

not be crystallized.¹⁷ Between 0 and 30 mole per cent. methylaniline, the pressure in the melting point tube became too great to avoid loss of sulfur dioxide. The solutions are orange and the solids are golden yellow, although the 50 mole per cent. solution gave a bright red solid.

Summary

Phase diagrams are presented for binary sys-

(17) J. C. Swallow and R. O. Gibson, (*J. Chem. Soc.*, 20 (1934)), obtained a glass on cooling methylaniline while P. M. Jaeger (*Z. anorg. allgem. Chem.*, **101**, 146 (1917)) claims to have crystallized this substance at -57° .

tems of sulfur dioxide with ethylene oxide, acetone, dioxane, anisole, diethyl sulfide and methylaniline.

The following new compounds are reported: dioxane-sulfur dioxide (1:1 and 1:2), ethylene oxide-sulfur dioxide, anisole-sulfur dioxide and diethyl sulfide-sulfur dioxide.

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Mechanism of the Reaction between Hydrogen Sulfide and Sulfur Dioxide in Liquid Media

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It has been known for some time that sulfur dioxide and hydrogen sulfide will not react with each other in either the gas or liquid phase unless an appropriate third substance is present. The reaction between these two gases to give sulfur and water progresses readily in a number of liquid media, but does not take place at all in the presence of others. Previous work in the investigation of the effect of various liquids upon this reaction has been carried out by Klein² and by Mathews.³

These workers have demonstrated that the catalytic effect is not dependent upon the dielectric constant of the liquid. Klein believed that an unstable compound must be formed between one or the other of the two gases and the liquid medium, but was unable to establish which reactant must form the addition compound. Mathews does not favor this viewpoint since methyl salicylate does not promote the reaction whereas methyl benzoate does. Mathews suggests that the activity of the catalyst depends upon its ability to dissolve the sulfur dioxide and the hydrogen sulfide. In the course of an examination of the reaction in this Laboratory additional data were obtained which make possible a proposed theory and explanation of which liquids will act as catalysts and which will not.

Experimental

The general method used in this study was to bubble a mixture of hydrogen sulfide and sulfur

(1) Post-Doctorate Fellow, Southern Acid and Sulphur Co., Inc. Project with The Ohio State University Research Foundation.

(2) D. Klein, *J. Phys. Chem.*, **15**, 1-19 (1911).

(3) E. Mathews, *J. Chem. Soc.*, 2270-2273 (1926).

TABLE I

- | | |
|----|---|
| A. | LIQUIDS IN WHICH HYDROGEN SULFIDE AND SULFUR DIOXIDE REACT IN TWO MINUTES OR LESS |
| a. | Water ^{1,2,3} |
| b. | Alcohols: methyl, ^{1,2} ethyl, ^{2,3} <i>i</i> -propyl, ² <i>i</i> -butyl, ^{2,3} <i>t</i> -butyl, ^{1,2} <i>n</i> -amyl, ³ <i>i</i> -amyl, ^{2,3} <i>t</i> -amyl, ² allyl, ² benzyl ² |
| c. | Basic nitrogen compounds: aniline, ^{1,2} pyridine, ¹ dimethylaniline, ¹ <i>o</i> -toluidine, ¹ molten diphenylguanidine ¹ |
| d. | Carbonyl derivatives: acetone, ^{1,2,3} methyl ethyl ketone, ^{2,3} carvone, ³ benzaldehyde ^{2,3} |
| e. | Ethers: dioxane ¹ |
| f. | Nitriles: benzyl cyanide ² |
| g. | Esters: propyl acetate, ³ amyl acetate, ^{1,2} ethyl butyrate, ² bornyl acetate, ² <i>i</i> -amyl nitrite ¹ |
| B. | LIQUIDS IN WHICH HYDROGEN SULFIDE AND SULFUR DIOXIDE REACT IN TWO TO THIRTY MINUTES |
| a. | Alcohol: glycerol ² |
| b. | Basic nitrogen compound: benzanilide in benzene ¹ |
| c. | Ether: diethyl ether ^{1,2,3} |
| d. | Nitriles: acetonitrile, ^{1,2,3} propionitrile, ³ valeronitrile ³ |
| e. | Esters: ethyl acetate, ^{2,3} <i>i</i> -butyl acetate, ³ methyl benzoate, ^{2,3} amyl benzoate, ² ethyl phthalate, ¹ methyl sulfate ² |
| f. | Nitro compounds: nitromethane ^{1,2} |
| C. | LIQUIDS IN WHICH HYDROGEN SULFIDE AND SULFUR DIOXIDE DO NOT REACT WITHIN THIRTY MINUTES |
| a. | Hydrocarbons and halogen derivatives: carbon tetrachloride, ^{1,2,3} chloroform, ^{1,2,3} benzene, ^{1,2,3} chlorobenzene, ² mineral oil, ¹ petroleum ether, ¹ amylene ³ ethyl chloride, ³ ethyl iodide ² |
| b. | Nitro compounds: nitrobenzene, ^{2,3} 2-nitro- <i>p</i> -cymene ¹ |
| c. | Acid derivative: methyl salicylate, ² benzoyl chloride, ³ acetyl chloride ³ |
| d. | Sulfur compounds: ethyl disulfide, ³ <i>n</i> -butyl mercaptan, ¹ carbon disulfide, ^{2,3} sulfuryl chloride, ³ diethyl sulfide ¹ |
| e. | Phosphorus compounds: phosphorus oxychloride ² |

