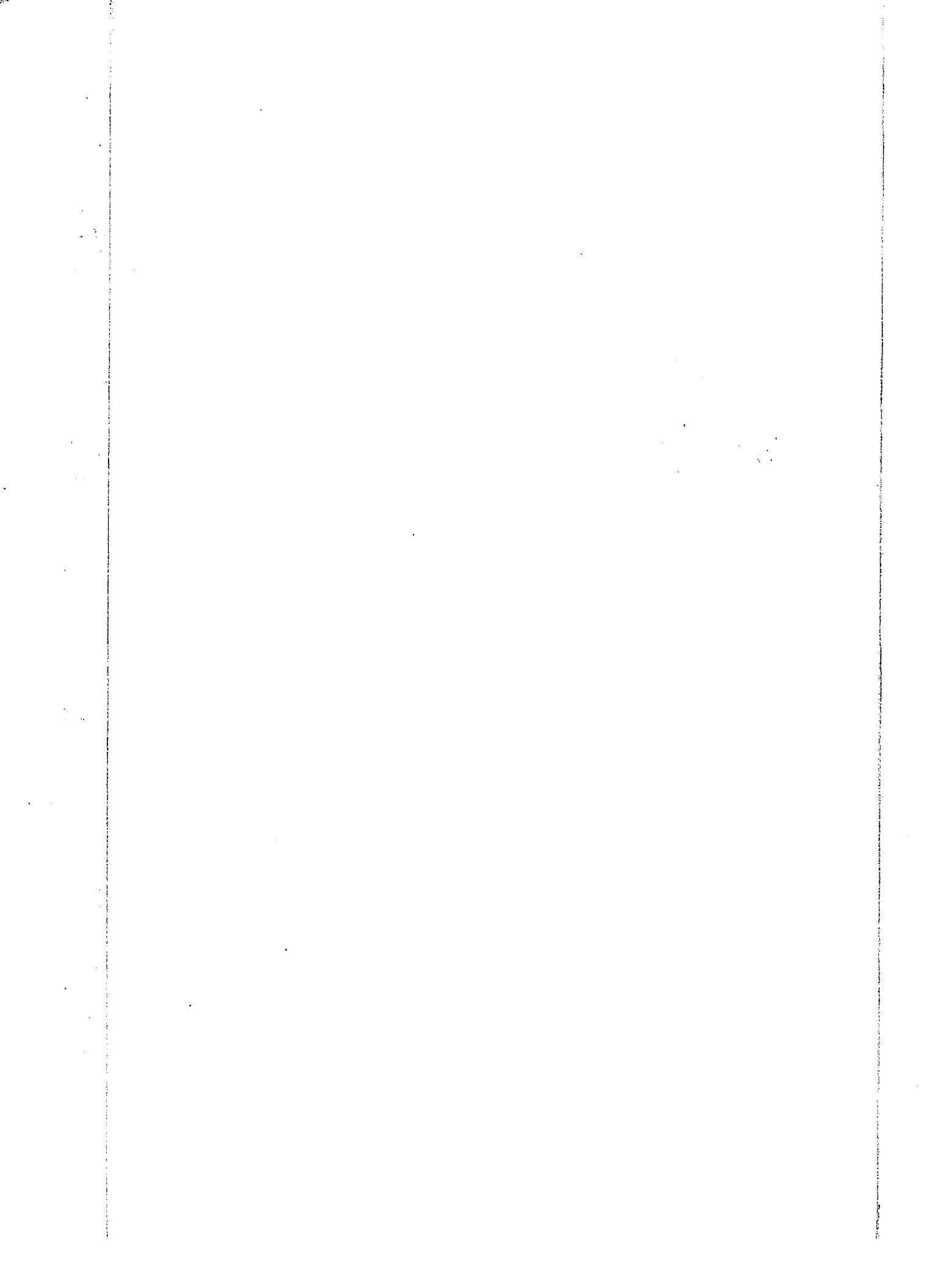
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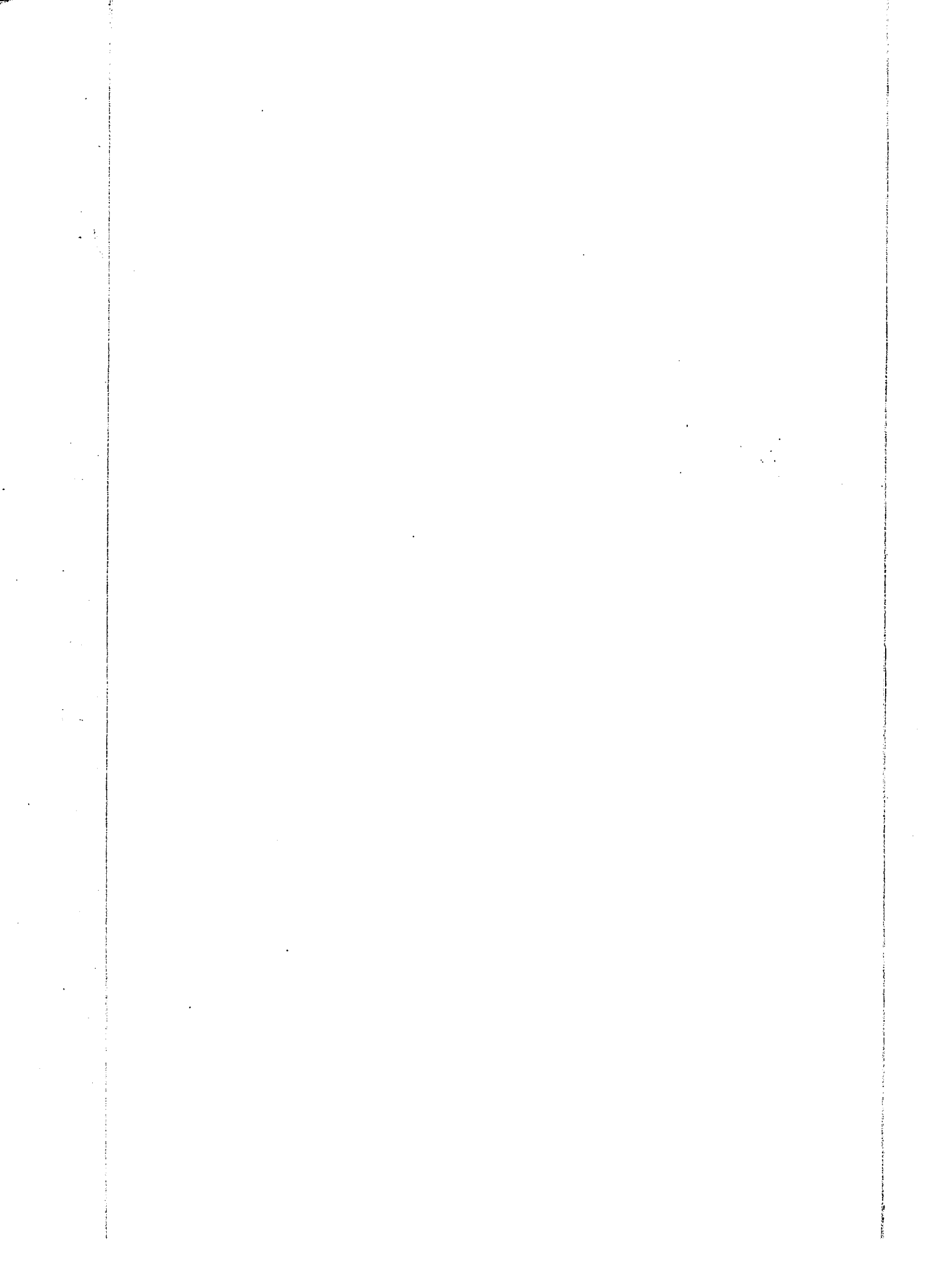
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THIOHYDROLYSIS IN SOLUTIONS  
IN LIQUID HYDROGEN SULFIDE

BY

Anderson Wheeler Ralston

A Thesis Submitted to the Graduate Faculty  
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject - Inorganic Chemistry

Approved

Signature was redacted for privacy.

In charge of Major work.

Signature was redacted for privacy.

Head of Major Department.

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Dean of Graduate College.

Iowa State College  
1927

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THIOHYDROLYSIS IN SOLUTIONS IN LIQUID  
HYDROGEN SULFIDE

Introduction

It is entirely conceivable and perhaps probable that every inorganic solvent has coupled with it a system of chemistry which is characteristic, and which contains some aspects which are uniquely its own. Most of our present day knowledge of chemistry, particularly inorganic, is built almost exclusively about the solvent water. In the study of other inorganic liquids as solvents lies a very broad and interesting source of investigation. The studies on liquid ammonia were probably pioneers in this field, which were followed by work on such solvents as: liquid hydrogen chloride, hydrogen cyanide, sulfur dioxide, vanadium oxychloride and liquid hydrogen sulfide. Numerous other inorganic liquids exist, the solvent action of which has received as yet very little attention, and a study of which will do much to further our knowledge of inorganic chemistry.

The properties of liquid hydrogen sulfide in this respect are of particular interest because of the close similarity in structure which exists between this hydride and water. Recent

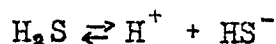
work (1)(2)(3)(4) has shown that liquid hydrogen sulfide dissolves numerous substances, and that many of these solutions are conductors of the electric current. Many individual cases have presented themselves in which compounds undergo reactions similar to hydrolysis in water and these reactions are now known under the general name "reactions of thiohydrolysis".

1. Steele, McIntosh and Archibald, Phil. Trans. Royal Soc. A., 205, 99, (1906)
2. Quam, Jour. Am. Chem. Soc. 47, 103, (1925)
3. Quam with Wilkinson, Jour. Am. Chem. Soc. 47, 989, (1925)
4. Biltz, Z. anorg. allgem. chem., 147, 171, (1925)

Purpose and Outline of the Investigation

The purpose of this work has been to carry out a systematic study of certain classes of inorganic and organic compounds using liquid hydrogen sulfide as the solvent medium and to establish a comparison between the action of these compounds in this solvent and like compounds in water, more especially as regards the phenomenon of hydrolysis in water and thiohydrolysis in liquid hydrogen sulfide.

Pure liquid hydrogen sulfide is a rather poor conductor of the electric current, but the fact that it does conduct is significant since it shows that the liquid is in equilibrium with its ions thus:



This being the case it is entirely reasonable to suppose that liquid hydrogen sulfide is potentially able to act as a hydrolyzing medium, and that compounds which are hydrolyzed by water should show somewhat analogous reactions in this medium.

Certain rather fundamental differences between water and liquid hydrogen sulfide must be recognized at the start, such as: reactions proceed much more slowly in liquid hydrogen sulfide than in water because of lower temperature and ionic concentration, thus necessitating a longer period of time before equilibrium conditions are realized; liquid hydrogen sulfide is a relatively strong reducing agent, and consequently many com-

pounds which hydrolyze in water react in an entirely different manner in liquid hydrogen sulfide. These reactions of reduction have no parallel in aqueous chemistry.

