

Eastman's *p*-phenylenediamine was sublimed at 200° under reduced pressure (2 mm.); the pure white product melted at 140°.

Summary

1. The quantitative absorption curves for ether solutions of *p*-nitrosoanisole, the methyl ether of quinoneoxime and of quinoneoxime have been determined. The spectroscopic results indicate that quinoneoxime and *p*-nitrosophenol are in tautomeric equilibrium in ether solutions in the ratio of approximately seven parts of the former to three parts of the latter.

2. The quantitative absorption spectra of ether solutions of quinone, quinoneoxime, quinonedioxime, quinonechlorimine and quinonedichloro-diimine together with the curve for the tautomeric mixture of quinoneoxime, and *p*-nitrosophenol have been obtained. The conclusion is drawn from these data that the diketonic or quinonoid formula represents the correct structure for quinone and the quinone derivatives.

3. The quantitative absorption curves for the ether solutions of hydroquinone, *p*-aminophenol, *p*-phenylenediamine, hydroquinone monomethyl ether and hydroquinone dimethyl ether have been obtained.

4. The frequencies of maximum absorption for all the compounds studied in this investigation have been ascertained and these values are presented in a table.

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REACTIONS IN LIQUID HYDROGEN SULFIDE. IX. REACTIONS BETWEEN PERSULFIDES OF HYDROGEN AND ORGANIC COMPOUNDS

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The persulfides of hydrogen bear the same relationship to liquid hydrogen sulfide as does hydrogen peroxide to water. Since hydrogen sulfide dissolves organic bodies very readily, more readily than does water, one would expect that the hydrogen persulfides would react with organic compounds more readily than does hydrogen peroxide but in a similar manner.

Up until the work of Bloch and Höhn,² Schenck and Falcke³ and Brunner and Vuillenmuir⁴ the properties of the hydrogen persulfides were either little known or the data given were incorrect.

The reactions of hydrogen peroxide on organic compounds were in-

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

² Bloch and Höhn, *Ber.*, **41**, 1961-1980 (1908).

³ Schenck and Falcke, *ibid.*, **41**, 2600 (1908).

⁴ Brunner and Vuillenmuir, *Schweiz. Med. Wochschr.*, **46**, 436 (1908).

vestigated by Fenton⁵ and Walton and Jones,⁶ who showed that in the presence of ferrous salts the following reactions took place with hydrogen peroxide. Glycolic acid is changed to glyoxylic acid, tartaric acid to dihydroxymalic acid, primary amines to aldehydes, piperidine to glutaric acid, benzene to phenol, benzonitrile to benzamide, azo compounds to azoxy compounds and phenol to dihydroxyphenol or quinone.

It will be noticed that all of the above reactions are of an oxidizing nature, either removing hydrogen or adding oxygen. Walton and Jones⁶ also showed that substances which will catalyze reactions of hydrogen peroxide in water solution will catalyze similar reactions in organic solvents.

In endeavoring to duplicate similar reactions with persulfides, alkaline solutions cannot be used because alkalis will decompose the persulfides very rapidly. Catalysts such as ferrous salts cannot be used because the persulfides are decomposed by them. Walton and Parsons⁷ showed that the persulfides are decomposed by many oxides and inorganic salts. It was found, however, that solutions of the persulfides in organic solvents without catalysts could be used in bringing about similar reactions.

Experimental

Preparation of the Persulfides.—The persulfides were prepared by the method of Walton and Parsons⁷ by heating a mixture of sodium sulfide and sulfur and water for several hours on a water-bath. The flask containing the mixture was closed with a Bunsen valve to prevent the entrance of air. This made it unnecessary to pass hydrogen through the solution during the heating. The solution of the sodium persulfide thus formed was allowed to run beneath the surface of concentrated hydrochloric acid kept at a temperature of -10 to -4° . As soon as a brown film started to form on the surface of the acid, showing that the persulfides were beginning to decompose, a fresh supply of acid was used. An emulsion of the persulfides was first formed which settled after several hours to form a yellow liquid. This was washed with distilled water in a separatory funnel and dried over phosphorus pentoxide. The material thus obtained is a mixture of the di- and the trisulfides and these may be separated and purified by fractional distillation in quartz apparatus as described by Walton and Parsons. The yield of the trisulfide obtained in this way was about 10% of the total crude persulfides. The crude persulfide mixture and the pure trisulfide react in the same manner so that in most of the work only the crude material was used.

Reactions of Liquid Hydrogen Sulfide on Styrene and Amylene.—Ten grams of each of these two bodies were sealed in glass tubes with four cubic centimeters of liquid hydrogen sulfide at the temperature of an ether-solid carbon dioxide bath, and allowed to come to room temperature and stand for two weeks. In neither case was any reaction apparent. When the hydrogen sulfide was allowed to evaporate, the styrene and amylenes were recovered unchanged. This shows the stability of these two unsaturated bodies toward liquid hydrogen sulfide and indicates that any reduction or oxidation brought about by the persulfides could not be due to the hydrogen sulfide formed by the decomposition of the persulfide.

⁵ Fenton, *J. Chem. Soc.*, 65, 899 (1894); 67, 774 (1895).

⁶ Walton and Jones, *THIS JOURNAL*, 38, 1956 (1916).

⁷ Walton and Parsons, *ibid.*, 43, 2546 (1921).

