# LIQUID HYDROGEN SULFIDE AS A REACTION MEDIUM

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The amount of work which has been done with liquid hydrogen sulfide as a reaction medium is small, due chiefly to the fact that while hydrogen sulfide is an inorganic compound its properties when it is used as a solvent are more like those of an organic substance. Very few inorganic substances are soluble in it. A second reason is that its boiling point of −60°C. requires either that the experiments be carried out at a low temperature or that the material be sealed in tubes and the work be done at room temperature with a pressure of about twenty atmospheres.

## PREPARATION OF LIQUID HYDROGEN SULFIDE

The apparatus used for the preparation of the liquid hydrogen sulfide is that of Antony and Magri as modified by Quam, and is shown in figure 1. The apparatus consists of three parts: a generator for preparing the hydrogen sulfide, a purifying train, and a liquefaction and delivery reservoir.

The gas is generated in the usual manner by the reaction of dilute hydrochloric acid on ferrous sulfide. The acid is stored in C, the sulfide in G and between the generator and the drier a pressure gauge is placed for protection against excess pressure.

The gas is washed by passing it through water in two Dreschel bottles, $K_1$ and $K_2$, which remove any hydrochloric acid spray that may have been carried over. It is next partly dried by passing through two bottles, $L_1$ and $L_2$, containing calcium chloride and then through two bottles, $N_1$ and $N_2$, containing aluminum sulfide, and finally through two bottles, $O_1$ and $O_2$, containing phosphorus pentoxide. The aluminum sulfide not only removes water left from the calcium chloride, but also in doing so liberates an equivalent amount of hydrogen sulfide and takes out any hydrogen chloride set free from the calcium chloride.

The condenser is in the form of a glass coil which is cooled by immersing it in a mixture of ether and solid carbon dioxide contained in a Dewar tube. By raising the levelling bulb it is possible to get slightly more pressure for the liquefaction. The liquid collects in the larger part of the condenser P and may be forced out from it into storage tubes or reaction tubes by closing the stopcock T and allowing the gas pressure from the generator to force the liquid out through the tube R. If it does not start readily, it is only necessary to lower the Dewar tube for a little while, thus raising the temperature somewhat, whereupon the vapor pressure of the liquid will force the liquid out.

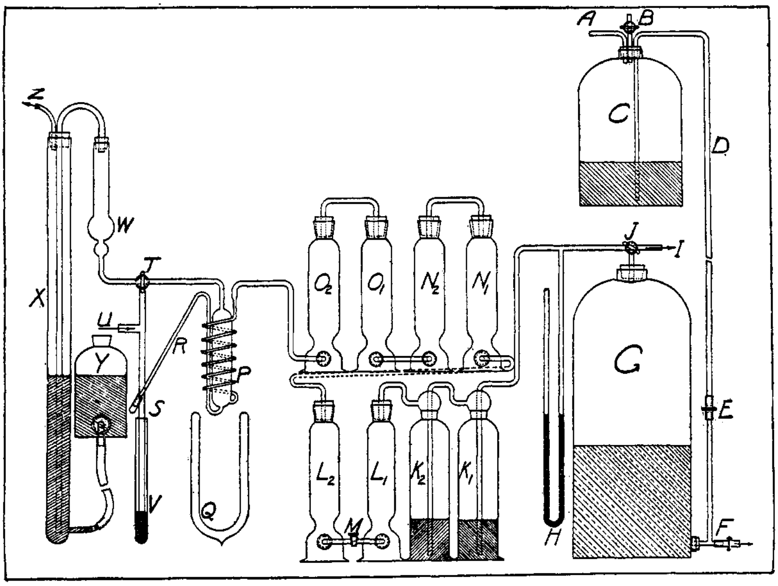


Fig. 1. Apparatus for the Liquefaction of Hydrogen Sulfide

## PHYSICAL PROPERTIES OF LIQUID HYDROGEN SULFIDE

The physical constants of liquid hydrogen sulfide are as follows: melting point, −82.9°; boiling point, −59.4°; critical temperature, 100.4°; critical pressure, 89 atmospheres; density of the liquid at −60°, 0.96; dielectric constant, 10.2; viscosity, 0.00412 dynes per centimeter; surface tension, 25.434 dynes per centimeter.

