Behavior of Trimethylene Sulfide in Heptane and Naphtha Solutions

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Trimethylene sulfide readily reacts with mercuric chloride, methyl iodide, potassium permanganate, and 30 per cent hydrogen peroxide giving stable derivatives. Bromine gives a product which readily decomposes at −15° C. Mercuric iodide does not react. Nitric and hydrochloric acids give highly polymerized products. The polymers from hydrochloric acid exhibit colloidal properties in aqueous medium. This member of the thiophane series behaves like the higher members of this series in that it resembles the alkyl sulfides more than thiophene in its chemical properties. It differs from tetramethylene and pentamethylene sulfides in its behavior with concentrated nitric and concentrated hydrochloric acids.

IN A previous paper the authors reported the behavior of certain thiophanes in hydrocarbon solutions (*1*). In the present paper are given the results obtained on a lower member of the thiophane series, using the same solvents and the reagents (with the addition of hydrochloric acid) that were used in the previous study.

A member of the alkyl sulfides and the thiophene series was studied along with trimethylene sulfide, using the same conditions throughout. The compounds used in this comparative study were ethyl sulfide and thiophene. One-half molar solutions of the sulfides were investigated with the following reagents: mercuric chloride, mercuric iodide, 30 per cent hydrogen peroxide in glacial acetic acid, nitric acid (sp. gr., 1.42), potassium permanganate, bromine in carbon tetrachloride, methyl iodide, and hydrochloric acid. The solvents used were pure *n*-heptane and three different naphthas. The heptane was obtained from the Eastman Kodak Company and boiled at 98° to 98.5° C. The naphthas were obtained from oil companies. The physical characteristics of these naphthas have been previously given (*1*). The trimethylene sulfide was prepared in this laboratory. It boiled at 94.5° to 95.5° C.

Trimethylene sulfide exhibits a peculiar behavior with concentrated nitric and concentrated hydrochloric acids which is not shown with tetramethylene and pentamethylene sulfides; neither ethyl sulfide nor thiophene shows this tendency. It seems, therefore, that strong acids favor polymerization of this sulfide. Trimethylene sulfide differs from tetramethylene and pentamethylene sulfides in that it does not yield an addition product with mercuric iodide under the conditions observed. The sulfide yields a ready precipitate with methyl iodide, whereas tetramethylene and pentamethylene sulfides require considerable time for such formation.

The nature of the polymerized product of trimethylene sulfide produced by the action of concentrated hydrochloric acid on the sulfide was studied. Its behavior with certain electrolytes in aqueous medium is given in Table I. In Table II are given data on the derivatives of trimethylene sulfide and ethyl sulfide in heptane and naphtha solutions.

EXPERIMENTAL PROCEDURE

MERCURIC CHLORIDE. To a solution of the sulfide in 5 ml. of the hydrocarbon was added an equivalent amount of mercuric chloride dissolved in absolute alcohol. The precipitate was filtered and dried in a vacuum desiccator overnight. Usually the melting point was not altered by recrystallization from absolute alcohol when heptane was used as a solvent, but, when the naphthas were used as solvents, several recrystallizations were necessary. By using a 0.237 molar solution of mercuric chloride in alcohol it was possible to detect trimethylene sulfide in concentrations of 40 parts per million. Trimethylene sulfide forms a monosalt with mercuric chloride under the above conditions, whereas ethyl sulfide forms mainly the di- salt; thiophene does not react.

MERCURIC IODIDE. A solution of the sulfide in the hydrocarbon was treated with a saturated solution of mercuric iodide in absolute alcohol. Trimethylene sulfide did not react with this reagent, nor did thiophene. Ethyl sulfide yielded a compound which was isolated as previously described by Bost and Conn (*1*). With this reagent, trimethylene sulfide differs from tetramethylene and pentamethylene sulfides.