A survey of inorganic compounds will show that probably no single class is as versatile in its reactions with water as the chlorides, some of which are insoluble, others dissolve without appreciable hydrolysis while others are completely hydrolyzed. Of the organic types showing reactivity with water the esters and nitrils are characteristic examples. From these considerations, therefore, it was determined to make a complete and systematic study of the reactions of the inorganic chlorides with liquid hydrogen sulfide and also the thiohydrolysis of nitrils and of thio esters. It is believed that a study of these classes of compounds will do much towards a comparison of liquid hydrogen sulfide and water as a hydrolyzing medium.

(8)

PART I.

COMPARISON OF THE ACTIONS OF CHLORIDES  
WITH LIQUID HYDROGEN SULFIDE AND WITH WATER



COMPARISON OF THE ACTIONS OF CHLORIDES  
WITH LIQUID HYDROGEN SULFIDE AND WITH WATER

Preparation of the Liquid Hydrogen Sulfide

The liquid hydrogen sulfide used in the course of the investigation was prepared in an apparatus similar to that employed by Quam (5) with the exception that during several of the runs the potassium sulfide solution used to wash the generated gas was replaced by distilled water. For storage the liquid was placed in especially designed, thick-walled tubes of from 25 to 50 cubic centimeters capacity which were then sealed while cold (low temperatures were maintained by the use of solid carbon dioxide and ether), wrapped in a towel and placed in a steel tube which was then immersed in water. Large galvanized iron containers were constructed for this purpose each having a capacity of eight steel bombs, and containing approximately thirty gallons of water. For use these tubes were removed from the steel containers, and the temperature reduced by means of the cooling mixture. It is at this point that the greatest danger in handling the liquid is experienced since the sudden change in the temperature of the tube is apt to cause it to crack. All tubes employed, however, were tested several times by alternately raising and lowering their

temperature so as to reduce this danger to a minimum.

#### General Manipulation

The reaction tubes were much smaller in size and contained from five to ten cubic centimeters of the liquid. The reacting substance was either introduced directly into the tube, as in the case of most stable solids, or sealed in a glass capsule which was broken in the liquid hydrogen sulfide after room temperature had been reached. After various periods of time these tubes were cooled down, opened, the liquid hydrogen sulfide boiled off and the reaction products removed. These products were then purified and analyzed.

The conductivity measurements were made using a Wheatstone Bridge arrangement, induction coil and telephone receivers. Conductivity cells were constructed of soft glass and were similar in design to those employed by Quam (6). The cell constants were obtained by using 0.02 N KCl at 25°C., and employing the value  $2.768 \times 10^{-9}$  reciprocal ohms for the specific conductance. The temperature was kept constant with an ether carbon dioxide mixture. In all cases sufficient time was allowed for solution to take place if the substance was soluble. When solubility was apparent excess solute was employed and readings were taken until constant

6. Quam with Wilkinson (loc. cit.)

values showed the solution to be saturated under the experimental conditions.

### Preparation of the Chlorides

The majority of the chlorides used in these experiments were obtained by purifying and dehydrating stock samples. Since the anhydrous salts were desired it was necessary either to heat the chloride for a period of several hours at  $105^{\circ}\text{C}$ . or if hydrolysis took place under these conditions, as in the case of lithium chloride, the double salt with ammonium chloride was prepared and the ammonium chloride removed by sublimation. Quite a number of the chlorides were, however, made in this laboratory and brief mention of the methods employed will be made. Anhydrous ferric chloride, stannic chloride, selenium tetrachloride and antimony pentachloride were prepared by direct chlorination of the elements. Boron trichloride was prepared by direct chlorination of amorphous boron which had been prepared by the reduction of boron trioxide with a mixture of powdered aluminum and magnesium. The liquid boron trichloride was kept over mercury for several days to remove the dissolved chlorine. Tellurium tetrachloride was prepared according to Lenher (7)

7. Lenher, Jour. Am. Chem. Soc., 24, 188 (1902).

by the action of sulfur monochloride and metallic tellurium. It was washed repeatedly with carbon disulfide until the washings left no residue upon evaporation.

### Data and Comparisons

#### Lithium Chloride

Action with Liquid  
Hydrogen Sulfide:

Action with Water:

-77°

Insoluble and non-  
reactive.

Very soluble and  
slightly hydrolyzed.

25°

Insoluble and non-  
reactive.

Conductivity according  
to Kohlrausch (8).

Conductivity -77°

N/32 Eq. cond. 103.8

Nil

N/64 Eq. cond. 106.5

#### Potassium Chloride

-77°

Insoluble and non-  
reactive

Very soluble and not  
appreciably hydrolyzed.

25°

Insoluble and non-  
reactive.

Conductivity Kohlrausch (9)

8. F. Kohlrausch, L. Holhom and H. Dusselhorst, Wied. Ann. 64, 417 (1898).
9. F. Kohlrausch, L. Holhom and H. Dusselhorst (ibid).

(13)

Conductivity  $-77^{\circ}$

N/32 Eq. cond. 127.4

Nil.

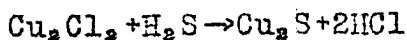
N/64 Eq. cond. 130.3

Cuprous Chloride

$-77^{\circ}$

Reacts to form cuprous sulfide, thus:

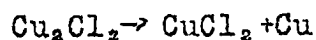
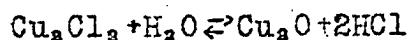
Very slightly soluble.



According to Bodlander (10) it is partially hydrolyzed and partially decomposed in contact with water, thus:

$25^{\circ}$

Reacts in a similar manner, but more rapidly.



Conductivity  $-77^{\circ}$

Shows an appreciable conductance due to HCl formed during above reaction.

Cupric Chloride

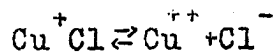
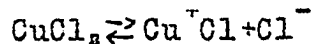
$-77^{\circ}$

Insoluble and non-reactive.

Very soluble and highly ionized. Ionizes in two stages: Evans (11)

Conductivity  $-77^{\circ}$

Nil.



10. G. Bodlander, Zeit. physik. Chem., 27, 58, (1898).
11. Evans, Proc. Roy. Soc., 57, 131, (1894).

(14)

Silver Chloride

-77°

Reacts to form yellow colloidal silver sulfide.

Insoluble.

25°

Forms black silver sulfide.

Conductivity -77°.

Shows an appreciable conductance due to HCl formed.

F. V. Von Hahn (12) found that silver sulfide hydrosols pass through a range of colors from yellow to green.

Strontium Chloride

-77°

Insoluble and non-reactive.

Soluble and yields a conducting solution.

25°

Insoluble and non-reactive.

Conductivity -77°

Nil.

12. F. V. Von Hahn, Koll. Zeit., 27, 171 (1920).

(15)

Barium Chloride

-77°

Insoluble and non-reactive.

Soluble and yields a conducting solution.

25°

Insoluble and non-reactive.

Conductivity -77°

Nil.

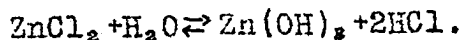
Zinc Chloride

-77°

Slightly soluble and nonreactive.

Soluble and slightly hydrolyzed according to the equation:

25°



Increased solubility but nonreactive.

F. L. Perrot (13) said that the state of equilibrium is rapidly attained.

Conductivity -77°

$0.643 \times 10^{-6}$

Cadmium Chloride

-77°

Insoluble and non-reactive.

Soluble, W. Bern (14) states that  $\text{CdCl}_2$  is hydrolyzed slightly at low temperature and that the amount of hydrolysis increases as the temperature is raised.

Conductivity -77°

Nil.

13. F. L. Perrot, Bull. soc. chim. (3)13, 975, (1895).
14. W. Bern, Zeit. physik. Chem., 27, 51, (1898).

(16)

Mercurous Chloride

-77°

Reacts to form HgSH with the consequent formation of HCl.

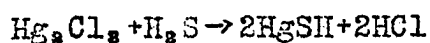
Very slightly soluble. According to Kohlrausch (15) a liter of water dissolves 0.02 g. at 18°.

25°

Reaction goes to completion forming olive green HgSH or H<sub>2</sub>S.H<sub>2</sub>S.

Conductivity -77°

Shows conductivity due to HCl formed in the reaction:



Since HgSH and Hg<sub>2</sub>SH<sub>2</sub>S both have the same percentage composition it was impossible to distinguish between them by chemical analysis. It is of interest to note in this connection that Antony and Sestini (16) state that hydrogen sulfide acting upon a mercurous salt below zero degrees C. gave mercurous sulfide, which above that temperature decomposed into mercuric sulfide and mercury. In the case of the liquid hydrogen sulfide the compound obtained was very stable at room temperature.

15. Kohlrausch, Zeit. physik. Chem., 50, 356, (1905).
16. Antony and Sestini, Gazz. chim. ital., 24, 1, 193



(17)

Mercuric Chloride

-77°

Slightly soluble and non-reactive.

Soluble and very slightly ionized.

25°

Very slightly hydrolyzed.

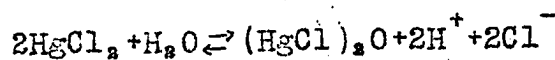
Soluble and reactive to give mercuric sulfide.

Hydrolysis takes place according to Lew (17) as follows:

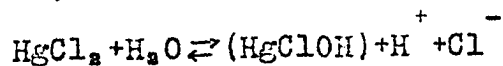
Conductivity -77°

Either,

$.031 \times 10^{-6}$



or,



Mercuric Bromide

-77°

Soluble and non-reactive.

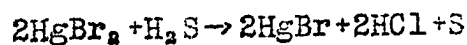
Soluble but slightly ionized.

Solubility greater than mercuric chloride.

Slightly hydrolyzed.

25°

Soluble, and reduced according to the equation:



Conductivity -77°

$5.160 \times 10^{-6}$

17. H. Lew, Zeit. physik. Chem., 30, 226, (1899).

(18)

Mercuric Iodide

-77°

Appreciably soluble  
and nonreactive.

Soluble but slightly  
ionized.

Solubility greater  
than mercuric chloride  
or bromide.

Hydrolyzed.

25°

Dissolved immediately,  
and on cooling a large  
amount of the yellow  
modification separated  
out.

Conductivity -77°

$9.985 \times 10^{-6}$

According to W. D. Bancroft (18) when mercuric  
iodide is precipitated from organic solutions the yel-  
low form is always first obtained which later changes  
to the red.

Boron Trichloride

-77°

Reacts with extreme  
violence to form the  
addition product  
 $\text{BCl}_3 \cdot 12\text{H}_2\text{S}$  which de-  
composes at  $-46^\circ\text{C}$ . in-  
to  $\text{BCl}_3$  and  $\text{H}_2\text{S}$ . De-  
termined by ratio.

