the direction that would be expected on the basis of catalytic decomposition of hydrogen peroxide during the slow process of dissolving the mineral.

Summary

The direct potentiometric titration of hydrogen peroxide with ceric sulfate has been shown to be accurate in solutions moderately acidified with hydrochloric, sulfuric, nitric or acetic acid. The reverse titration is also accurate in sulfuric and nitric acid solutions.

The hydrogen peroxide–ceric sulfate reaction may be applied in the indirect determination of lead peroxide.

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REACTIONS IN LIQUID HYDROGEN SULFIDE. VI. REACTIONS WITH ORGANIC COMPOUNDS

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Hydrogen sulfide has been found by different workers to be a good solvent for organic substances[2] and for this reason it was thought important to study the reactions between liquid hydrogen sulfide and members of the different types of organic compounds.

Experimental

Several examples of each of the types of organic compounds were placed in glass tubes of 50-cc. capacity and, after cooling to −77° with a mixture of ether and solid carbon dioxide, liquid hydrogen sulfide was added. The tubes were then sealed and allowed to come to room temperature. After standing for several weeks they were again cooled, opened, the excess of hydrogen sulfide was allowed to evaporate and the residues were examined for evidence of reaction.

The following types of organic compounds were studied: saturated hydrocarbons, unsaturated hydrocarbons, alcohols, phenols, ethers, aldehydes, ketones, alkyl and aryl halides, acids, acid anhydrides, esters, sugars, nitro compounds, Grignard reagent, amides, amines and acyl halides.

Hydrocarbons.—Benzene, toluene, naphthalene, anthracene, gasoline, kerosene and vaseline are all soluble and non-reactive in liquid hydrogen sulfide. The unsatu-

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[1] This paper is from a portion of the work presented to the Graduate Faculty of Iowa State College in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] McIntosh and Steele, *Proc. Roy. Soc. London*, **73**, 450 (1904); Archibald and McIntosh, *ibid.*, **73**, 454 (1904); Antony and Magri, *Gazz. chim. ital.*, **75**, 206 (1905); Steele, McIntosh and Archibald, *Phil. Trans. Roy. Soc.*, **205A**, 99 (1906); Magri, *Atti. accad. Lincei*, (V) **16**, 171 (1907); Quam, This Journal, **47**, 103 (1925); Quam and Wilkinson, *ibid.*, **47**, 989 (1925); Ralston and Wilkinson, *ibid.*, **50**, 258 (1928).

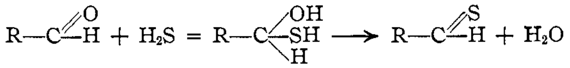
rated hydrocarbons amylene and trimethylethylene are miscible in liquid hydrogen sulfide but do not react with it unless the temperature is raised to room temperature and even then the reaction is a slow one. If after standing at room temperature for several weeks the tubes are again cooled to −77°, a white solid separates out which has a strong mercaptan odor. This solid decomposes and disappears on bringing it to room temperature. Since neither amylene nor trimethylethylene is a solid at −77, the formation of a solid is evidence that a reaction has taken place. Probably this is an addition reaction at the double bond, but no analytical data could be obtained because of the instability of the compounds.

Alcohols.—Methyl, ethyl, *iso*butyl, and *iso*-amyl alcohols and glycerin are miscible in liquid hydrogen sulfide at −77°, while allyl and furyl alcohols are miscible at room temperature. After standing for two months, the first three of these gave a precipitate of sulfur on cooling, showing that some decomposition had taken place. The allyl alcohol gave a small amount of a viscid liquid that had a strong mercaptan odor, which would indicate that an addition product had formed at the double bond.

Phenols.—Phenol, cresol, and *m*-aminophenol are soluble in liquid hydrogen sulfide, the latter but slightly, however; none of them gave any indication of reaction.

Ethers.—Ethyl ether, the only one tried, is miscible but non-reactive in liquid hydrogen sulfide.

