these equilibria approached one another until a maximum was reached. Beyond this point polymerization occurred with a prolongation of reaction time and the yield of ester subsequently decreased.

An explanation for this gradual approach to a maximum is offered on the basis of the following considerations: that the concentration of boron fluoride necessary for bringing about a reverse of the condensation reaction having a reaction velocity equal to that of the condensation reaction, is greater than that used for the condensation itself. Thus in those reactions where low concentrations of boron fluoride are used a state is reached in which the boron fluoride is absorbed by the ester and the concentrations are not sufficient to effect a reversal having a velocity equal to the condensation velocity. As the concentration of boron fluoride is increased in the ester the velocity of the reverse reaction is increased. When the proper amount of boron fluoride is present the velocity of the reverse reaction is equivalent to the velocity of the condensation reaction: there being sufficient boron fluoride on both sides of the reaction to cause the reverse and condensation reactions to proceed with equal velocities. Beyond this concentration of boron fluoride polymerization is more pronounced.

Summary

The influence of time and concentration of boron fluoride upon the condensation of acetic acid with cyclohexene at a constant temperature has been studied. The concentration of boron fluoride is shown to have a marked effect upon the quantity of ester obtained. An explanation was offered for the change in apparent equilibria with the quantity of boron fluoride used.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Sulfur Studies. XI. Some Sulfur Derivatives of Benzaldehyde

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Practically nothing is known about monomeric thioaldehydes since they polymerize immediately upon formation. However, the conditions under which they are formed profoundly influence the nature of the resulting polymerization and we have found that reactions by which one would expect to obtain monomeric thiobenzaldehyde lead to a variety of compounds such as the thioester, the mercaptan, the dithio acid, the disulfide, the cyclic trimer, and other polymers. It is the purpose of this paper to describe some of these reactions and to offer a mechanism for the formation of some of the compounds obtained.

Benzal chloride and sodium sulfide react in alcoholic solution to form monomeric thiobenzaldehyde, C_6H_5CHS. However, the compound cannot be isolated and it immediately undergoes polymerization or side reactions. A part polymerizes to β-trithiobenzaldehyde. Some undergoes the Cannizzaro reaction to give benzyl mercaptan, dithiobenzoic acid, and a small amount of benzyldithiobenzoate. A portion of the mercaptan then reacts with thiobenzaldehyde to form a small quantity of benzyl mercaptal of benzaldehyde.

It has been suggested that the Cannizzaro reaction proceeds through ester formation. Our work confirms this belief. That is, thiobenzaldehyde readily undergoes polymerization to dithiobenzoate, and in the presence of alkalies such as sodium sulfide, the ester is saponified to the thio alcohol and dithio acid. On the other hand, the Cannizzaro reaction involving thiobenzaldehyde can be arrested at the ester stage provided that the monomer is formed under conditions which do not produce saponification of the ester. This is accomplished by depolymerizing β-trithiobenzaldehyde by distilling it at 3 mm. in the presence of a few drops of sulfuric acid. A part of the monomer in the distillate immediately re-polymerizes to the trimer and the rest polymerizes to the ester. The Cannizzaro reaction can then be completed from this point if desired by adding sodium sulfide whereupon the thio acid and thio alcohol are immediately formed.

While β-trithiobenzaldehyde is mainly depolymerized by distilling at low pressure in the presence of sulfuric acid, some decomposition also occurs with the formation of stilbene and sulfur. Some tetraphenylthiophene is also formed by the interaction of stilbene and sulfur. When the distillation is carried out in the absence of sulfuric acid, decomposition into stilbene and sulfur with the resultant formation of tetraphenylthiophene is the main course of the reaction rather than depolymerization.

When hydrogen sulfide is passed into an alcoholic solution of benzaldehyde previously saturated with dry hydrogen chloride, trithiobenzaldehyde is formed exclusively.[1] By reducing the acid concentration other types of polymers, perhaps linear, are obtained in the form of pink gums along with varying quantities of the trimer. The pink gum cannot be purified by recrystallization or by vacuum distillation. The latter brings about complete decomposition, mainly into stilbene and sulfur. The monomer does not undergo the Cannizzaro reaction in acid solution.

Hydrogen sulfide reacts with benzaldehyde in the presence of small amounts of potassium hydroxide or sodium hydroxide to form thiobenzaldehyde. Most of the thiobenzaldehyde immediately polymerizes to form a viscous, pink oil; the remainder undergoes the Cannizzaro reaction. Upon distillation *in vacuo*, the pink oil is decomposed to form mostly stilbene and sulfur. However, some benzyl dithiobenzoate also is formed which indicates slight depolymerization.