Completely hydrolyzed  
with water to give  $\text{HCl}$   
and  $\text{H}_3\text{BO}_3$ .

S. B. Dumas (19) says  
that a solid hydrate is  
first found if a smaller  
quantity of water is em-  
ployed.

18. Bancroft, Jour. Phys. Chem., 1, 137, (1897)
19. Dumas, Ann. chim. phys. (2) 31, 346, (1826)

25°

Clear solution which  
on cooling down yields  
the product  $\text{BCl}_3 \cdot 12\text{H}_2\text{S}$ .

Conductivity  $-77^\circ$  $0.596 \times 10$ Aluminum Trichloride $-77^\circ$ 

Appreciably soluble,  
but nonreactive.

Hydrolyzed to give  
 $\text{Al}(\text{OH})_3$  and  $\text{HCl}$ .

Biltz (20) also reports  
 $\text{AlCl}_3$  as soluble.

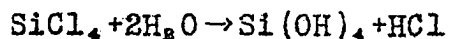
F. Wöhler and E. Baud  
(21) reported the for-  
mation of  $2\text{AlCl}_3 \cdot \text{H}_2\text{S}$   
and  $\text{AlCl}_3 \cdot \text{H}_2\text{S}$ .

Conductivity  $-77^\circ$  $2.092 \times 10^{-6}$ Silicon Tetrachloride $-77^\circ$ 

Completely miscible and  
nonreactive.

Completely hydrolyzed  
according to the equation:

25°



Very slow reaction took  
place over an interval  
of several weeks with  
the formation of  $\text{SiS}_2$ .

20. Biltz, (loc. cit.)

21. F. Wöhler and E. Baud, Ann. chim. phys. (8) 1, 28, (1904)

Conductivity  $-77^{\circ}$ 

Conc.	Sp. Cond. /X10 <sup>7</sup>
0.094	.3228
0.2184	.5929
0.3709	.8778
0.4573	1.290
0.5502	1.290
0.6556	1.290
0.7646	1.290
0.8464	1.290
1.2838	1.290
1.4632	1.290

Titanium Tetrachloride $-77^{\circ}$ 

Reacts with great violence to form addition products, which decompose explosively at room temperature.

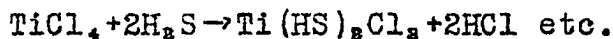
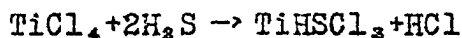
Analysis showed the compound to be  $2\text{TiCl}_4 \cdot \text{H}_2\text{S}$ .

König and von der Pfordten (23) have found that  $\text{TiCl}_4$  forms a series of compounds:

$\text{Ti}(\text{OH})\text{Cl}_3$ ,  
 $\text{Ti}(\text{OH})_2\text{Cl}_2$ ,  
 $\text{Ti}(\text{OH})_3\text{Cl}$  and finally  
 $\text{Ti}(\text{OH})_4$  stands between silicon and tin in its ease of hydrolysis with water.

 $25^{\circ}$ 

Partially reduced to black  $\text{TiCl}_3$  and partially thiohydrolyzed according to the equations:



Biltz (23) has shown the existence of  $\text{TiCl}_4 \cdot 2\text{H}_2\text{S}$  and  $\text{TiCl}_4 \cdot \text{H}_2\text{S}$  by the reaction of titanium tetrachloride

22. König and von der Pfordten, Ber., 22, 1485, (1899)  
 23. Biltz, (loc. cit.)

(21)

and liquid hydrogen sulfide at low temperatures. The difference here is due to different experimental conditions. Pfordten (24) has shown that gaseous hydrogen sulfide forms a series of products corresponding to those obtained with liquid hydrogen sulfide at room temperature.

Tin Tetrachloride

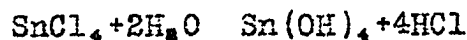
-77°

Completely miscible and nonreactive.

First forms hydrates and with excess water proceeds thus:

25°

Very slow reaction with the formation of minute amounts of stannic sulfide.



Less hydrolyzed than  $\text{SiCl}_4$  or  $\text{TiCl}_4$ .

Conductivity -77°

Conc.	Sp. Cond. x 10 <sup>7</sup>
0.0040	0.965
0.1416	1.007
0.2481	1.062
0.5134	1.062

Lead Chloride

-77°

Insoluble and nonreactive.

Very slightly soluble in cold water, rather soluble in hot water.

Conductivity -77°

Slightly hydrolyzed.

Nil.

24. Pfordten, Ann., 234, 257 (1886)

(22)

Phosphorus Trichloride

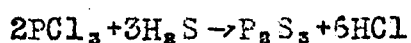
-77°

Completely miscible  
and nonreactive.

Hydrolyzed with cold  
water to give HCl and  
H<sub>3</sub>PO<sub>3</sub>

25°

Reacted immediately  
to give P<sub>2</sub>S<sub>3</sub> and HCl,  
thus:

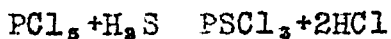


The equivalent conductivities of PCl<sub>3</sub>, As Cl<sub>3</sub>,  
SbCl<sub>3</sub> and BiCl<sub>3</sub> have been previously determined by Quam  
and Wilkinson (25) and have not been repeated in this  
investigation.

Phosphorus Pentachloride

-77°

Reacts slowly with the  
formation of PSCl<sub>3</sub> ac-  
cording to the equation:



Reacts to form POCl<sub>3</sub>  
which is further hydro-  
lyzed to give meta and  
ortho phosphoric acids  
and hydrogen chloride.

25°

Same reaction as at the  
lower temperature. It  
is, therefore, evident that  
PSCl<sub>3</sub> is extremely stable  
towards liquid hydrogen  
sulfide.

25. Quam with Wilkinson, (loc. cit.)

(23)

Arsenic Trichloride

-77°

Immediate reaction with the formation of arsenic trisulfide.

Hydrolyzed with water to give  $H_3AsO_3$  and HCl.

25°

Reacts the same as at the lower temperature.

It is evident that the thiohydrolysis of arsenic trisulfide goes to completion. One would expect that at the lower temperature some of the known arsenic, sulfur and chlorine compound might be formed such as: SCl or  $2AsS^0ClAs_2S_3$  (26), but such does not appear to be the case.

Antimony Trichloride

-77°

Soluble and nonreactive.

Forms first  $SbOCl$  which is decomposed with warm water into antimonic acid and hydrogen chloride.

25°

Extremely soluble and nonreactive.

Biltz (27) has also found that  $SbCl_3$  is soluble in liquid hydrogen sulfide. On boiling off the hydrogen sulfide lemon yellow crystals of the composition  $SbS^0Cl.7SbCl_3$  were formed. This compound had been previ-

26. Ovard, Compt. rend. 116, 1516, (1893)  
27. Biltz, (loc. cit.)

(24)

ously isolated by Schneider (28).

Antimony Pentachloride

-77°

Reacted slowly to form  $SbSbCl_5$  and HCl.

Decomposed by warm water into antimonious and hydrochloric acids.

25°

Reacted in a similar manner to give  $SbSbCl_5$  and HCl.

Bismuth Trichloride

-77°

Reacted to form the addition compound  $2BiCl_3 \cdot H_2S$  which is stable in liquid hydrogen sulfide, but is decomposed at atmospheric conditions giving:  $BiSbCl_5$ ,  $BiCl_3$  and  $2HCl$ .

Forms  $BiOCl$  which is stable towards water.

25°

A duplication of the reaction at the lower temperature occurred.

The formation of this addition compound explains why Quam (29) obtained no conductance with  $BiCl_3$  and liquid hydrogen sulfide although a reaction was observed to have taken place.

28. Schneider, Pogg., 108, 407, (1858)  
29. Quam, (loc. Cit.)

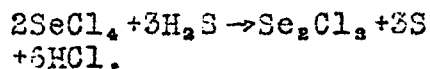


(25)

Selenium Tetrachloride

-77°

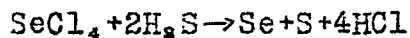
Reacts to form selenium monochloride and sulfur according to the equation:



Hydrolyzed first yielding the oxychloride and finally meta selenous acid and hydrogen chloride.

25°

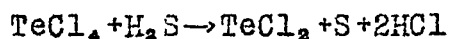
Reduced to selenium according to the equation:



Tellurium Tetrachloride

-77°

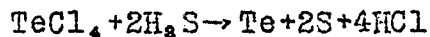
Reduced to form tellurium dichloride according to the equation:



First hydrolyzed to the oxychloride and then tellurous and hydrochloric acids.

25°

Reduced to elemental tellurium, thus:



Chromic Chloride

(green)

-77°

Insoluble and non-reactive.

Conductivity -77°

Dissolves to give various ions such as  $\text{CrCl}_2 + \text{Cl}$  etc. Hydrolysis value between

(26)

Nil.

aluminum chloride  
and ferric chloride.

Chromium Chloride

(violet)

-77°

Insoluble and non-  
reactive.

Slightly soluble and  
partially hydrolyzed.

25°

Completely inert.

Conductivity -77°.

Nil.

Manganous Chloride

-77°

Insoluble and non-  
reactive.

Soluble and according  
to Bruner (30) slight-  
ly hydrolyzed.

Conductivity -77°.

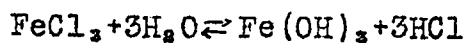
Nil.

Ferric Chloride

-77°

Very soluble and  
slowly reduced at  
this temperature.

Soluble and hydrolyzed,  
thus:



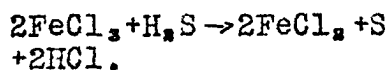
25°

Immediately reduced  
to ferrous chloride,

30. Bruner, Jour. physik. Chem., 32, 133, (1900).

(27)

thus:



Conductivity  $-77^\circ$

$209.890 \times 10^{-6}$

Cobaltous Chloride

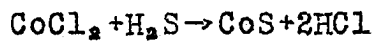
$-77^\circ$

Insoluble and nonre-  
active.

Soluble and slightly  
hydrolyzed.

$25^\circ$

Reacts to form the  
sulfide, thus:



Conductivity  $-77^\circ$

Nil.

Summary

Liquid hydrogen sulfide is much more reactive with these compounds than would first be supposed. This is especially true at room temperature. It is seen that reactivity with this solvent falls naturally into three general classes:

1. An addition product is formed which may or may not be soluble in the liquid hydrogen sulfide. Examples are:  $\text{BCl}_3 \cdot 12\text{H}_2\text{S}$ ,  $2\text{TiCl}_4 \cdot \text{H}_2\text{S}$ ,  $2\text{BiCl}_3 \cdot \text{H}_2\text{S}$ , etc.
2. Reactions of thiohydrolysis take place such as  $\text{PCl}_5$  to  $\text{PSCl}_3$ ,  $\text{Hg}_2\text{Cl}_2$  to  $\text{HgSH}$ , or  $\text{AsCl}_3$  to  $\text{As}_2\text{S}_3$ .
3. Reduction of the halide by the liquid hydrogen sulfide, such as:  $\text{SeCl}_4$  to  $\text{Se}$  or  $\text{FeCl}_3$  to  $\text{FeCl}_2$ .