Aldehydes.—Acetaldehyde, butylaldehyde, acrylaldehyde, benzaldehyde, *m*-nitrobenzaldehyde, trinitrobenzaldehyde, *p*-tolualdehyde, cinnamaldehyde and furfuraldehyde all dissolve in liquid hydrogen sulfide and react with it. In every case after standing for several days a second liquid layer formed and if the tube was again cooled white crystals of the compound $H_2S{\cdot}xH_2O$ were formed. This reaction took place with every aldehyde studied and was accompanied by the development of the odor of a mercaptan. With benzaldehyde, *p*-tolualdehyde, cinnamaldehyde and furfuraldehyde the reaction was carried to such an extent that after driving off the excess of hydrogen sulfide and bringing to room temperature a gelatinous mass remained. In the case of furfuraldehyde this was purified by recrystallizing from ethyl acetate and found to be furfural thioaldehyde, C_4H_3OCSH.[3] The reaction must consist of the addition of hydrogen sulfide to the aldehyde and then dehydration of the resulting compound.



$$\mathrm{R{-}\overset{\diagup\!\!\diagup O}{C}{-}H + H_2S = R{-}\underset{\diagdown H}{\overset{\diagup OH}{C}}{-}SH \longrightarrow R{-}\overset{\diagup\!\!\diagup S}{C}{-}H + H_2O}$$

Ketones.—Acetone, diethyl ketone, acetyl ketone, acetophenone and benzophenone were all soluble in liquid hydrogen sulfide and, while the last two showed no evidence of reaction, the first three developed a small amount of pink color and a mercaptan odor.

Alkyl and Aryl Halides.—Ethyl chloride, bromide and iodide, methyl iodide, *iso*-butyl bromide, *n*-propyl iodide, *n*-butyl iodide, benzyl chloride, benzyl iodide, allyl bromide and iodide were all soluble in liquid hydrogen sulfide and, with the exception of the allyl halides, all were non-reactive. These latter reacted because of the presence of the double bond.

Acids.—A number of organic acids such as acetic, propionic, benzoic and cinnamic were found to be soluble but non-reactive except the last, which contains a double bond.

Acid Anhydrides.—Acetic, benzoic, succinic and malic acid anhydrides were soluble in liquid hydrogen sulfide, the latter being but slightly so. There was no evidence of reaction except a slight decomposition of the hydrogen sulfide giving free sulfur.

Esters.—Ralston and Wilkinson[4] have shown that esters are soluble in liquid hydrogen sulfide and are thiohydrolyzed just as they are hydrolyzed in water.

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[3] Meints and Wilkinson, THIS JOURNAL, **51**, 803 (1929).

[4] Ralston and Wilkinson, *ibid.*, **50**, 2160 (1928).

Salts.—Most metal salts of organic acids are insoluble in liquid hydrogen sulfide.

Sugars.—Sucrose, glucose, maltose, lactose, mannose, arabinose and raffinose are insoluble in liquid hydrogen sulfide and show no evidence of reacting with it.

Grignard Reagents.—Ethylmagnesium bromide, phenylmagnesium bromide and benzylmagnesium chloride, either solid or dissolved in ether, all react vigorously with liquid hydrogen sulfide giving the corresponding hydrocarbon and a white solid suspended in the liquid. This solid, on evaporating the liquid slowly, gives off hydrogen sulfide and takes up water from the air readily. A study of the products of this reaction is being made.

Amides.—Acetamide, *n*-butyramide, acetanilide, benzanilide and phthalimide are all soluble but give no evidence of reaction. Picramide reacts slowly, liberating sulfur due to the presence of the nitro group.

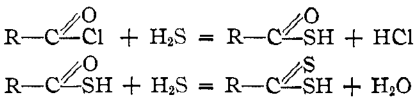
Amines.—Diethylamine, *sec.*-butylamine, *iso*butylamine and di-*n*-butylamine all react with liquid hydrogen sulfide and form either viscid liquids or crystalline solids which decompose readily, giving off hydrogen sulfide.

Dimethylaniline, diethylaniline, diphenylamine, α-naphthylamine, β-naphthylamine and benzidine are soluble but do not react with liquid hydrogen sulfide. Aniline and benzylaniline react similarly to the alkylamines, forming white crystalline compounds which decompose rapidly, giving off hydrogen sulfide and forming a red liquid which slowly decomposes. Phenylhydrazine reacts with liquid hydrogen sulfide to form yellow-white crystals of the compound $C_6H_5NHNH_2 \cdot H_2S$. After evaporating off the hydrogen sulfide a red liquid is obtained which slowly gives off ammonia, deposits sulfur and leaves liquid aniline according to the equation

$$C_6H_5NHNH_2 + H_2S = C_6H_5NHNH_2 \cdot H_2S = C_6H_5NH_2 + NH_3 + S$$

The red liquid is an intermediate product between the addition compound and aniline. This breaks down very slowly on standing and more rapidly if shaken vigorously. A similar red solution is obtained when phenylhydrazine is saturated with hydrogen sulfide gas. The odor of ammonia is not then perceptible until the mixture has stood for three or four days.