## LIQUID HYDROGEN SULFIDE AS A SOLVENT

The first extensive study of the solvent power of liquid hydrogen sulfide was made by Walker, McIntosh, and Archibald (1), who reported the solubility of some ninety organic compounds including hydrocarbons, halides, acids, esters, acyl chlorides, nitriles, alcohols, ethers, aldehydes, ketones, nitro and amino compounds.

Antony and Magri (2) reported that as a solvent liquid hydrogen sulfide does not resemble water very much but resembles more carbon disulfide, alcohol, ether and benzene. Salts of metals with strong acids are insoluble in it, while nonmetallic substances in general are soluble. The halides of the nonmetals, nitrogen compounds such as naphthylamine and nitronaphthalene, hydrocarbons, alcohols and ethers are soluble. Salts of metals such as copper and lead, and oxidizing agents such as chromates, dichromates, chromic acid and permanganates, are unchanged in liquid hydrogen sulfide. Solid bromine reacts and iodine dissolves to give a dark red solution.

Quam (3) repeated some of this work and extended it to a large number of compounds, both organic and inorganic. In his study he divided the compounds into four groups according to their ability to dissolve in hydrogen sulfide and react with it. His work brought out very well the fact that the substances which dissolve best in liquid hydrogen sulfide are organic in character.

The first group, containing the substances which are soluble without apparent reaction, consists chiefly of organic compounds, with the exception of hydrogen chloride, hydrogen bromide, zinc chloride and a few sulfides. Aluminum chloride should be in this group instead of the last, as it is somewhat soluble and nonreactive.

In the second group are given the compounds that are soluble and react for one of three reasons: (*a*) because of their oxidizing power; (*b*) because of the presence of an amino group; or (*c*) because thiohydrolysis takes place.

The third group contains those elements and compounds that are insoluble but react with the hydrogen sulfide. Any reaction is due either to oxidation or to the formation of a sulfide of the metal.

The last group, which contains the substances which are insoluble and nonreactive, consists almost entirely of inorganic bodies, with the exception of the carbohydrates. Contrary to what one might expect, the sulfides of both metals and nonmetals are insoluble in hydrogen sulfide, with the exception possibly of ammonium hydrosulfide, and its solubility is quite low. Another striking thing shown by the table is the insolubility of the metal salts, such as the chlorides, and the solubility of the chlorides of the nonmetals in groups four, five and six of the periodic table. With the exception of carbon tetrachloride these chlorides are all hydrolyzed in water, some of them almost completely. In liquid hydrogen sulfide, however, they are quite stable except when their oxidizing power causes decomposition. Ralston determined the solubility of thiol and dithio organic acids in liquid hydrogen sulfide and found that they were all very soluble.

## CONDUCTANCE IN LIQUID HYDROGEN SULFIDE

The conductance of pure liquid hydrogen sulfide was determined first by Magri (4), who reported the specific conductance as less than $4.1 \times 10^{-7}$. Quam and Wilkinson (5), using a very sensitive galvanometer and a 110 volts D.C. current, reported it as less than $1 \times 10^{-11}$. Satwalekar, Butler and Wilkinson (6) with a similar set-up obtained a value of $3.7 \times 10^{-11}$. The conductance of a good grade of conductivity water is about $0.7 \times 10^{-6}$, showing that the value for the conductance of pure water is about 20,000 times greater than it is for liquid hydrogen sulfide.