NITRIC ACID. To 5 ml. of the hydrocarbon solution of the sulfide in an apparatus, as previously described (*1*), was added an equivalent amount of nitric acid (sp. gr., 1.42) to form the sulfone. Better results were obtained with ethyl sulfide when fuming acid was used. A precipitate was obtained with trimethylene sulfide, but it was neither the expected sulfone nor the sulfoxide of trimethylene sulfide. The authors were unable to obtain a pure sample, and attempts to prove the constitution of the compound were futile. The product is apparently a polymer or a mixture of polymers of trimethylene sulfide which may be accompanied by partial oxidation. The sulfone of ethyl sulfide was obtained, but thiophene failed to yield a product.

HYDROCHLORIC ACID. A 10-ml. portion of the sulfide in heptane (approx. 1.5 molar) and 2 ml. of concentrated hydrochloric acid (sp. gr., 1.18) were placed in a 12-inch (30.5-cm.) tube. The tube was surrounded by a freezing mixture and hydrochloric acid gas passed in for 30 minutes. This was sufficient for complete saturation. While cold, the tubes were sealed and left standing a few days. By this time the aqueous portion in the tube containing the trimethylene sulfide was a very viscous, clear liquid, adhering to the walls of the tube, and it could not be removed by vigorous shaking. When the tube was opened and treated with water, a heavy, flocculent, snow-white precipitate was obtained. It was not possible to filter this product. It melted completely at 100° C., but, when held at 80° C. for 2 hours, the compound liquefied and would not solidify on cooling. Attempted distillation resulted in decomposition with the evolution of hydrogen sulfide and some unsaturated products. The precipitate was washed once with water by decantation. A second treatment with water effected its dispersion in the aqueous medium. It was possible to reprecipitate the product quickly in its original form by addition of certain electrolytes. By repeatedly washing the precipitate it was found that it could be dispersed in the aqueous medium again, and by addition of the electrolyte to this redispersed system it was possible to reprecipitate the original product. Table I shows the behavior of this compound with several electrolytes.

Table I. Behavior of $(C_3H_6S)_y$ with Electrolytes in Aqueous Medium

Electrolyte Added	Pectized	Peptized after Washing	Reprecipitated
HCl	Yes	Yes	Yes
$NaCl$	Yes	Yes	Yes
KCl	Yes	Yes	Yes
$BaCl_2$	Yes	Yes	Yes
$HgCl_2$	Yes	No	...
H_2SO_4	Yes	Yes	Yes
Na_2SO_4	No	...	...
K_2SO_4	No	...	
Na_2CO_3	Yes	No	...
K_2CO_3	Yes	No	...
$KCNS$	Yes	No	...
NH_4NO_3	Yes	No	...
$CuSO_4$	Yes	No	...
$Na_2S_2O_3$	Yes	No	...
$NaC_2H_3O_2$	No	...	...

Since this behavior with these electrolytes gave no indication about the nature of the charge on the dispersed phase, it was necessary to make this determination by cataphoresis experiments. A portion of the product was dispersed in water and placed in a U-tube equipped with platinum electrodes. A potential gradient of one volt per centimeter was imposed across the system for 48 hours. At this time considerable precipitate had accumulated on the positive pole, but as soon as the circuit was broken it disappeared.

Solubility tests in many of the ordinary solvents were made. It was insoluble in ethyl and methyl alcohols, acetone, ether, petroleum ether, benzene, toluene, chloroform, carbon tetrachloride, ethyl acetate, pyridine, bromobenzene, and acetic acid. It was very slightly soluble in carbon disulfide.

Treatment of the heptane portion of the sealed tube with mercuric chloride solution gave a copious, white precipitate which shrinks at 110° C. and partially melts at 118° C. The addition product of trimethylene sulfide and mercuric chloride shrinks from 92° to 95° C. Similar but impure products were obtained with trimethylene sulfide in naphthas 1, 3, and 7 with hydrochloric acid.

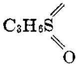
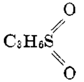
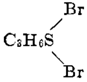
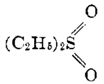
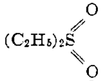
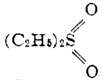
Contrary to the behavior of trimethylene sulfide with hydrochloric acid under the above described conditions, tetramethylene, pentamethylene, and ethyl sulfides were recovered from the tubes unchanged. Thiophene imparted a black color to the hydrochloric acid portion of the tube.