Acyl Halides.—All of the acyl halides studied dissolve in liquid hydrogen sulfide and react with it more or less readily. This corresponds to the reaction with water to form the acid. In addition a second reaction takes place whereby the oxygen of the halide is replaced by sulfur, forming the dithio-acid.



$$R\text{—}C\overset{O}{\lessdot}Cl + H_2S = R\text{—}C\overset{O}{\lessdot}SH + HCl$$

$$R\text{—}C\overset{O}{\lessdot}SH + H_2S = R\text{—}C\overset{S}{\lessdot}SH + H_2O$$

Benzyl chloride and bromide, α-bromopropionyl bromide, phthalic chloride, succinyl chloride, benzenesulfonyl chloride and phenylacetyl chloride all reacted and gave varying amounts of yellow to red liquids containing the dithio acids.

Acetyl chloride and acetyl bromide both reacted readily with liquid hydrogen sulfide, forming a deep orange-colored liquid. When the tubes were opened and the hydrogen sulfide pressure thus reduced, fine white crystals were formed mingled with the red liquid. These were purified by recrystallizing from ether.

Anal. Calcd. for $(CH_3CS)_2S$: S, 64.01; C, 31.97; H, 4.02. Found: S, 63.98. 63.84; C, 32.27, 32.6; H, 4.14, 4.12.

This would show that the compound is the anhydride of dithioacetic acid. This compound has not been prepared before. The following are the properties observed: melting point, 225°; readily soluble in acetone, benzene, carbon disulfide, chloroform, carbon tetrachloride and ethyl acetate. It is fairly soluble in ether, petroleum ether and hot alcohol. Cold solutions of aniline and the amines dissolve it. It is insoluble in water, dilute acids or alkalies and inorganic solvents in general. Molecular weight determinations by the freezing point lowering method, when dissolved in benzene, gave values of 269, 270 and 272, which show that it is somewhat associated in benzene solution since the simple formula for $(CH_3CS)_2S$ has a molecular weight of but 150.

Conclusions

1. The solubilities of the different types of organic compounds in liquid hydrogen sulfide have been observed.
2. The presence of a double bond in the organic compound is usually shown by the development of the odor of a mercaptan.
3. The aldehydes, amines and acyl halides are the only types that show much evidence of reacting with the liquid hydrogen sulfide.
4. The amines give unstable addition products with hydrogen sulfide.
5. The aldehydes tend to substitute a sulfur atom for the sulfur of the aldehyde group to form a thio-aldehyde.
6. The acyl halides tend to substitute an SH group for the halide and an S for the oxygen and form dithio acids to a small amount. Acetyl chloride and bromide form the dithioacetic acid, which then loses hydrogen sulfide and forms the thioanhydride.

AMES, IOWA

NOTES

A Sensitive Test for Magnesium.[1,2]—K. Suitsu and K. Okuma[3] state that the azo dye, *o,p*-dihydroxy-azo-*p*-nitrobenzene gives a very sensitive test for the magnesium ion. This reagent has been used in the courses of qualitative analysis at this University for two years with excellent results. The authors claim to be able to detect $^1/_{500}$ mg. of magnesium by means of this test.

The dye is readily prepared by diazotizing *p*-nitraniline and coupling it with the theoretical quantity of resorcinol dissolved in dilute sodium hydroxide solution. The solution is acidified and the precipitated dye filtered off. The product may be purified by recrystallization from methyl alcohol as a dark red powder, m. p., 199–200°. A convenient concentration for ordinary use is a 0.5% solution of the dye in 1% sodium hydroxide. Some deterioration of the reagent occurs in solution after a year's standing.

The solution to be tested for magnesium is made slightly acid with dilute hydrochloric acid and one drop of the reagent added. On making

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[1] Hahn, *Ber.*, **57**, 1394 (1924); **60**, 975 (1927), describes a somewhat similar test for magnesium using 1,2,5,8-tetrahydroxy-anthraquinone.

[2] Since this note has been accepted for publication, the Eastman Kodak Company has informed me that they intend placing the reagent on the market.

[3] Suitsu and Okuma, *J. Soc. Chem. Ind. Japan*, **29**, 132–138 (1926); *C. A.*, **20**, 3000 (1926).