Walker, McIntosh, and Steele (7) tried the conductance of solutions in hydrogen sulfide of a very large number of organic compounds, and found them all to be very poor conductors. The only solutions that showed appreciable conductance were those of piperidine, pyridine, quinoline and nicotine. These substances are all basic in nature and with the hydrogen sulfide form addition compounds which are sulfides and which are dissociated. Acetonitrile, aldehydes, and ketones unite with hydrogen sulfide and therefore their solutions conduct slightly. Antony and Magri (2) tried the conductance of a number of substances in liquid hydrogen sulfide and found that many nonmetallic compounds are soluble and give conducting solutions: a solution of iodine is a good conductor; one of phosphorus triiodide is less good; solutions of chloroform and of tetramethylammonium chloride also conduct. Chipman and McIntosh (8) found that solutions of iodine and of antimony trichloride showed good conductance, as did also those of tripropylamine and isobutylamine. The curves show that the equivalent conductance increases with increase in concentration, which is the reverse of what takes place in water solutions. With iodine the usual form of curve is obtained. When equivalent conductance increases with concentration it is assumed that a compound has been formed between the solute and the solvent. Walden (9) accounted for the conductance of the iodine solutions of this nature by the ionization of the iodine molecule into $I^+$ and $I^-$, which conduct the current.

TABLE 1

*Conductances of saturated solutions of some inorganic halides in liquid hydrogen sulfide*

| SUBSTANCE | ($\lambda \times 10^6$) |
|---|---|
| $HgCl_2$ | 0.031 |
| $SnCl_4$ | 0.106 |
| $SiCl_4$ | 0.129 |
| $ZnCl_2$ | 0.634 |
| HCl | 0.881 |
| $AsCl_3$ | 1.15 |
| $AlCl_3$ | 2.09 |
| $HgBr_2$ | 5.16 |
| $HgI_2$ | 9.99 |
| $FeCl_3$ | 209.9 |
| $SbCl_3$ | 424.0 |
| 0.02 *N* KCl (in $H_2O$) | 2397.0 |

Because of the very high resistance of solutions in liquid hydrogen sulfide, special cells were constructed with low cell constants. The platinum electrodes were 18 mm. square and were separated and held about 2 mm. apart by small glass rods fused between them. The unit was held rigidly in place by forcing a small glass tube in between the electrode and the cell wall.

The specific conductances of saturated solutions of a few of the inorganic bodies which are soluble in liquid hydrogen sulfide were determined by Ralston (10) and are given in table 1. For comparison the conductance of a 0.02 *N* KCl solution in water is given.

TABLE 2

*Conductances of halides in liquid hydrogen sulfide* ($\lambda \times 10^3$)

| MOLAR CONCENTRATION | $PCl_3$ | $PBr_3$ | $AsCl_3$ | $SbCl_3$ |
|---|---|---|---|---|
| 0.01 | | | 1.2343 | 165.7 |
| 0.05 | | | | 583.6 |
| 0.0538 | | 0.6643 | | |
| 0.069 | 0.2055 | | | |
| 0.1 | | | 1.6387 | 14148.3 |
| 0.1086 | | 0.365 | | |
| 0.162 | | 0.1679 | | |
| 0.20 | | | 1.918 | |
| 0.2155 | | | | |

TABLE 3

*Conductances of solutions of alkyl ammonium chlorides* ($\lambda \times 10^3$)

| MOLAR CONCENTRATION | $CH_3NH_3Cl$ | $(CH_3)_2NH_2Cl$ | $(C_2H_5)_3NHCl$ |
|---|---|---|---|
| 0.0104 | | | 1532.7 |
| 0.0113 | | 641.5 | |
| 0.0133 | 21.25 | | |
| 0.0140 | | | 8357.0 |
| 0.0340 | | 15256.0 | |
| 0.0448 | | | 42969.0 |
| 0.0468 | 78.42 | | |
| 0.0508 | | | 66004.0 |
| 0.0544 | 132.6 | | |

The equivalent conductances of the chlorides of the phosphorus family were determined by Quam (5) and the values are shown in table 2. These chlorides are all hydrolyzed readily in water, but in liquid hydrogen sulfide many of them are stable without undergoing thiohydrolysis. The conductance increases with the increase in the atomic weight of the element until bismuth is reached, but the conductance of bismuth trichloride in liquid hydrogen sulfide is zero. The conductances of both the arsenic and the antimony chlorides increase with increasing concentrations, as was found by Chipman and McIntosh (8).