Fromm and Forster[2] report the preparation of benzyl dithiobenzoate by refluxing an alcoholic solution of C_6H_5CSSNa and sodium hydroxide with an excess of benzyl chloride. They describe the ester as being white prisms, m. p. 55°. Since the other known esters of dithiobenzoic acid are red oils, we repeated the work of Fromm and Forster and obtained in good yield benzyl sulfide, m. p. 50°, instead of the ester. The sulfide was identified by conversion into the sulfone by the method of Bost, Turner and Norton.[3] One would not expect to obtain the ester under the experimental conditions specified by Fromm and Forster since as rapidly as the ester was formed, it would be saponified by the sodium hydroxide, at the elevated temperature, with the formation of C_6H_5CSONa and $C_6H_5CH_2SNa$. The mercaptide would then react with the excess benzyl chloride to form benzyl sulfide. By modifying the experimental conditions, we have obtained the ester in good yield as a red oil, b. p. 179–180° at 3 mm.

Experimental Work

The Reaction of Sodium Sulfide and $C_6H_5CHCl_2$.—Seven and eight-tenths grams of sodium sulfide and 16.1 g. of $C_6H_5CHCl_2$ were dissolved in 125 cc. of anhydrous ethyl alcohol and allowed to stand at room temperature in an atmosphere of nitrogen for a week or longer. A red supernatant liquid and a white precipitate resulted. The same results were also obtained by refluxing six to eight hours. After the reaction was complete, the precipitate was filtered off in an atmosphere of nitrogen and later showed to be sodium chloride and β-trithiobenzaldehyde. A search was made immediately for the monomeric thiobenzaldehyde in the red alcoholic solution. This was done by examining a portion with 2,4-dinitrophenylhydrazine (since benzal chloride, the oxobenzaldehyde, and the thiobenzaldehyde all give the same hydrazone, the first two compounds would interfere with the test and their presence or absence had to be determined); by testing for a thiocarbonyl group with Grote's reagent;[4] and by a fractional vacuum distillation with the subsequent identification of the compounds thus obtained. Benzyl mercaptan and benzyl dithiobenzoate were identified in the distillate. No monomer of thiobenzaldehyde was isolated. The remaining red alcoholic solution was examined as follows: an equal volume of 4% aq. sodium hydroxide solution was added and the whole was then extracted with benzene. Dithiobenzoic acid was isolated from the aqueous portion. The benzene extract was permitted to evaporate spontaneously and the residue was then recrystallized from ethyl alcohol. Benzyl disulfide, benzyl mercaptal of benzaldehyde, and benzyl dithiobenzoate were identified in this portion.

The Reaction of Benzaldehyde and Hydrogen Sulfide in the Presence of Acids.—Hydrogen sulfide passed into an alcoholic solution of benzaldehyde previously saturated with dry hydrogen chloride gives exclusively trithiobenzaldehyde. We have tried varying concentrations of hydrogen chloride from a few bubbles to complete saturation with the hope of finding an acid concentration in which the monomeric thiobenzaldehyde would be stable. The runs were carried out by saturating 5 cc. of benzaldehyde in 20 cc. of absolute ethyl alcohol at −5° with hydrogen sulfide. A few bubbles of dry hydrogen chloride were then passed in while the passage of hydrogen sulfide was continued. An intense blue color formed and rapidly faded with the formation of a sticky white precipitate and a pink gum. Upon increasing the quantity of hydrogen chloride the blue color faded more rapidly. The sticky white precipitate was soluble in benzene from which it was deposited as a pink gum upon complete evaporation of the benzene. Some trithiobenzaldehyde also was formed. Other runs were carried out at room temperature with the same results. Other runs were carried out in which sulfuric acid, zinc chloride, acetic acid, magnesium perchlorate, and phosphorus pentoxide were substituted for hydrogen chloride and gave results identical with above.

The Action of Hydrogen Sulfide upon Benzaldehyde in Presence of Potassium Hydroxide.—Concentration: 0.5 g. KOH; 20 cc. C_6H_5CHO; 100 cc. absolute ethyl alcohol. Hydrogen sulfide was passed in at room temperature for

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[1] E. Baumann and E. Fromm, *Ber.*, **22**, 2600 (1889).

[2] E. Fromm and Forster, *Ann.*, **394**, 340 (1912).

[3] R. W. Bost, J. O. Turner and R. D. Norton, THIS JOURNAL, **54**, 1985 (1932).

[4] I. W. Grote, *J. Biol. Chem.*, **93**, 25 (1931).

four days. A large quantity of a viscous, pink oil separated during this time and the alcohol layer was colored red. Benzyl mercaptan was identified as one of the products of the reaction by vacuum distillation of a portion of the red alcohol layer. The mercaptan thus obtained was converted into the benzyl 2,4-dinitrophenyl thioether by the method of Bost, Turner and Norton.[3] To the remaining red alcohol layer, an equal volume of 4% aq. sodium hydroxide was added whereupon benzyl disulfide precipitated and was filtered off. The aqueous solution was acidified with hydrochloric acid and then extracted with benzene. The red benzene extract was shaken with lead acetate solution. A precipitate formed which was recrystallized from hot toluene. Red needles resulted, m. p. 205°, which were lead dithiobenzoate.