¹ Present work. ² Klein. ³ Mathews.

dioxide through the liquid to be examined. The hydrogen sulfide was generated from calcium sulfide; the sulfur dioxide was taken from a commercial cylinder. Both gases were dried over phosphorus pentoxide before mixing. Approximately 10 mg. per minute of each gas was used. The liquids were dried with appropriate reagents to assure absence of moisture. Those liquids which have been shown in this and previous studies to bring about a reaction are listed in parts A and B of Table I. The liquids which did not catalyze the reaction are listed in part C of Table I.

Discussion

Klein² has suggested that one or both of the gases must react with the solvent, but has not gone further with a mechanism for the reaction. Mathews³ was surprised by the fact that methyl benzoate would catalyze the reaction whereas methyl salicylate would not. A wide variety of the solvents tried give addition compounds with sulfur dioxide, but it is of interest that some of these like the amines⁴ catalyze the reaction and others, such as diethyl sulfide,⁵ do not.

Of the compounds studied, it already has been reported that amines, aldehydes, ketones and nitriles,⁶ all of which promote the reaction, form addition compounds with hydrogen sulfide. Moreover, a careful consideration of all the solvents which do promote the reaction shows that every one is capable of combining with hydrogen sulfide by means of a hydrogen bridge. Huggins⁷ has pointed out that sulfur does not form such dative bonds with hydrogen and that mercaptans thus differ from alcohols. Walker, *et al.*,⁸ have found that substances which tend to react with hydrogen sulfide to give such molecular compounds form conducting solutions in liquid hydrogen sulfide.

It, therefore, becomes apparent that the function of a solvent which promotes this combination of hydrogen sulfide and sulfur dioxide is to react with hydrogen sulfide to form a compound with a hydrogen bridge which can ionize to give hydrosulfide or (much less likely) a sulfide ion. The liquid must act as a Brönsted base toward hydrogen sulfide to promote the reaction.

(4) J. R. Bright, Ph.D. Thesis, The Ohio State University, 1940.

(5) N. F. Albertson and W. C. Fernelius, *THIS JOURNAL*, **65**, 1687 (1943).

(6) J. A. Wilkinsol, *Chem. Rev.*, **8**, 241 (1931).

(7) M. L. Huggins, *J. Org. Chem.*, **1**, 454 (1936).

(8) J. W. Walker, D. McIntosh and E. Archibald, *J. Chem. Soc.*, **85**, 1098-1105 (1904).

Upon this basis it is possible to account for the discrepancy proposed by Mathews. Methyl benzoate can form a hydrogen bridge with hydrogen sulfide but methyl salicylate cannot, since a bridge already exists between the hydroxyl group and the ester group through internal chelation.

The difference in behavior of nitromethane (catalytic) and nitrobenzene (not catalytic) is especially interesting in view of the work of Copley, Zellhoefer and Marvel,⁹ on the solubility of CHCl_2F in various solvents. The solubility is abnormally large in the case of nitrobutane, showing that the nitro group is able to act as a donor center to the hydrogen atom. However, substitution of a phenyl group to give nitrobenzene causes a marked lowering in solubility.

Further support is given to the mechanism by the fact that a number of substances which catalyze the reaction in the liquid form do not do so in the solid state. Water and alcohol have been shown to be in this category, previously, and in this work it was shown that solid diphenylguanidine will not catalyze the reaction although the molten material will. The reaction is not catalyzed by the limited surface of the solid, but requires the much more extensive reaction possible with the liquids. The solids which are reported in the patent literature as catalysts for this reaction, such as alumina, are all of a nature favorable to the retention of a tenaciously held layer of adsorbed moisture under the conditions of preparation and operation.

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Summary

1. The reaction between hydrogen sulfide and sulfur dioxide in liquid media has been extended to a number of additional liquids.

2. The mechanism of the reaction is shown to be (a) the formation of compounds between the hydrogen sulfide and the liquid medium through a hydrogen bridge, (b) the release of hydrosulfide ions by the addition compounds, (c) reaction between sulfur dioxide or its addition compounds and the hydrosulfide ion.

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(9) M. J. Copley, G. F. Zellhoefer and C. S. Marvel, *THIS JOURNAL*, **61**, 3552 (1939).