Of the chlorides studied those of the alkali and alkaline earth groups showed decided inactivity,  $\text{KCl}$ ,  $\text{BaCl}_2$ ,  $\text{SrCl}_2$  etc. Silver, cuprous and mercurous chlorides on the other hand are all reactive even at the low temperature. While zinc chloride is soluble and yields a conducting solution, cadmium chloride is markedly inert. The halides of mercury are all soluble at the lower temperature yielding conducting solutions, the order of conductivity being  $\text{I} < \text{Br} < \text{Cl}$ . At room temperature these halides show no

resemblance in reaction, for while the chloride forms the sulfide, the bromide is reduced and the iodide is unreactive. Boron and aluminum trichloride both yield conducting solutions. While silicon and tin tetrachlorides are very soluble at low temperatures titanium tetrachloride forms an addition compound. At higher temperatures titanium tetrachloride is both reduced and hydrolyzed while silicon and tin tetrachloride form the respective sulfides, but only to a small extent.

With the chlorides of the fifth group one finds marked instability towards the hydrogen sulfide, especially at the higher temperature. In some cases intermediate products of hydrolysis are found which are stable in the liquid. Antimony trichloride presents, however, a marked exception since it is extremely soluble but unreactive with the liquid. Selenium and tellurium tetrachlorides are both reduced. Manganous and chromic chlorides are stable but cobalt forms the sulfide at the higher temperature, while ferric chloride is reduced to ferrous chloride.

It is very noticeable that in cases where thiohydrolysis does take place the sulfide is usually formed and not the hydrosulfides or thioacid. The only two instances of the possible formation of hydrosulfides or thioacids were

reactions with mercurous chloride and titanium tetrachloride, while numerous cases of the direct formation of sulfides were evidenced. In this respect thiohydrolysis in liquid hydrogen sulfide differs very markedly from hydrolysis in water. Liquid hydrogen sulfide is not as strong a hydrolyzing agent as water since many compounds which are easily hydrolyzed with water are stable or are hydrolyzed with difficulty in the hydrogen sulfide, and as further evidenced by the stability of intermediate products of hydrolysis such as  $\text{PSCl}_3$  and  $\text{SbSCl}_3$ , etc. in the liquid hydrogen sulfide.

Perhaps the greatest dissimilarity in the two solvents is the reducing power of the hydrogen sulfide, which is very vigorous at room temperature. Many compounds which are almost completely hydrolyzed by water are on the other hand reduced by the hydrogen sulfide such as:  $\text{TiCl}_4$ ,  $\text{SeCl}_4$ ,  $\text{TeCl}_4$ ,  $\text{FeCl}_3$ , etc. This makes a true comparison of the hydrolyzing power of liquid hydrogen sulfide and water rather difficult since this reduction masks any power of hydrolysis which the hydrogen sulfide may possess with these compounds.

PART II.

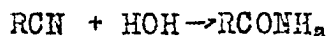
ACTION OF LIQUID  
HYDROGEN SULFIDE ON NITRILES

## ACTION OF LIQUID HYDROGEN SULFIDE ON NITRILES

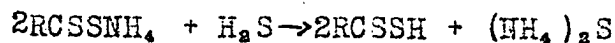
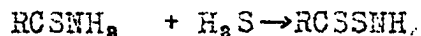
Theoretical Considerations

Since nitriles are hydrolyzed with water to carboxylic acids in the presence of acids or bases, an investigation of these reactions with liquid hydrogen sulfide under like conditions is of extreme interest.

In an acid or alkaline solution or with superheated steam nitriles react thus:



When a nitrile is sealed up with liquid hydrogen sulfide, and the tube allowed to remain at room temperature, one duplicates the conditions necessary for the cyanide hydrolysis with water since the nitrile is in contact with the hydrogen sulfide at a temperature some eighty-five degrees above the boiling point of the latter. If any similarity with aqueous chemistry manifests itself under these conditions one would expect the dithio acid to be found according to the equation:





Bernthsen (1) showed that gaseous hydrogen sulfide reacts with acetic nitrile in solution to give thioacetamide and since one increases the contact by dissolving the nitrile directly in the hydrogen sulfide the probability of the above reaction taking place is quite strong.

Reactivity would be at once indicated by the appearance of the characteristic orange red solution of the dithio acid in the liquid hydrogen sulfide, and the separation of insoluble ammonium sulfide.

A study of these reactions is of extreme importance since it not only offers further data for the comparison of reactions in liquid hydrogen sulfide and in water, but also, since it affords a possible method of preparation of numerous dithio acids which are at present very difficult to synthesize.

1. Bernthsen, Ann., 192, 45, (1878).

Experimental Part

Samples varying from five-tenths to one gram of the nitrile were placed in dry pressure tubes and cooled down in the ether-carbon dioxide bath. Liquid hydrogen sulfide was then admitted and the tubes observed for six hours at the lower temperature. The tubes were then sealed and allowed to remain at room temperature for several days, frequent observations being made. The tubes were then cooled down, opened and dry gaseous hydrogen chloride introduced after which treatment the tubes were again sealed and kept at room temperature until reaction had apparently ceased. The tubes were again cooled and the excess hydrogen sulfide removed at its boiling point. The products were then separated from the ammonium sulfide with ether, and the free acid extracted from the ether with sodium hydroxide solution. The acid was then obtained by acidifying the sodium hydroxide solution with hydrochloric acid and extracting with ether. In two cases identification of the acids was made by determination of the boiling point, and in one case by analysis.

Observations

The observations are best portrayed by the following table.

All the nitriles studied were completely miscible and unreactive with pure liquid hydrogen sulfide at 25°C. Observations were made for seventy-two hours.

TABLE I.

Liquid Hydrogen Sulfide Plus Hydrogen Chloride

Nitrile:	-77°	25°	Color of Acid:	Remarks
Aceto	Miscible and non-reactive	Reactive, yielding an orange red solution.	Orange red	Reaction completed after 24 hours. (NH <sub>4</sub> ) <sub>2</sub> S separated.
Propio	Miscible and non-reactive	Reactive, yielding an orange red solution.	Orange red	Reaction completed after 24 hours. (NH <sub>4</sub> ) <sub>2</sub> S separated.
Valerio	Miscible and non-reactive	Slowly reactive, yielding an orange red solution.	Orange red	Reaction completed after 40 hours. (NH <sub>4</sub> ) <sub>2</sub> S separated.
Benzo	Slowly reactive	Immediate reaction, yielding a red solution.	Red	Reaction completed after 10 hours. (NH <sub>4</sub> ) <sub>2</sub> S separated.

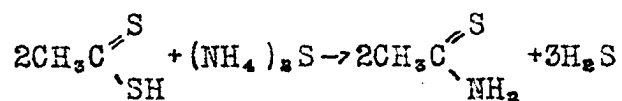
Proof of the Formation of  
Dithiocarboxylic Acids.

In order to show that the dithiocarboxylic acids were actually formed the products from the reaction of liquid hydrogen sulfide with propio and benzo nitriles were isolated by the method previously described. The product isolated from the action of propio nitrile boiled at  $49^{\circ}$ , at 20 mm. pressure. Only a very small amount of the acid was obtained. In order to check this boiling point a sample of dithiopropionic acid was prepared by treating magnesium ethyl bromide with carbon disulfide, hydrolyzing and extracting the product by a method similar to that employed by J. Houben and H. Pohl (2) for the preparation of dithioacetic acid. The acid prepared in this manner had a boiling point of  $59^{\circ}$  at 30 mm. pressure.

A small amount of product boiling at  $290^{\circ}$  at 25 mm. pressure was obtained from the action of liquid hydrogen sulfide and benzo nitrile. On analysis of a sample by means of Carius sulfur determination, the percentage of sulfur was found to be 41.11%, which is rather close to the theoretical percentage of 41.64 for sulfur in dithiobenzoic acid. Benzo nitrile was much more reactive than any of the aliphatic nitriles studied. The small yields obtained were

2. J. Houben and H. Pohl, Ber. 40, (2) 1303, (1907).

due to two causes: first, some of the nitrile formed the intermediate product, the thio amide, showing that the optimum conditions for the reaction have not as yet been realized; secondly, the ammonium sulfide formed reacted with the acid after the removal of the hydrogen sulfide. This reaction is reversed as follows:



A study of more efficient means of separation of the acid will of course eliminate this difficulty.

Conclusions

It has been shown that when nitriles are placed in contact with liquid hydrogen sulfide in the presence of hydrogen chloride the nitrile is reactive, the products of the reaction being: the corresponding dithiocarboxylic acid, the thioamide and ammonium sulfide. The presence of the thioamide shows that the optimum conditions for the reaction are a matter of further investigation. The function of the hydrogen chloride is as yet unknown, save that it is known that the reaction does not take place in its absence. The hypothesis that the thiohydrolysis in this case is dependent upon the acidity of the solution seems most probable. To prove this other acid and also basic catalysts should be employed.

The work done in this laboratory on this subject serves merely as an introduction into an important field, and a further study of the reactions from the standpoint of determining the optimum condition as regards time, temperature and catalysts would yield very interesting and important results. Since this reaction enables one to pass directly from the nitrile to the dithiocarboxylic acid its contribution to sulfur chemistry cannot be over-estimated.

PART III.

CONDUCTIVITIES OF ORGANIC  
THIOACIDS IN LIQUID HYDROGEN SULFIDE

CONDUCTIVITIES OF ORGANIC  
THIOACIDS IN LIQUID HYDROGEN SULFIDEIntroduction

It has been found by Guam and Wilkinson (1) that acetic acid is a nonconductor in liquid hydrogen sulfide at low temperatures while thioacetic acid solutions have a rather appreciable conductivity value. It is, therefore, evident that the substitution of one sulfur for one oxygen atom in the acetic molecule markedly influences the degree of dissociation of the acid in this solvent. Reasoning from this it seems logical to assume that the replacement of the second oxygen of the acetic acid molecule to give a dithiocarboxylic acid should be attended by a further increase of dissociation in liquid hydrogen sulfide.

Acetic acid and its homologues are classed as weak acids in water solution, and further as one ascends the homologous series the acidic properties become noticeably less. It is thus of extreme interest and importance to determine if this same relationship exists in the sulfur system.