Since the solubility of ammonium chloride in liquid hydrogen sulfide is practically zero, the conductance is also zero. If the hydrogen atoms are substituted by alkyl groups, the solubility increases and the conductance also. The values obtained by Quam for the equivalent conductances (5) of hydrogen sulfide solutions of alkylammonium chlorides are shown in table 3.

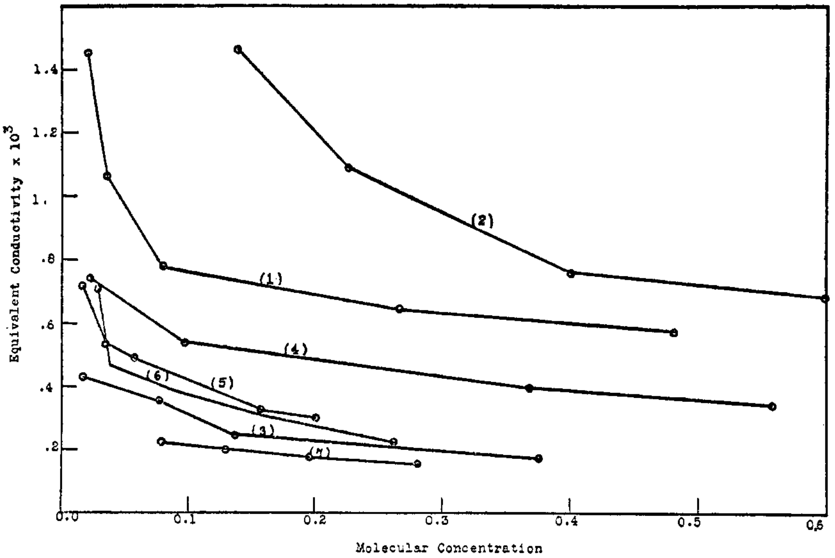


FIG. 2. EQUIVALENT CONDUCTANCES OF THIO ACIDS IN LIQUID HYDROGEN SULFIDE

(*1*) Thiolacetic acid; (*2*) dithioacetic acid; (*3*) dithiopropionic acid; (*4*) dithioisobutyric acid; (*5*) dithiovaleric acid; (*6*) dithioisocaproic acid; (*7*) dithiobenzoic acid.

### CONDUCTANCE OF THIOACIDS

A number of thiol and dithio organic acids were prepared and their equivalent conductances in hydrogen sulfide were determined by Ralston at different dilutions. The results obtained are shown in the curves in figure 2.

In the homologous series the conductance decreases with increasing molecular weight with the exception of propionic acid, whose conductance is apparently lower than it should be for the series. However the same is true for the oxygen acids dissolved in water as the value for propionic acid is low there also.

For comparison, these values and the values for the similar oxygen acids dissolved in water at similar dilutions (32 liters) are given in table 4. It will be observed that the values for the oxygen acids in water solutions are from 1000 to 10,000 times greater than for the thio acids in liquid hydrogen sulfide. Benzoic acid dissolved in water is a fairly strong acid, but the dithiobenzoic acid dissolved in hydrogen sulfide is quite weak. Thiolacetic acid is a much stronger acid when dissolved in water than when it is dissolved in hydrogen sulfide.

TABLE 4

*Comparison of the conductance of thio acids and oxygen acids*

| IN WATER | $\lambda$ | IN HYDROGEN SULFIDE | $\lambda \times 10^8$ |
|---|---|---|---|
| Acetic | 8.7 | Dithioacetic | 1.00 |
| Propionic | 7.4 | Dithiopropionic | 0.41 |
| Isobutyric | 7.9 | Dithiobutyric | 0.72 |
| Valeric | 7.7 | Dithiovaleric | 0.57 |
| Isocaproic | 7.5 | Dithioisocaproic | 0.62 |
| Benzoic | 22.3 (64) | Dithiobenzoic | 0.22 |
| Thiolacetic | 42.1 | Thiolacetic | 1.29 |

The decomposition voltage of a solution of antimony chloride dissolved in liquid hydrogen sulfide is 1.9 ± .1 volts. None of the other halides soluble in liquid hydrogen sulfide gave a reproducible value for its decomposition voltage.