Reaction of Hydrogen Persulfides with Styrene.—To find the effect of the persulfides on a double bond between two carbon atoms styrene was treated with some of the crude persulfide. Twenty grams of the crude sulfide was added to forty grams of styrene dissolved in 180 cc. of benzene. The mixture became warm and was colored first yellow and then green and finally became milky. After standing for a few hours the mixture was refluxed at the temperature of boiling benzene for six hours. Upon cooling, crystals of sulfur were precipitated, leaving a clear yellow solution. Ammonia gas was passed through the solution for five minutes and a heavy orange precipitate was formed. This was filtered off and discarded and the benzene removed from the filtrate by vacuum distillation. The liquid residue, weighing 42 g., was purified by dissolving in ether and passing ammonia gas into this solution until no more sulfur precipitated. The sulfur was filtered out and the ether evaporated, leaving a clear light yellow liquid. This was heated in a water-bath under a pressure of 30 mm. to remove any unchanged styrene. The ether solution could be changed into a wine colored one by passing ammonia gas into it but no sulfur could be precipitated. The yellow color would return to the solution if either air or illuminating gas was passed into the solution to remove the ammonia. A similar product may be made by adding pure styrene to the persulfide without the addition of a solvent containing the temperature is kept below 40°. An analysis of the liquid for the sulfur content showed 37.44 and 37.40% while the calcd. for the compound $C_8H_8-CH-CH_2$ is 38.12% and for the compound $C_8H_8-CH-CH_2$ is 23.55%. Bloch,

Höhn and Bugge⁸ reported a similar compound but their analysis for the percentage of sulfur was much lower (29.8). This is probably due to the use of $(NH_4)_2S$ in dissolving out the excess of sulfur instead of precipitating it with ammonia gas. Undoubtedly some of their compound was decomposed and part of the sulfur they removed came not from free sulfur but from the chemically combined sulfur.

The material could not be distilled as it decomposes to give styrene and sulfur. It does not add bromine and is stable toward hypochlorites and alkalis. Concentrated nitric acid oxidizes it completely to water, carbon dioxide and sulfuric acid. A molecular weight determination gave a value of 252, showing that some polymerization had occurred. The persulfide in this reaction has acted as an oxidizing agent, adding sulfur at the double bond. There was no evidence of there being any reducing action to form ethylbenzene.

Reaction of the Persulfides with Amylene.—As another compound containing a double bond between two carbon atoms amylenes, the unsymmetrical methylethylethylene, was used. Both the pure trisulfide and the crude mixture of the persulfides gave the same reaction with the body.

Ten grams of the pure trisulfide was added to 50 cc. of amylenes. No reaction took place at first but after a few hours standing a compound with an odor similar to a mercaptan was formed. After a week the crystals of sulfur which had formed were filtered off and the greenish yellow liquid was heated in a water-bath under a vacuum but nothing was distilled over. When the liquid was treated with ether, sulfur was precipitated in a large amount. On passing ammonia gas into the ether solution a colloidal orange precipitate formed which after standing for several days settled to a clear liquid with a strong odor of a mercaptan. After removing the ether the light yellow liquid did not add bromine, and was stable toward hypochlorites, alkalis and dilute acids. An analysis of this liquid for the per cent. of sulfur showed 45.38 and 44.84 while the theoretical for the compound $C_8H_{10}S$ is 31.37% and for $C_8H_{10}S_2$ is 47.76%. The boiling point of the liquid is 132–135° under a pressure of 8 mm. although different preparations of the liquid vary

⁸ Bloch, Höhn and Bugge, *J. prakt. Chem.*, **82**, 473–485 (1908).

some from this. The liquid is probably not entirely pure but contains some of both the mono- and di-sulfur compound. Here again the action of persulfides is one of oxidation or addition of sulfur at the double bond.

Reaction of the Persulfides with Azobenzene.—As hydrogen peroxide forms azoxybenzene from azobenzene the similar reaction between the persulfides and azobenzene should give a thioazoxybenzene. When benzene solutions of the persulfides and the azobenzene were mixed, no reaction was apparent for an hour. After standing for three hours and then refluxing at the temperature of boiling benzene for twenty minutes and cooling, crystals of sulfur were deposited. The sulfur was filtered out and the benzene removed by distillation. The solid residue was purified by recrystallizing several times from 95% ethyl alcohol. The crystals thus obtained melted at 126° and a mixed melting point determination showed it to be hydrazobenzene. No sulfur was added at the double bond as in the case of the peroxide on azobenzene.

Reaction of the Persulfides with Benzenediazonium Chloride.—In order to observe the effect of the persulfides on a triple bond between two nitrogen atoms the compound benzene diazonium chloride was used. If the dry material is added to the liquid persulfide at room temperature the reaction is of explosive violence. If the solid is cooled and the sulfide added slowly the reaction is somewhat slower and by dissolving in either carbon disulfide or benzene it becomes quite mild. From a carbon disulfide solution a large amount of hydrogen chloride is liberated, a red liquid forms, and a buff colored solid with the odor of a mercaptan remains. This solid is explosive on heating, showing that some of the diazonium compound still remains unacted upon. The difficulty in studying this reaction is in finding some medium which will dissolve both the persulfide and the diazonium chloride. The former dissolves quite readily in organic solvents but the latter being of the nature of a salt is insoluble in such solvents. This reaction is being studied further.

Conclusions

1. While liquid hydrogen sulfide does not react with either styrene or amylene the persulfides do react, adding the group —S—S— at the double bond. This reaction is essentially one of oxidation similar to the action of hydrogen peroxide.

2. The persulfides form hydrazobenzene from azobenzene, which is essentially a reducing reaction and differs from the reaction with hydrogen peroxide, .

3. With diazonium chloride the reaction with the persulfides is so vigorous that it takes place with explosive violence unless it can be regulated by the use of a solvent such as carbon disulfide.

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