1. Guam and Wilkinson, Jour. Am. Chem. Soc. 47, 989, (1925).

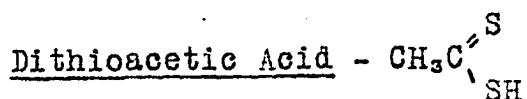


Purpose of the Investigation

It is apparent that acids of the type RCSSH bear the same relationship to liquid H<sub>2</sub>S as acids of the type RCOOH have to water. It is the purpose of this investigation to determine the effect on conductivity of compounds of this type in liquid hydrogen sulfide when oxygen atoms in the molecule are substituted by sulfur, and furthermore, to establish some definite generalization in regard to increase in molecular weight of the acids and their conductivities in this solvent.

Preparation of the AcidsThioacetic Acid:

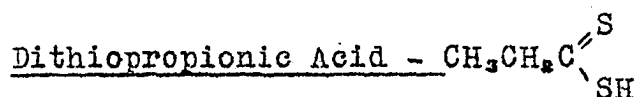
The thioacetic acid was prepared by a method similar to that first employed by Schiff (2). Acetic acid was heated for several hours with phosphorus pentasulfide and the resulting mixture distilled several times using a fractionating column. The acid which was used had a boiling point of 93°- 95°C. which checks the boiling point of thioacetic acid, 93°C.



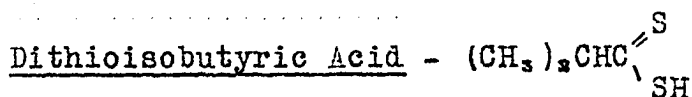
The dithioacetic acid was prepared according to

2. Schiff, Ber. 28, 1205, (1895).

J. Houben and H. Pohl (3). One molecular weight of methyl magnesium iodide was treated with an excess of carbon disulfide and the resulting compound hydrolyzed. The ether solution was then extracted with twenty-five percent sodium hydroxide solution and the free acid was then obtained by acidifying with hydrochloric acid and extracting with ether. The ether was then removed, and the acid distilled under a vacuum. The acid boiled at 40° at 19 mm. which checks the boiling point of that obtained by Houben and Pohl 37° at 15 mm. pressure.



This acid was prepared by methods exactly similar to those used in the preparation of dithioacetic acid with the exception that ethyl magnesium bromide was substituted for the methyl magnesium iodide used in the former case. The acid boiled at 59° under 30 mm. pressure.

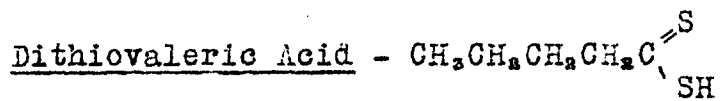


This acid was prepared by a similar method using isopropyl magnesium bromide and carbon disulfide. It boiled at 58° under 20 mm. pressure. J. Houben and H. Pohl (4) found that normal dithiobutyric acid boiled at 59° under 13 mm.

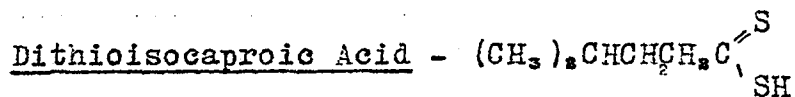
3. J. Houben and H. Pohl, Ber. 40, 2, 1303, (1907).

4. J. Houben and H. Pohl, Ber. 40, 2, 1725, (1907).

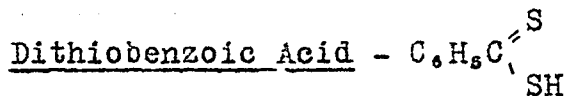
pressure.



A similar method of preparation was employed using n butyl magnesium bromide and carbon disulfide. The acid boiled at  $80^\circ$  under 10 mm. pressure. J. Houben and H. Pohl (5) found that dithioisovaleric acid boiled at  $84^\circ$  under 33 mm. pressure.



This acid was prepared using the same method. It boiled at  $85^\circ$  under 14 mm. pressure. J. Houben and H. Pohl (6) report its boiling point as  $84^\circ$  under 10 mm. pressure.



Prepared by the use of phenyl magnesium bromide and carbon disulfide. Boiled at  $290^\circ$  under 10 mm. pressure.

5. J. Houben and H. Pohl, (ibid.).
6. J. Houben and H. Pohl, (ibid.).

General Manipulation

The liquid hydrogen sulfide was prepared as previously described. Conductivity apparatus and cells were similar to those employed in the previous work. The acids were added by means of a weighing pipette.

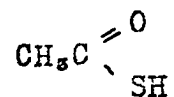
(45)

Conductivities

Acetic Acid -77°

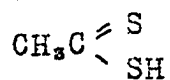
Nil

Thioacetic Acid -77°



Conc.	Eq. Cond.
	$\sqrt{\times 10^3}$
0.0207	1.450
0.0365	1.060
0.0795	0.755
0.2653	0.650
0.2669	0.620
0.4833	0.578
0.5746	0.573
1.0331	0.554

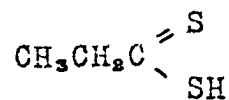
Dithioacetic Acid -77°



Conc.	
0.1405	1.461
0.2252	1.092
0.4005	0.760
0.4462	0.761
0.4826	0.735
0.6513	0.529

(45)

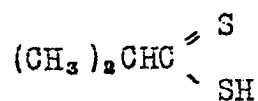
Dithiopropionic Acid -77°



Conc.

0.0157	0.431
0.0544	0.397
0.0764	0.351
0.1376	0.250
0.2814	0.210
0.3300	0.188
0.3781	0.175

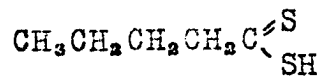
Dithioisobutyric Acid -77°



Conc.

0.0244	0.742
0.0982	0.539
0.1687	0.509
0.2326	0.492
0.3714	0.397
0.4464	0.385
0.5588	0.347
0.8289	0.339

Dithiovaleric Acid -77°



Conc.

0.0181	0.722
0.0348	0.541
0.0567	0.489
0.1082	0.412
0.1561	0.332
0.2012	0.302

(47)

Dithioisocaproic Acid -77°

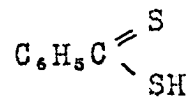


Conc.

0.0288  
0.0386  
0.0897  
0.1308  
0.1603  
0.2888

0.708  
0.458  
0.392  
0.376  
0.311  
0.218

Dithiobenzoic Acid -77°



Conc.

0.0789  
0.1854  
0.2333  
0.2800

0.227  
0.182  
0.166  
0.159

Conclusions

From the results obtained it is apparent that the substitution of sulfur for oxygen atoms in the acetic acid molecule greatly increases the conductivity in liquid hydrogen sulfide. It is also shown that as the molecular weight of the dithio acid is increased there is a decrease in conductivity. Dithiopropionic acid is an exception to this rule since its equivalent conductance is much less than would be expected. This generalization is the same as one meets in the conductivity of acetic acid and its homologues in water. It is of interest to note that propionic acid is also lower in conductivity in the aqueous system. The conductances of acetic acid and its homologues corresponding to the ones studied in this investigation are as follows:

Acid	$\wedge$ (32)	$\wedge$ (1024)
Acetic	8.7	46
Propionic	7.4	38.7
Isobutyric	7.9	43.6
Valeric	7.7	42.6
Isocaproic	7.5 $\wedge$ (27.8)	29.6 $\wedge$ (442.5)
Benzoic	22.3 $\wedge$ (64)	79.6 $\wedge$ (512)

The conductivities of the thio acids in liquid hydrogen sulfide are of the order of one thousandth of the conductivities of the above acids in water.



Benzoic acid, which has the highest equivalent conductivity in aqueous solution, appears to differ in the sulfur system, since dithiobenzoic acid has the lowest conductivity in liquid hydrogen sulfide.

In general it can be said that these acids appear to have a similar relation to liquid hydrogen sulfide as the oxygen acids display towards water. Reasoning from this it would be expected that trichloroacetic acid would have an appreciable conductivity in liquid hydrogen sulfide, but Quam and Wilkinson (7) found its conductivity to be "nil", and this result has been verified in this laboratory. A possible explanation is that the introduction of the three chlorines in place of the three hydrogens so modifies the nature of the molecule as to render it insoluble in the liquid hydrogen sulfide.

7. Quam and Wilkinson, (loc.cit.).

PART IV.

THIOHYDROLYSIS OF ESTERS  
IN LIQUID HYDROGEN SULFIDE

THIOHYDROLYSIS OF ESTERS  
IN LIQUID HYDROGEN SULFIDE

Theoretical Considerations

It is well known that esters are appreciably hydrolyzed in water, the degree of hydrolysis depending on the temperature, the acidity of the solution and the concentration of the products of hydrolysis. Since liquid hydrogen sulfide has been shown in numerous instances to act as a hydrolyzing medium it is not unreasonable to suppose that there may be some similarity in reactions of esters with water and with liquid hydrogen sulfide. Because reactions in liquid hydrogen sulfide proceed more slowly than with water a longer period of time will probably be required for equilibrium to be attained.

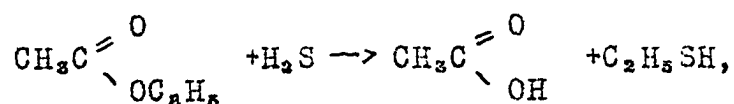
One of the standard methods of determining the degree of hydrolysis is by conductivity measurements. In the case where one of the products of the hydrolysis is a nonconductor in solution the method is much simplified. Thus if the conductivity of the hydrolyzed ester is expressed by  $\wedge_b$  and the conductivity of the unhydrolyzed ester by  $\wedge$  then the increase in conductivity,  $\wedge_b - \wedge$ , is due to hydrolysis of the ester. If hydrolysis were complete the conductivity due to hydrolysis would be  $\wedge_A + \wedge_B$  when  $\wedge_A$  and  $\wedge_B$  are the equivalent conductivities of the acid and base respectively. The

degree of hydrolysis can, therefore, be expressed by the equation:

$$x = \frac{\Lambda_b - \Lambda}{\Lambda_a - \Lambda}$$

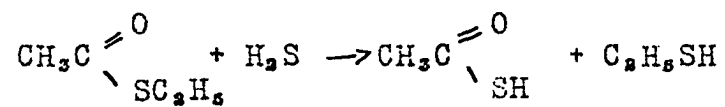
One can obtain  $\Lambda_b$  directly by measuring conductivity values of solutions of the esters, and  $\Lambda$  is obtained by measuring the conductivity values of the ester in a solution saturated with the weak base so that hydrolysis is prevented.