## THIOHYDROLYSIS

### *Thiohydrolysis of chlorides*

The metathetical reaction between hydrogen sulfide and other substances has been called thiohydrolysis to bring out its relationship to hydrolysis. The reaction with the chlorides, especially those of the elements in the fourth, fifth and sixth groups of the periodic table, brings out the similarities and also the differences in the two reactions. Carbon tetrachloride is insoluble in water but miscible with liquid hydrogen sulfide in all proportions, and reacts with neither of the solvents. All of the other chlorides in the fourth group hydrolyze in water to form the insoluble hydrated oxides, while in hydrogen sulfide they all dissolve with but very little action.

In the phosphorus family the chlorides of phosphorus and arsenic hydrolyze in water to form soluble acids, while the chlorides of antimony and bismuth hydrolyze to form the insoluble oxychlorides. In hydrogen sulfide phosphorus trichloride reacts very slowly at low temperatures, but at room temperatures both phosphorus trichloride and arsenic trichloride react to give the sulfides immediately. Antimony trichloride dissolves at room temperature but does not react in the liquid state, although it will react with the vapor when the liquid is removed to form the compound $SbSCl \cdot 7SbCl_3$. Bismuth trichloride reacts immediately with the hydrogen sulfide to form the compound $BiSCl \cdot BiCl_3$.

TABLE 5

*Thiohydrolysis of halides*

| COMPOUND ADDED | COMPOUND FORMED BY THIOHYDROLYSIS | COMPOUND FORMED BY HYDROLYSIS |
|---|---|---|
| $SiCl_4$ | $SiCl_4$ is soluble in $H_2S$, but does not react | $Si(OH)_4$  $SiO_2 + 2H_2O$ |
| $TiCl_4$ | $2TiCl_4 \cdot H_2S$  $TiCl_2 + S$ | $Ti(OH)_4$  $TiO_2 + 2H_2O$ |
| $SnCl_4$ | $SnCl_4$ dissolves in $H_2S$. There is a slight reaction forming $SnS_2$ | $Sn(OH)_4$  $SnO_2 + 2H_2O$ |
| $PCl_3$ | $P_2S_3$ | $P(OH)_3$ |
| $PCl_5$ | $PSCl_3$ | $POCl_3$ |
| $AsCl_3$ | $As_2S_3$ | $AsOCl \cdot H_2O$  $H_3AsO_3$ |
| $SbCl_3$ | $SbSCl \cdot 7SbCl_3$ | $SbOCl$ |
| $SbCl_5$ | $SbSCl_3$ | $H_3SbO_4$  $SbOCl_3$ |
| $BiCl_3$ | $BiSCl \cdot BiCl_3$ | $BiOCl$ |
| $SeCl_4$ | $SeSCl_2$  $Se_2Cl_2$  $Se + S$ | $H_2SeO_3$ |
| $TeCl_4$ | $TeCl_2 + S$  $Te + S$ | $H_2TeO_3$ |

The chlorides of elements in the sixth group of the periodic table are all hydrolyzed in water and thiohydrolyzed in hydrogen sulfide. None of the products formed are simple, but those resulting from the thiohydrolysis are the more complex because of the reducing power of the hydrogen sulfide. A comparison of these reactions is given in table 5.

### *Thiohydrolysis of esters (11)*

Just as esters are hydrolyzed in water solution so are they thiohydrolyzed in liquid hydrogen sulfide. In order to make the comparison more complete the esters of thiolacetic acid were used rather than the oxygen acid esters. The products of the reactions are the thiol acids and the thioalcohols or mercaptans. The degree of hydrolysis was measured by determining the conductance of the solution of the ester alone in hydrogen sulfide and then of the ester solution saturated with the mercaptan. The calculation of the degree of hydrolysis is made by the following expression