Potassium Permanganate. The method employed in this oxidation was essentially that employed in a previous paper (*1*). Trimethylene sulfide readily yielded the expected sulfone. When heptane was used as a solvent, usually one crystallization was sufficient, whereas in the case of the naphthas from two to four recrystallizations were necessary. Thiophene gave no definite products.

Hydrogen Peroxide. A 10-ml. portion of the hydrocarbon solution of the sulfide was treated with the equivalent of 30 per cent hydrogen peroxide dissolved in glacial acetic acid to form the sulfone. The reaction product was heated on a steam bath for 3 hours and then transferred to an evaporating dish, and the acid-solvent mixture was removed. The residue was taken up in anhydrous ether, and the latter removed in a vacuum desiccator. When naphthas were used as solvents, three or four recrystallizations were necessary. Trimethylene and ethyl sulfides yield sulfones; thiophene does not.

Methyl Iodide. To a 5-ml. portion of the sulfide in hydrocarbon solution was added the equivalent amount of methyl iodide to form the iodomethylate. Trimethylene sulfide yielded a ready precipitate. It differed from tetramethylene and pentamethylene sulfides in that it was necessary for these sulfides to stand 24 hours before precipitation began, and several days before it was complete. The melt-

Table II. Derivatives of Sulfides in Heptane and Naphtha Solutions

Reagent	Compound Formed	Crystalline Form	Crystal Solvent	Melting Point ° *C.*
		TRIMETHYLENE SULFIDE		
$HgCl_2$	$C_3H_6S{\cdot}HgCl_2$	White powder	Alcohol	92–95 (shrinks)
HgI_2	Very unstable product, if formed at all			
HNO_3	Product not identified			
HCl	Highly polymerized products exhibiting colloidal behavior in aqueous medium			
$KMnO_4$	 $C_3H_6S\begin{smallmatrix}{=}O\\{=}O\end{smallmatrix}$	Long slender needles	Alcohol	75
H_2O_2	 $C_3H_6S\begin{smallmatrix}{=}O\\{=}O\end{smallmatrix}$	Long slender needles	Alcohol	75
CH_3I	$C_3H_6S.CH_3I$	Needles	Alcohol	98–100
Br_2	 $C_3H_6S\begin{smallmatrix}-Br\\-Br\end{smallmatrix}$	Orange-yellow ppt., very unstable	....	....
		ETHYL SULFIDE		
$HgCl_2$	$(C_2H_5)_2S{\cdot}2HgCl_2$	Colorless needles	Alcohol	119.5 (*2*)
HgI_2	$(C_2H_5)_2S{\cdot}HgI_2$	Lemon-yellow needles, decompose on standing	Alcohol	62 (approx.) (*5*)
HNO_3	 $(C_2H_5)_2S\begin{smallmatrix}{=}O\\{=}O\end{smallmatrix}$	Colorless leaflets, darken on standing	Ether	70 (*4*)
$KMnO_4$	 $(C_2H_5)_2S\begin{smallmatrix}{=}O\\{=}O\end{smallmatrix}$	Colorless leaflets, darken on standing	Ether	70
H_2O_2	 $(C_2H_5)_2S\begin{smallmatrix}{=}O\\{=}O\end{smallmatrix}$	Colorless leaflets, darken on standing	Ether	70
H_2O_2	$(C_2H_5)_2S=O$	Lemon-yellow oil	Ether	4–6 (*3*)
CH_3I	$(C_2H_5)_2S{\cdot}xCH_3I$	Red oil at ordinary temp.		
Br_2	Oil unstable at ordinary temperature			

ing points of the products obtained when heptane was used as a solvent were not altered by recrystallization from absolute alcohol; however, repeated recrystallizations were necessary when the naphthas were used as solvents. Ethyl sulfide gives an oil under the above conditions but thiophene does not react.