It has been shown by Quam and Wilkinson that solutions of mercaptans in liquid hydrogen sulfide are nonconductors. It has further been shown that acetic acid is a nonconductor at low temperatures while thioacetic acid is a conductor. In considering, therefore, the hydrolysis of an ester such as ethyl acetate in liquid hydrogen sulfide, thus:



it is evident that since both acetic acid and ethyl mercaptan are nonconductors a conductivity method cannot be employed. However, if one studies the thioesters a conductivity method is directly applicable since in this case one of the products is thioacetic acid which is a relatively strong conductor in liquid hydrogen sulfide. In the case of

ethyl thioacetate the reaction proceeds thus:



and since the thioacetic acid is a conductor while the ethyl mercaptan is not, one has direct recourse to the method expressed by the formula:

$$x = \frac{\Lambda_b - \Lambda}{\Lambda_a - \Lambda}$$

Experimental PartPreparation of the Esters:

The thiol esters were prepared by a method previously employed by Obermeyer (1) for the preparation of methyl thiolacetate. An alcoholic solution of lead acetate was added to an alcoholic solution of the mercaptan until no further precipitation of lead mercaptid took place. The lead mercaptid was then filtered off, washed with ether and dried in a vacuum desiccator. The lead mercaptid was then treated with ice-cooled acetyl chloride, the reaction flask being immersed in an ice salt mixture. After the reaction had subsided the resulting lead chloride was filtered off and the solution distilled. The ester was then placed in contact with calcium carbonate to remove any acetic acid and redistilled. In the case of esters of higher molecular weight, as butyl and iso butyl, the mercaptan was refluxed with acetyl chloride for several hours, and the resulting solution distilled and purified as previously described.

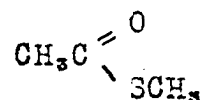
The esters employed had the following boiling points:

Methyl	95°-96°.
Ethyl	115°-116°
n Propyl	135°-137°
iso Propyl	122°-123°
n Butyl	154°-155°
iso Butyl	144°-145°
Phenyl	110°-111° at 8 mm.

1. Obermeyer, Ber. 20, 2921, (1887).

Determination of Conductivities:

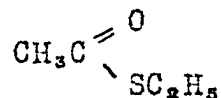
The conductivities were determined with an apparatus similar to that employed for the chlorides and thio acids. The same type of cells were also employed. The temperature was kept constant at  $-77^{\circ}\text{C}$ . by means of an ether-carbon dioxide mixture. Determinations of the equivalent conductances of the hydrolyzed ester at various dilutions were first made. Another run was then made using as solvent for the ester, a saturated solution of the corresponding mercaptan in the liquid hydrogen sulfide. The conductivity of the thioacetic acid had been previously determined in Part III. The data were then plotted, equivalent conductivity against concentration, and from these values the degrees of thiohydrolysis were calculated.

Conductivity Data:Methyl Thiolacetate

Conc.	Eq. Cond. $\sqrt{x} \ 10^3$
0.0188	0.116
0.0601	0.047
0.1207	0.029
0.1925	0.022
0.3187	0.022
0.5671	0.011

Ester plus Mercaptan

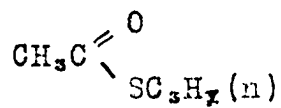
0.4568	0.004
0.5153	0.004
0.5222	0.003

Ethyl Thiolacetate

0.0223	0.187
0.0581	0.082
0.1028	0.094
0.2171	0.056
0.4832	0.038
0.6108	0.032

Ester plus Mercaptan

0.3132	0.007
0.5218	0.006
0.6800	0.005
0.7175	0.005

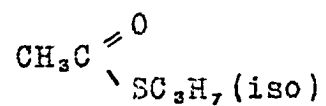
n Propyl Thiolacetate

0.0149	0.719
0.2097	0.103
0.3026	0.089
0.3698	0.092
0.4647	0.084
0.5731	0.083
0.6637	0.078
0.7572	0.077
0.8458	0.075
0.9376	0.075



Ester plus Mercaptan

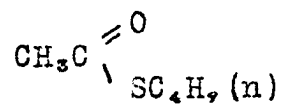
0.0770	0.021
0.1833	0.019
0.2204	0.016
0.2439	0.026
0.2881	0.022
0.3442	0.018
0.3825	0.021

Isopropyl Thiolacetate

0.0068	1.072
0.0885	0.253
0.1775	0.171
0.2534	0.134
0.3596	0.125
0.4300	0.122
0.5334	0.116
0.5924	0.139
0.6756	0.114
0.7465	0.113

Ester plus Mercaptan

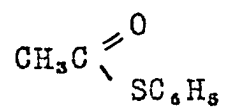
0.0817	0.025
0.0983	0.024
0.1218	0.023
0.2616	0.024
0.3001	0.023
0.4542	0.016
0.8763	0.011

n Butyl Thiolacetate

0.0154	1.185
0.0455	0.984
0.0610	0.819
0.1291	0.416
0.1882	0.349
0.2179	0.345
0.2668	0.341
0.2952	0.333
0.4634	0.273

Ester plus Mercaptan

0.0506	0.057
0.1142	0.034
0.1742	0.028
0.2329	0.022
0.3698	0.015
0.4698	0.012
0.5410	0.011
0.6353	0.009

Phenyl Thiolacetate

No Conductivity.

Degree Hydrolysis:

Table I.

Ester

: Conc. : : mol/l. :	: Methyl :	: Ethyl :	: n Propyl :	: iso : Propyl :	: n Butyl :
: 0.02 :	: 7.70 :	: 13.72 :	:	: 59.20 :	:
: 0.05 :	: 6.00 :	: 10.64 :	: 73.20 :	: 55.92 :	: 75.61 :
: 0.1 :	: 3.91 :	: 8.31 :	: 59.21 :	: 30.11 :	: 75.10 :
: 0.2 :	: 2.48 :	: 6.84 :	: 20.83 :	: 22.42 :	: 51.00 :
: 0.3 :	: 2.40 :	: 6.40 :	: 12.60 :	: 19.61 :	: 51.84 :
: 0.4 :	: 2.11 :	: 5.97 :	: 10.79 :	: 19.72 :	: 49.83 :
: 0.5 :	: 1.53 :	: 5.63 :	: 11.25 :	: 21.18 :	: 46.20 :
: 0.6 :	:	: 4.34 :	: 11.20 :	: 20.86 :	:
: 0.7 :	:	:	: 13.08 :	: 20.42 :	:
: 0.8 :	:	:	: 11.05 :	:	:
: 0.9 :	:	:	: 10.35 :	:	:

Conclusions:

From these results it appears that thiohydrolysis of esters of the type studied does take place. It is also evident that as the "R" group increases the hydrolysis values become greater. Phenyl thioacetate, on the other hand, exhibits no conductivity. The following assumptions have been made in attributing the observed conductivity to hydrolysis and also in calculating the degree of hydrolysis by use of the formula employed.

1. That conductivity is due to dissociation of the ester in the liquid hydrogen sulfide, and not to any

ionization of the hydrogen sulfide in the ester.

2. That the lowering of the conductance of the ester by addition of the corresponding mercaptan is due to a reversal of the hydrolysis and not to a change in nature of the solvent.

3. That the thioacetic acid is dissociated to the same extent at all concentrations.

Sample Calculation

Methyl Thiolacetate

Conc.

$$0.02 \quad \frac{.11433-.004}{1.48-.004} = .0770$$

$$0.05 \quad \frac{.0616-.004}{.964-.004} = .0600$$

$$0.10 \quad \frac{.0343-.004}{.78-.004} = .0391$$

$$0.30 \quad \frac{.0195-.004}{.650-.004} = .0240$$

$$0.40 \quad \frac{.0165-.004}{.596-.004} = .0211$$

$$0.50 \quad \frac{.01335-.004}{.615-.004} = .0153$$

GENERAL CONCLUSIONS

GENERAL CONCLUSIONS

Many substances have been found to undergo reactions of thiohydrolysis in liquid hydrogen sulfide, and in numerous instances reactions very similar to those taking place in a water system have been observed. With inorganic compounds liquid hydrogen sulfide has been found to be a much weaker hydrolyzing medium than water, although a true comparison is very hard to draw.

Many substances have also been found to be soluble in liquid hydrogen sulfide, and in the majority of cases these solutions were found to be conductors of the electric current. One must not, however, form the conclusions from this work that liquid hydrogen sulfide is a good ionizing medium since the substances studied in this laboratory have been very carefully selected from the standpoint of their probability of yielding conducting solutions in this solvent. If these solutions had been made at random quite a different conclusion would be drawn since Walker, McIntosh and Archibald (2) have shown that liquid hydrogen sulfide is a remarkably poor ionizing medium for the majority of compounds. In fact, the authors go so far as to say that combination with this

2. Walker, McIntosh and Archibald, Jour. Chem. Soc. 85, 1098, (1904).

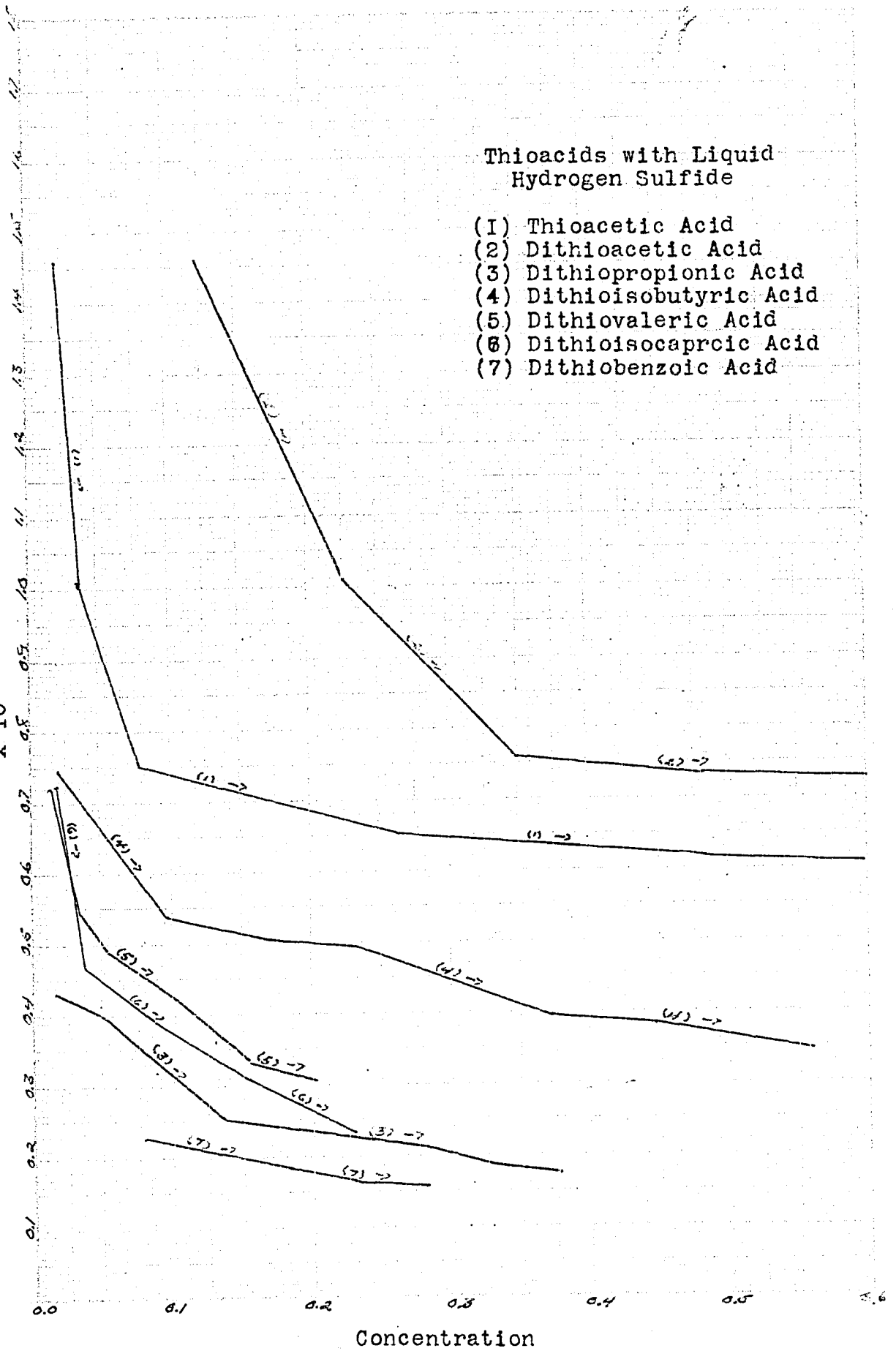
solvent is necessary before conducting solutions are obtained. This conclusion, however, seems rather broad in view of the work of Quam and Wilkinson (3) and that presented in this thesis.