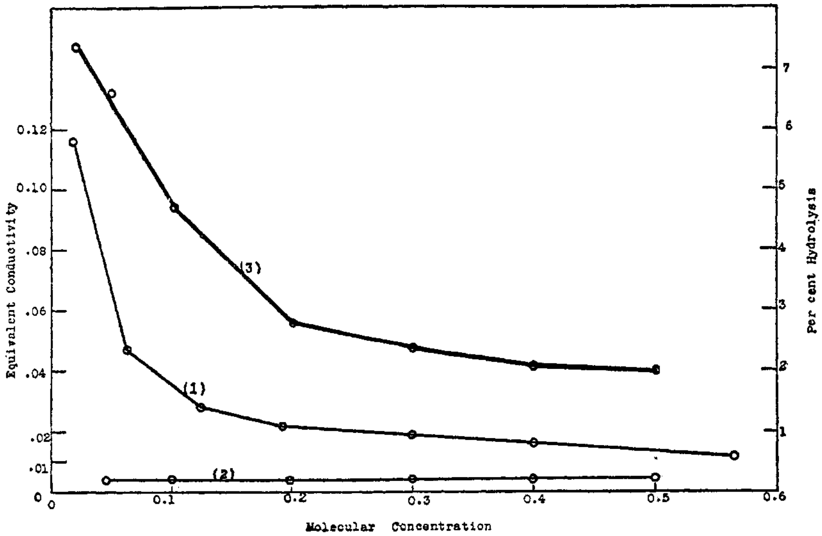


FIG. 3. HYDROLYSIS OF METHYL THIOLACETATE
(*1*) Ester; (*2*) ester plus mercaptan; (*3*) per cent hydrolysis.

$$\frac{\lambda_e - \lambda}{\lambda_a - \lambda} = h$$

where $h$ is the degree of hydrolysis, $\lambda_e$ is the conductance of the ester solution, $\lambda_a$ the conductance of the acid of the same concentration and $\lambda$ the conductance of the ester solution saturated with the mercaptan. The mercaptan was found to be a nonconductor when dissolved in the hydrogen sulfide. The value $\lambda$ is therefore the conductance of the unhydrolyzed ester. $\lambda_e$ is the conductance of the ester which has not been thiohydrolyzed, increased by the conductance of the acid that has been formed by the thiohydrolysis, while $\lambda_a$ is the value for the conductance if all of the ester has been thiohydrolyzed. The curves which were obtained for the thiohydrolysis of methyl thiolacetate are given in figure 3, and the data for several of the other esters which were studied are given in table 6. It is to be noticed that as the molecular weight of the ester increases the per cent of thiohydrolysis increases.

TABLE 6

*Thiohydrolysis of esters of thiolacetic acid in liquid hydrogen sulfide*

| | PER CENT OF HYDROLYSIS | | |
|---|---|---|---|
| | 10 liters | 5 liters | 2 liters |
| Methyl thiolacetate | 4.52 | 2.80 | 1.22 |
| Ethyl thiolacetate | 10.10 | 8.56 | 5.24 |
| *n*-Propyl thiolacetate | 49.3 | 17.2 | 11.7 |
| Isopropyl thiolacetate | 30.8 | 20.5 | 18.2 |
| *n*-Butyl thiolacetate | 68.0 | 56.7 | 53.3 |

## REACTIONS WITH LIQUID HYDROGEN SULFIDE

There is some disagreement as to the reaction between liquid sulfur dioxide and liquid hydrogen sulfide. It is well known that in the gaseous condition they react to form water and free sulfur. Lang and Carson (12) reported that when the two substances were mixed and kept cold, sulfur separated out. Mathews (13) reported that unless some third substance, such as water, alcohol, ether, amyl alcohol, acetone, amyl acetate or ethyl acetate is present in the liquid phase to act as a solvent, no reaction takes place. It has been the experience in this laboratory that the two liquids do not react at low temperatures but that as the temperature rises they react with explosive violence.