Vacuum Distillation of Pink Oil.—A special distilling apparatus had to be used in this work due to the fact that a number of compounds distilled over together once depolymerization or decomposition began, and some of these compounds were solids which immediately solidified in the side-arm. The side-arm of the distilling flask had an inside diameter of 2 mm. and at a distance of about 15 mm. from the neck was bent downward so as to make a vertical connection with a bulb to receive solids and high boiling liquids. A horizontal connection at the bend led to an ice trap to condense the more volatile components. All connections and joints were made of ground glass. The neck was a separate piece with ground glass connections so as to permit the use of different size distilling bulbs. An oil-bath was used to heat the distilling flask. The pressure was 3 mm. Decomposition started at about 120° with a change of color to deep red. Heating was continued to 200°. The following compounds were identified in the distillate: benzyl mercaptan, benzyl disulfide, stilbene, and benzyl dithiobenzoate. The mercaptan was in the more volatile portion. The disulfide, stilbene, and the ester distilled over together and had to be separated by fractional recrystallization from ethyl alcohol. The residue left in the distilling flask was recrystallized from ethyl alcohol and gave sulfur and tetraphenylthiophene.

Vacuum Distillation of β-Trithiobenzaldehyde.—The distillation was carried out in the apparatus described above and at a pressure of 3 mm. Depolymerization and decomposition started upon melting (225°). Sulfur, stilbene, tetraphenylthiophene, a few drops of benzyl dithiobenzoate, and a few drops of benzaldehyde were identified as the decomposition products.

Sulfuric acid catalytically depolymerizes paraldehyde and we have attempted to do the same with β-trithiobenzaldehyde. Ten grams of the trimer and 3 drops of concd. sulfuric acid were distilled at a pressure of 3 mm. β-Trithiobenzaldehyde and benzyl dithiobenzoate were the main products of distillation. A few drops of benzaldehyde and a small quantity of stilbene were also formed. Depolymerization instead of decomposition undoubtedly occurred in this distillation since the large quantities of stilbene, sulfur, and tetraphenylthiophene were not formed as was the case of the distillation carried out in the absence of sulfuric acid. However, the distillate immediately polymerized to the trithiobenzaldehyde, or underwent the Cannizzaro reaction.

Another vacuum distillation of the trimer in which phosphoric acid was used as the depolymerizing agent gave the same results.

Preparation of Benzyl Dithiobenzoate.—When the calculated quantity of benzyl chloride is added to a solution of 5.2 g. of dithiobenzoic acid in 50 cc. of ethyl alcohol and 35 cc. of 10% aq. sodium hydroxide at 80° and shaken, a red oil separates. This oil boils at 179–180° at 3 mm.; decolorizes Feigel's solution; upon standing in contact with concd. ammonium hydroxide for six days gives benzamide, benzyl mercaptan, and hydrogen sulfide. This red oil is benzyl dithiobenzoate. Sulfur found: 26.07%. Calcd.: S, 26.20%.

Saponification of Ester.—Three grams of sodium sulfide was dissolved in 40 cc. of absolute alcohol and 1 cc. of benzyl dithiobenzoate was added. The temperature was about 25°. In a few minutes the bright red color of the ester had changed to the darker red color of the acid. After a few hours, the reaction seemed to be complete and an equal volume of water was added. No precipitation of the ester occurred showing that the soluble sodium dithiobenzoate and sodium benzyl mercaptide had been formed. The dithio acid was isolated as described previously; the mercaptan was converted into the insoluble benzyl disulfide by bubbling air through a portion of the solution followed by filtration and recrystallization of the disulfide from alcohol. Incidentally, these reactions offer a satisfactory method for identifying benzyldithiobenzoate.

Action of Hydrogen Sulfide upon $(C_6H_5CH{=}NH\cdot HCl)_2\cdot SnCl_4$.—The aldimine stannichloride was prepared by the method of Stephens.[5] Hydrogen sulfide was passed into an alcoholic solution of the salt for twenty-four hours. A transparent plastic substance that melted between 100–110° was obtained. Some pink gum was also formed. No definite products could be isolated.

The work is being continued with certain high molecular weight aromatic aldehydes and also with certain aliphatic aldehydes to see if similar results are obtained.

Summary

1. Reactions designed to produce monothiobenzaldehyde in neutral or acid solutions lead to polymers of varying types depending upon the acid concentration.
2. Reactions designed to produce the monomer in alkaline solution lead to products which are accounted for on the basis of the Cannizzaro reaction.
3. Monomeric thiobenzaldehyde was formed but existed only for a short time in solution.
4. Benzyl dithiobenzoate has been prepared and characterized.
5. Evidence that the Cannizzaro reaction goes through ester formation as an intermediate was obtained.
6. Polymerized thioaldehydes have been depolymerized.

CHAPEL HILL, N. C. RECEIVED MARCH 1, 1937

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[5] H. Stephens, *J. Chem. Soc.*, **127**, 1874 (1925).