3. Quam with Wilkinson, Jour. Am. Chem. Soc. 47, 989, (1925).



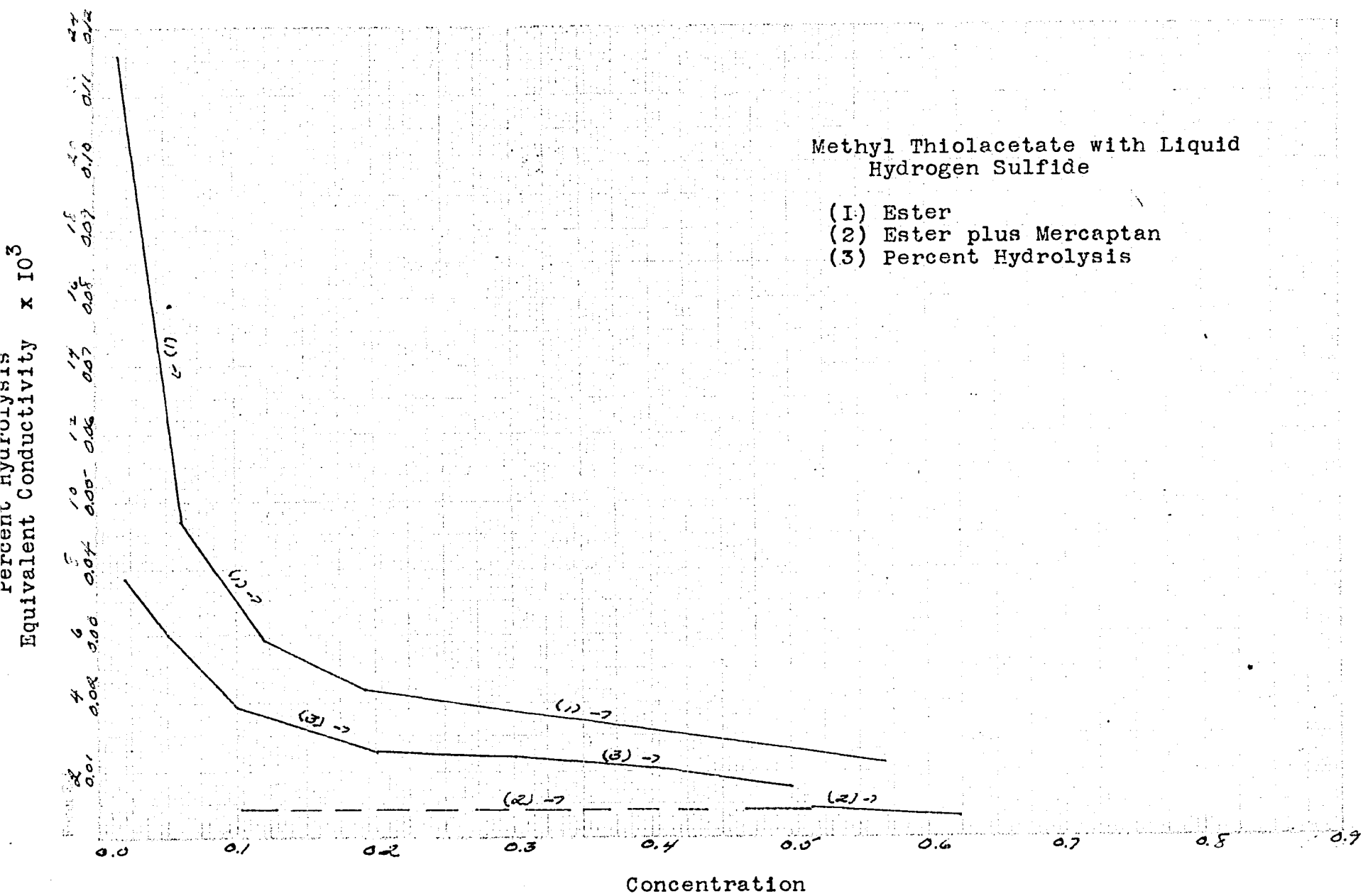
Equivalent Conductivity

$\times 10^3$

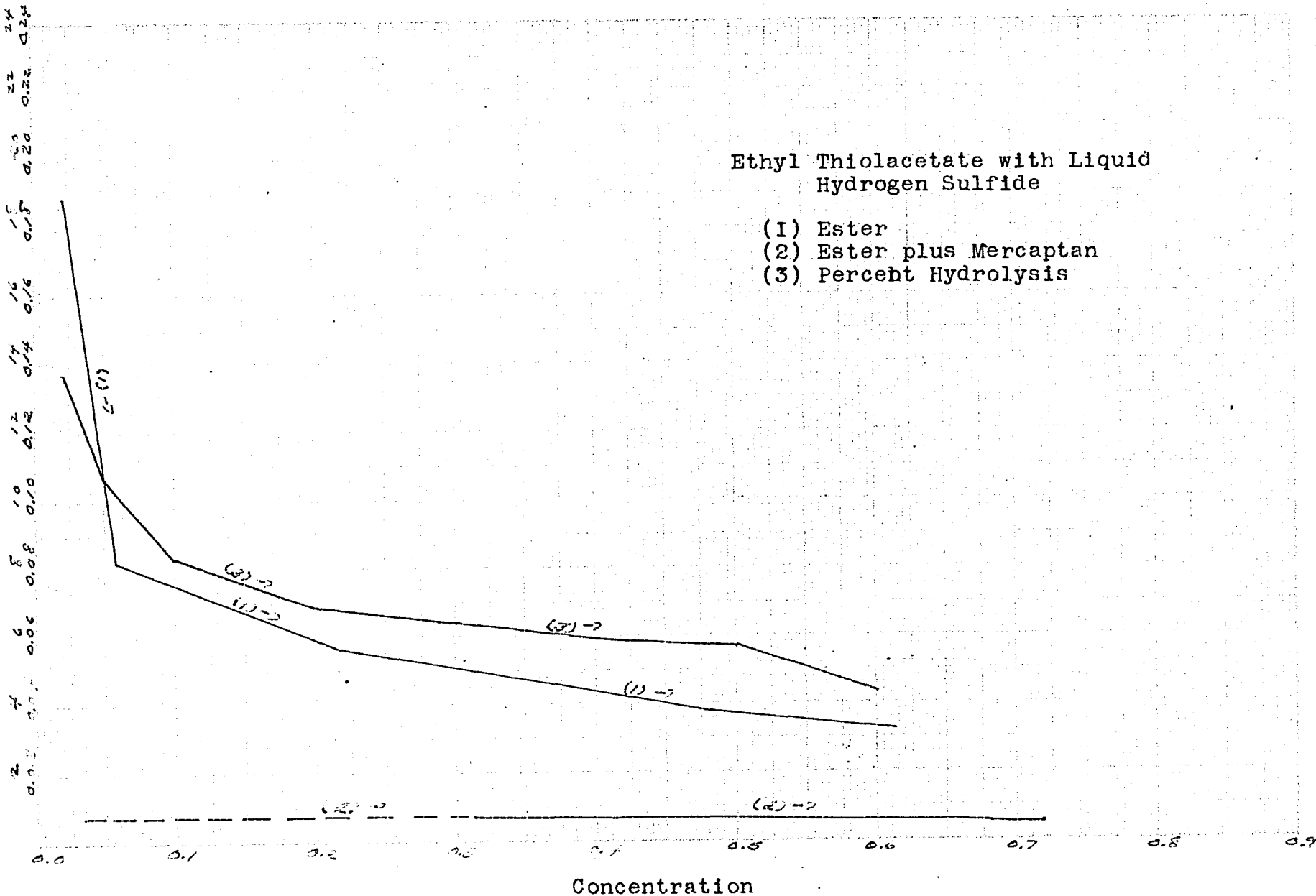


Methyl Thiolacetate with Liquid Hydrogen Sulfide

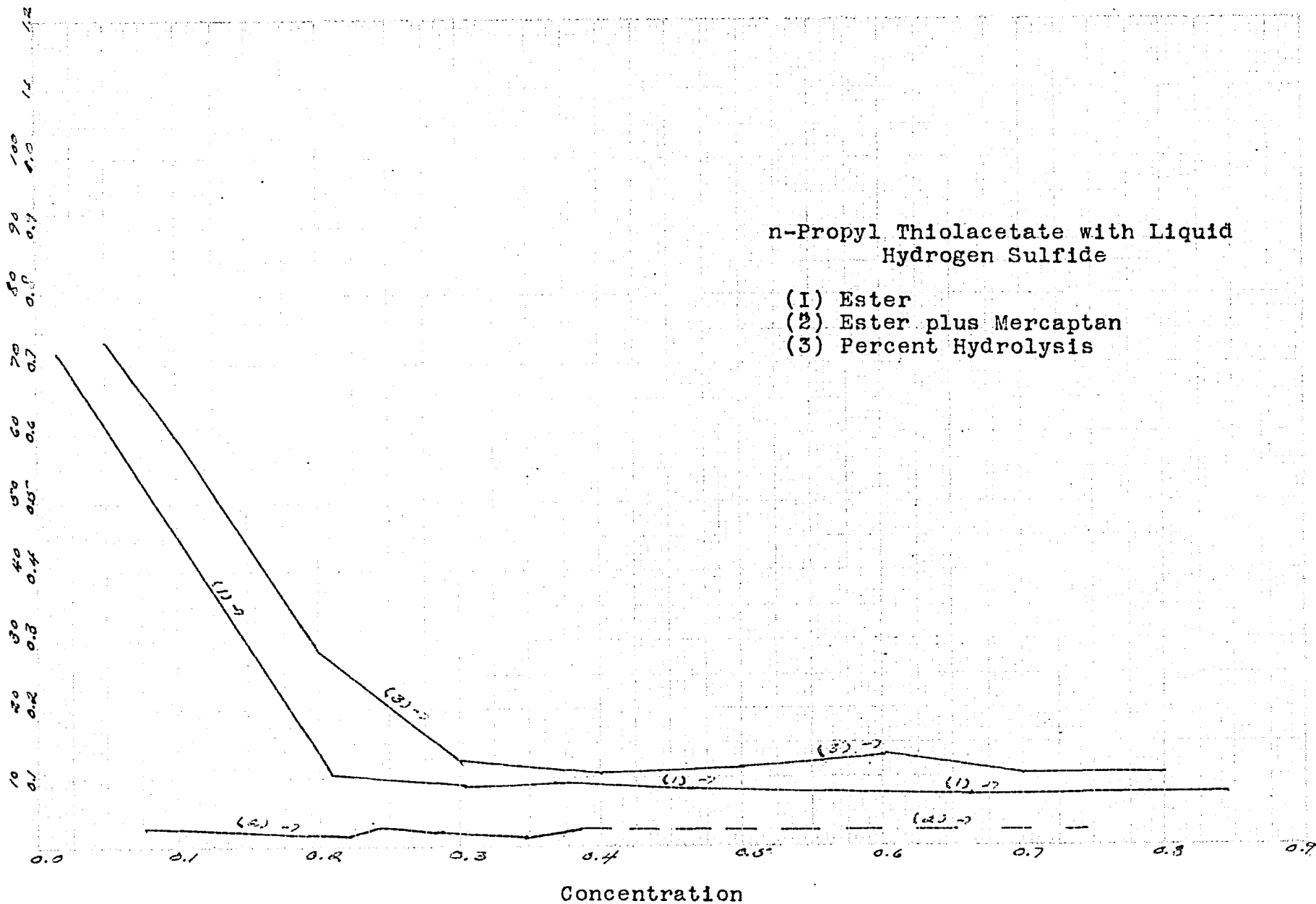
- (1) Ester
- (2) Ester plus Mercaptan
- (3) Percent Hydrolysis

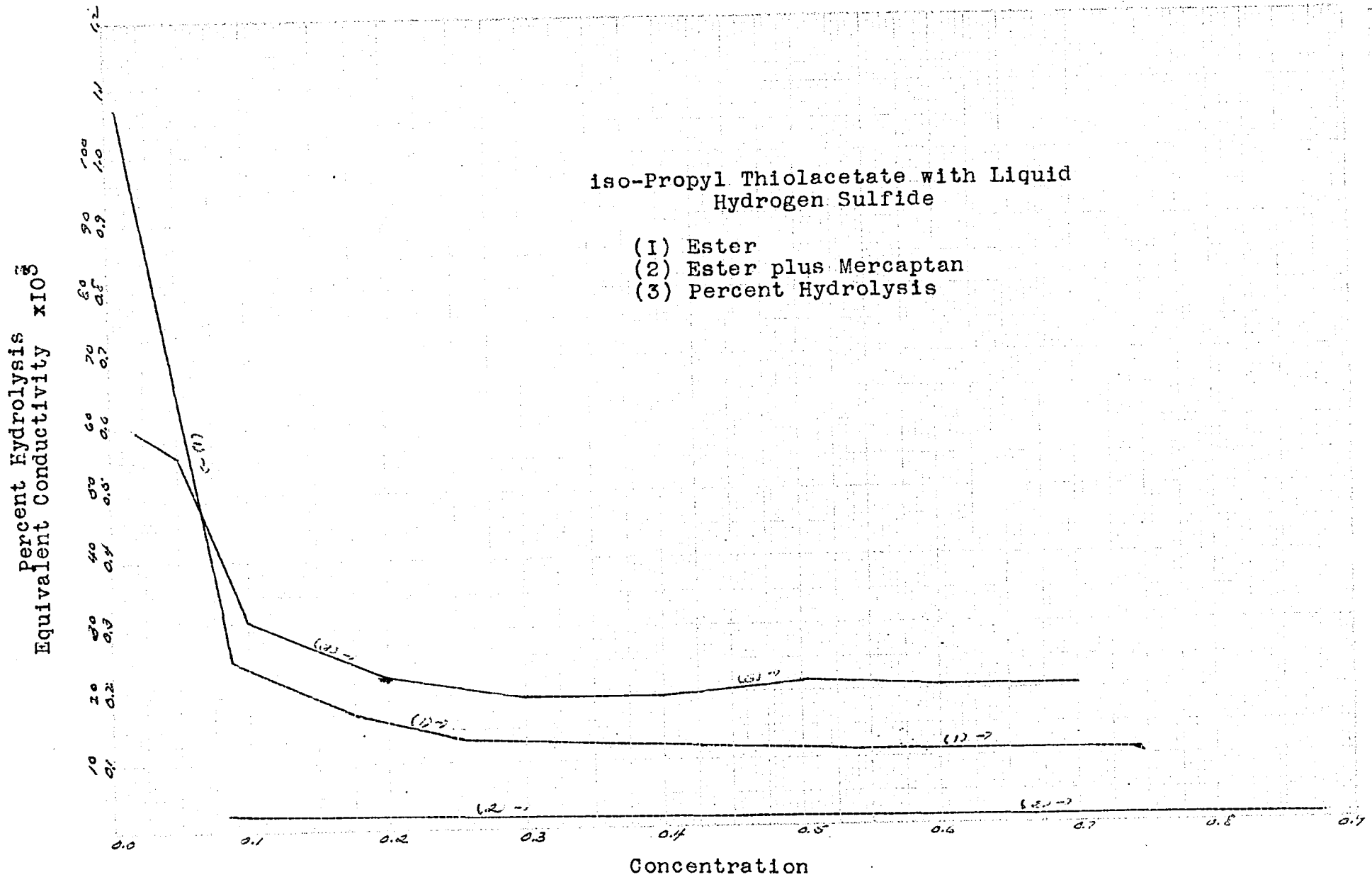