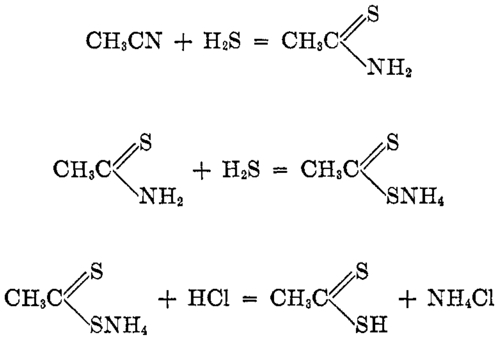
The hydrogen sulfide and sulfur dioxide were dried with phosphorus pentoxide and the tubes were cleaned and dried with alcohol and ether and then dried by passing warm air, dried with phosphorus pentoxide, through them. The sulfur dioxide and hydrogen sulfide were condensed directly in these dried tubes which had been cooled to $-78.5$°C., and the tubes were sealed immediately. As long as the tubes were kept cold no reaction took place, but when the tubes were removed from the cooling bath and the temperature allowed to rise every tube exploded. Such a tube was placed behind a glass screen and the progress of the reaction watched. Within five minutes from the time it was removed from the cooling bath it exploded. The reaction started at the boundary of the two liquids and increased in violence until the pressure was great enough to burst the tube.

Calcium oxide reacts with liquid hydrogen sulfide to form a mixture of calcium sulfide and calcium hydrosulfide. The mixture loses hydrogen sulfide very readily and one cannot obtain a homogeneous sample. Similarly, calcium carbide reacts with hydrogen sulfide to liberate acetylene and form a white solid which analysis indicates is calcium sulfide. There is also formed a small amount of a light yellow liquid which was thioacetaldehyde.

Cahours (14) treated furfuramide, dissolved in alcohol, with hydrogen sulfide gas and obtained a yellow crystalline substance whose analysis indicated it to be thiofurfural ($C_{10}H_4S_2O_2$). Baumann and Fromm (15) isolated a similar substance by passing hydrogen sulfide into an alcoholic solution of furfural. If the two liquids are sealed in a tube and allowed to come to room temperature and then to stand for a few days the mixture solidifies to a yellow crystalline mass. Two samples of this material, recrystallized from ethyl acetate, melted between 95° and 98° and contained 28.74 per cent and 28.57 per cent of sulfur. Baumann and Fromm reported a melting point of 90–92°. The theoretical per cent of sulfur in thiofurfural is 28.6.

Furan, furfuralcohol, pyromucic acid and the ethyl and nitro-ethyl esters of pyromucic acid all were treated in a similar manner with hydrogen sulfide. None of them reacted with it, thus indicating that it is the aldehyde oxygen that is replaced and not the oxygen in the ring. Borgeson (16) has shown that this reaction is characteristic of all aldehydes. He has also shown that acyl halides first undergo thiohydrolysis, and that the oxygen is then replaced by sulfur to give either the dithio acid or its anhydride.

Nitriles also thiohydrolyze to give the dithio acids. This is one of the easiest methods of preparing the dithio acids. The reaction is catalyzed by the presence of hydrochloric acid just as is the similar reaction with water. The reaction may be represented as follows:



$$CH_3CN + H_2S = CH_3C\begin{smallmatrix}\nearrow S \\ \searrow NH_2\end{smallmatrix}$$

$$CH_3C\begin{smallmatrix}\nearrow S \\ \searrow NH_2\end{smallmatrix} + H_2S = CH_3C\begin{smallmatrix}\nearrow S \\ \searrow SNH_4\end{smallmatrix}$$

$$CH_3C\begin{smallmatrix}\nearrow S \\ \searrow SNH_4\end{smallmatrix} + HCl = CH_3C\begin{smallmatrix}\nearrow S \\ \searrow SH\end{smallmatrix} + NH_4Cl$$

Since the ammonium chloride is insoluble in liquid hydrogen sulfide it separates out in the tube as a white solid, while the dithio acids are soluble. The following nitriles have been found to undergo this reaction: aceto-, propio-, valero-, succino- and benzo-nitrile; of these the last one reacted the most rapidly and gave the highest yield.

The Grignard reagents will react in liquid hydrogen sulfide just as easily as in water. Ethyl magnesium bromide and naphthyl magnesium bromide were treated with liquid hydrogen sulfide and the resulting hydrocarbons identified. The composition of the solid magnesium compound is quite variable, depending entirely upon the concentration of reagents used and the relative amount of hydrogen sulfide.

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