BROMINE. Ten-milliliter portions of the sulfides in hydrocarbon solutions were treated with bromine dissolved in carbon tetrachloride. Trimethylene sulfide readily yields the dibromide in the form of an orange-yellow precipitate. This product is highly unstable, as is also that of ethyl sulfide. These compounds decompose even at −15° C., evolving hydrogen bromide. Thiophene failed to yield any product.

LITERATURE CITED

(1) Bost and Conn, IND. ENG. CHEM., 23, 93 (1931).
(2) Faragher, Morrell, and Comay, *J. Am. Chem. Soc.*, 51, 2774 (1929).
(3) Pummerer, *Ber.*, 43, 1407 (1910).
(4) Saytzeff, *Ann.*, 167, 153 (1867).
(5) Smiles, *J. Chem. Soc.*, 77, 163 (1900).

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Absorption of Carbon Dioxide in Sodium Carbonate-Bicarbonate Solutions

I. Equilibrium in System Carbon Dioxide–Sodium Carbonate–Sodium Bicarbonate–Water

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Experiments have been performed to determine the equilibrium relationship between temperature, partial pressure of carbon dioxide in the gas phase, and chemical composition of the liquid, for a range of conditions approximating those encountered in the absorption process as operated in practice. The results of these experiments have been correlated with the work of McCoy and Smith (3) and an empirical equation,

$$\frac{X^2 C^{1.29}}{SP(1 - X)(185 - t)} = 10$$

representing the equilibrium relationship between temperature, partial pressure of carbon dioxide in the gas, and chemical composition of the liquid, has been developed.

CARBON dioxide of high purity is obtained from flue gases (or other gases containing carbon dioxide) by a process in which the carbon dioxide is separated from the other constituents of the flue gas by means of a liquid absorption medium which preferentially absorbs the carbon dioxide. An aqueous sodium carbonate-bicarbonate solution is a liquid absorption medium commonly employed. Accurate design of absorption equipment for this process is facilitated by a knowledge of the relationships between the various conditions under which the absorption is to take place and (1) the equilibrium which tends to be established between the carbon dioxide concentration in the gas and the concentration of carbonate and bicarbonate in the liquid, and (2) the rate at which carbon dioxide tends to be absorbed from the gas by the liquid. The present article treats the question of equilibrium; another article will consider the question of absorption rate.

The reversible reaction

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3 \qquad (1)$$

is utilized in the absorption process for producing essentially pure carbon dioxide from flue gas (which contains approximately 18 per cent carbon dioxide, 80 per cent nitrogen, and the balance carbon monoxide, oxygen, sulfur compounds, and organic matter). The process involves two stages. In the first stage, the flue gas is exposed to an aqueous solution containing sodium carbonate under conditions which favor the formation of sodium bicarbonate according to Equation 1; carbon dioxide is removed from the flue gas and is stored in the liquid as sodium bicarbonate. In the second stage, the liquid is removed from contact with the flue gas and is subjected to conditions which favor the decomposition of sodium bicarbonate with the formation of sodium carbonate, carbon dioxide, and water; the carbon dioxide is evolved from the solution accompanied only by water vapor, which is easily removed by condensation. To the designer of equipment for absorbing carbon dioxide in sodium carbonate-bicarbonate solutions, it is of considerable interest to know just where the reaction represented by Equation 1 will balance for the different conditions which are likely to be encountered when the equipment is put ihto operation.

WORK OF EARLIER INVESTIGATORS

The system under consideration consists of a gas phase and a liquid phase; it is a two-phase system containing three components. Application of the familiar phase rule of Gibbs reveals that there are three degrees of freedom; it follows that, when the system is at equilibrium, the ratio of sodium bicarbonate to sodium carbonate, the temperature, the partial pressure of carbon dioxide in the gas, the total sodium concentration in the liquid, and all other variables are fixed if any three independent variables are fixed. An equation showing the equilibrium relationship between certain variables has been developed from theoretical considerations by McCoy and Smith (*3*):

$$\frac{2\,X^2\,C}{SP\,(1 - X)} = M \qquad (2)$$