Percent Hydrolysis  
Equivalent Conductivity  $\times 10^3$

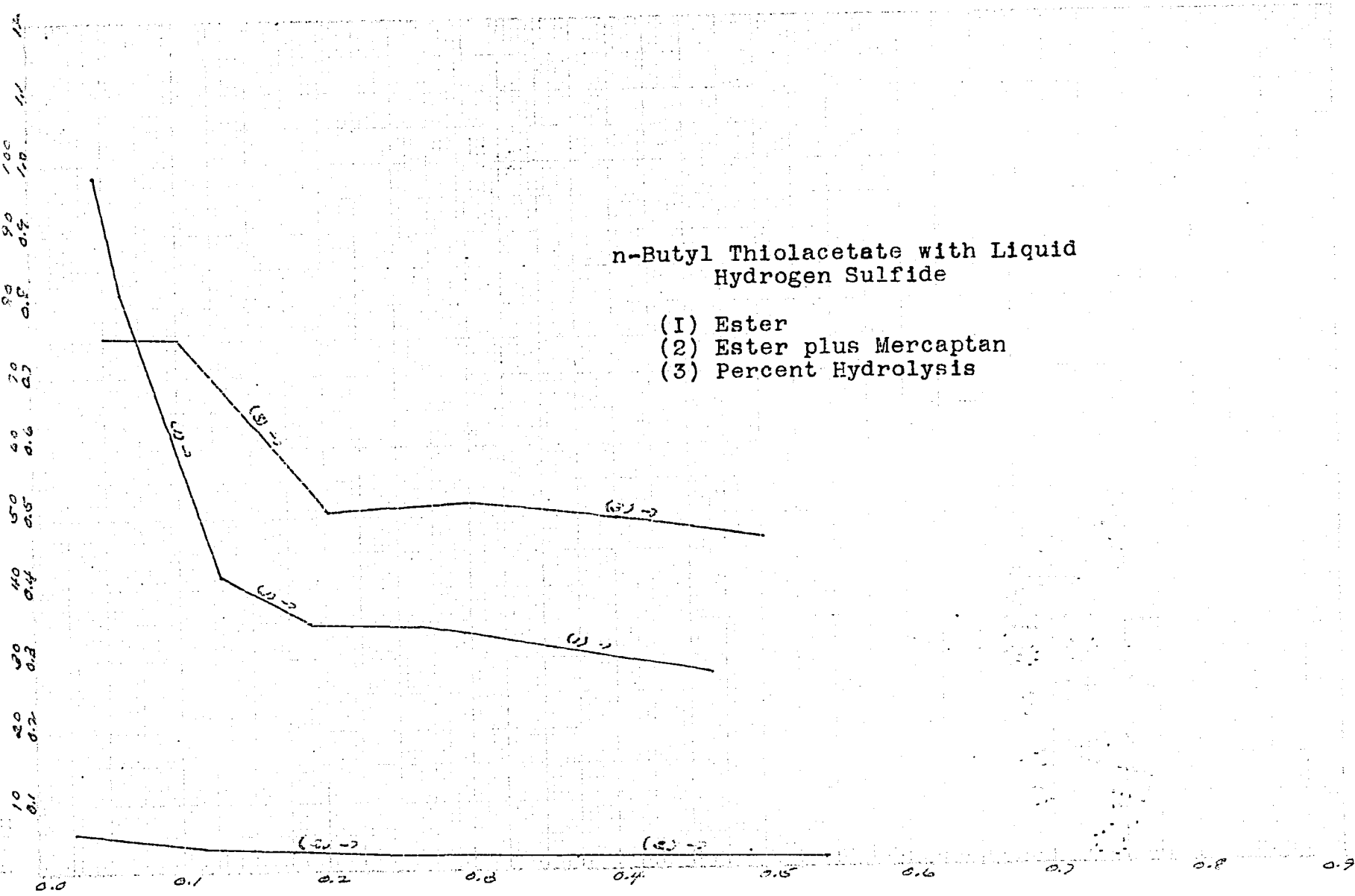


Percent Hydrolysis  
Equivalent Conductivity  $\times 10^3$





Percent Hydrolysis  
Equivalent Conductivity  $\times 10^3$



n-Butyl Thiolacetate with Liquid Hydrogen Sulfide

- (1) Ester
- (2) Ester plus Mercaptan
- (3) Percent Hydrolysis

Concentration