

meet this need,¹ and the results relating to gas purification thereby obtained are given below. All samples for analysis were taken under steady-state conditions.

Experimental

Oxygen Removal by Hot Copper.—In repeated attempts, no oxygen could be detected by this method in hydrogen passed at 110 cc./min. through a fused silica tube (diameter 7 cm., length, 22 cm.) filled with copper turnings at 600°. (The glass purification train, in which all joints were sealed, also contained sodium hydroxide pellets to remove hydrogen sulfide.)

With the copper at 230° and other conditions the same, the purified hydrogen contained 0.0017% oxygen by volume.

Oxygen removal in this way from nitrogen is facilitated by adding hydrogen so that the end product is water, not copper oxides.² Oxygen determinations were carried out on nitrogen thus purified in a pilot plant, the copper being near 400°. In one case, 0.0009% oxygen was found in the purified gas, which contained 25% by volume of hydrogen. In a second installation, the oxygen content was 0.0002% at the exit of the purifier with only 3% hydrogen present. Higher purity was not required in the pilot plant, and these oxygen contents probably are not valid lower limits.

Contamination in Transit.—The oxygen content of "oxygen-free" hydrogen being passed through about 10 feet of rubber tubing jumped to 0.0026%. At a distance from the purifier in a steel system believed to be tight, the second nitrogen mentioned above contained 0.0035% oxygen.

These data have been presented in the hope that some one will use the analytical method in a systematic study of oxygen removal, for it is capable of giving quantitative results on gases that could well appear oxygen-free by other quantitative methods.

(1) Winslow and Liebhafsky, *Ind. Eng. Chem., Anal. Ed.*, **18**, 565 (1946).

(2) So long as the metal is exposed, oxygen removal by copper at red heat can be very effective though repeated contact appears to be necessary for complete removal; v. Moser, "Die Reindarstellung von Gasen," Ferdinand Enke, Stuttgart, 1920, p. 79. When, owing to oxide formation, diffusion has become the rate-determining step oxygen removal necessarily suffers. There is no doubt that the addition of hydrogen facilitates the process. Hydrogen seems first to have been used for this purpose by Hulett, *This Journal*, **27**, 1415 (1905) who, however, used essentially an oxyhydrogen torch to prepare nitrogen from air.

Though equilibrium favors the formation of ammonia under our experimental conditions, the rate of formation is almost certainly negligible since the homogeneous reaction is too slow and since copper at 400° does not adsorb appreciable nitrogen; v. Frankenburger, *Z. Elektrochem.*, **39**, 276 (1933), and Dew and Taylor, *J. Phys. Chem.*, **31**, 281 (1927).

RESEARCH LABORATORY
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The Reaction of Sodium 1-Dodecanesulfinate with Mercuric Chloride¹

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Reports² indicate that German investigators thought their activated Buna-S recipes called Redox formulas were dependent in part on the presence of small amounts of sulfinic acid salts in

(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) Swann and Elias, Off. Pub. Bd., U. S. Dept. Commerce, Report PB 1636, 1945.

their emulsifier, Mersolat. In seeking methods of identifying and determining alkylsulfinic acids in the presence of alkylsulfonic acids, we have investigated the reaction of sodium 1-dodecanesulfinate with mercuric chloride. The formation of arylmercury chlorides from arylsulfonates by heating with aqueous mercuric chloride is well known³ although the analogous reaction of alkylsulfonates has apparently not been reported. We have found that sodium 1-dodecanesulfinate does react readily with mercuric chloride in boiling aqueous solution to give 1-dodecylmercury chloride in 49% yield. Thus, the reaction is demonstrated to be a useful one in the aliphatic sulfinic acid series.

Experimental

Sodium 1-Dodecanesulfinate.—This salt was prepared by the method of Allen.⁴ The crude salt showed at least 74% sulfinate content on potentiometric titration in acetic acid with sodium nitrite.^{5,6} An anhydrous sample of the salt was also prepared and analyzed both for the elements and for sulfinate content.

*Anal.*⁷ Calcd. for C₁₂H₂₅SO₂Na: C, 56.24; H, 9.83; Na, 8.97. Found: C, 56.30; H, 9.99; Na (as Na₂SO₄), 8.88.

The anhydrous material showed over 94% sulfinate by potentiometric titration.⁶

1-Dodecylmercury Chloride.—Using a modification of the procedure of Whitmore, Hamilton and Thurman,⁸ 1 g. (0.0037 mole) of pure dry sodium 1-dodecanesulfinate was added with mechanical stirring to a boiling solution of 50 cc. of water and 1 g. (0.0037 mole) of mercuric chloride. A flocculent white precipitate formed immediately and the stirring and heating were continued for two hours. The insoluble product was separated from the reaction mixture by filtration, dried and extracted three times with 20-cc. portions of boiling benzene. Evaporation of the solvent from the filtered benzene extracts gave 0.73 g. (0.0018 mole, 49.3% of the theoretical amount) of crude 1-dodecylmercury chloride, m. p. 106–111°. After crystallization twice from benzene and once from ethanol the product melted at 113–113.5°.

*Anal.*⁷ Calcd. for C₁₂H₂₅HgCl: C, 35.55; H, 6.21. Found: C, 35.73; H, 6.51.

Meals⁹ has reported the melting point of 1-dodecylmercury chloride as 114–114.5°.

(3) Connor in Gilman's "Organic Chemistry," 2nd ed., Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 918.

(4) Allen, *J. Org. Chem.*, **7**, 23 (1942).

(5) Koenigs, *Ber.*, **11**, 615 (1878).

(6) We are indebted to Dr. H. A. Laitinen, Mrs. Nancy Fritz and Mrs. Rita Leubner for these titrations.

(7) Microanalyses were done by Mr. H. S. Clark, Illinois State Geological Survey.

(8) Whitmore, Hamilton and Thurman, "Organic Syntheses," 2nd ed., Coll. Vol. 1, John Wiley and Sons, Inc., New York, 1941, p. 519.

(9) Meals, *J. Org. Chem.*, **9**, 211 (1944).

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Black "Soap" Films of Fatty Acids in Sulfuric Acid

BY LEON McCULLOCH

Bubble-films of soapy water become thinner on aging, passing through a series of color spectra,

until a spot becomes so thin as to be colorless or "black" when it usually breaks.

The higher fatty acids dissolve in cold concentrated sulfuric acid to give soap-like solutions. They are soap-like in that they foam and give bubble-films of great stability. This can be demonstrated as follows:

Into a 125-ml. Erlenmeyer flask place about 0.02 g. of stearic acid, keeping the neck of the flask clean, and pour in 20 ml. of 95% sulfuric acid. Seal the neck of the flask with an oxygen torch. The stearic acid solution is colorless when pure, and darkens slowly only after many days. (Apparently there is no sulfonation of the stearic acid at first. Experiments indicate that the fatty acid is recovered when the sulfuric acid is poured into water.)

When the flask is shaken the solution foams, giving a foam which persists for an hour or more. Occasionally a horizontal film remains across the flask out of contact with other bubbles. Such a horizontal film sometimes remains permanent for days, making it possible to observe the changes which occur.

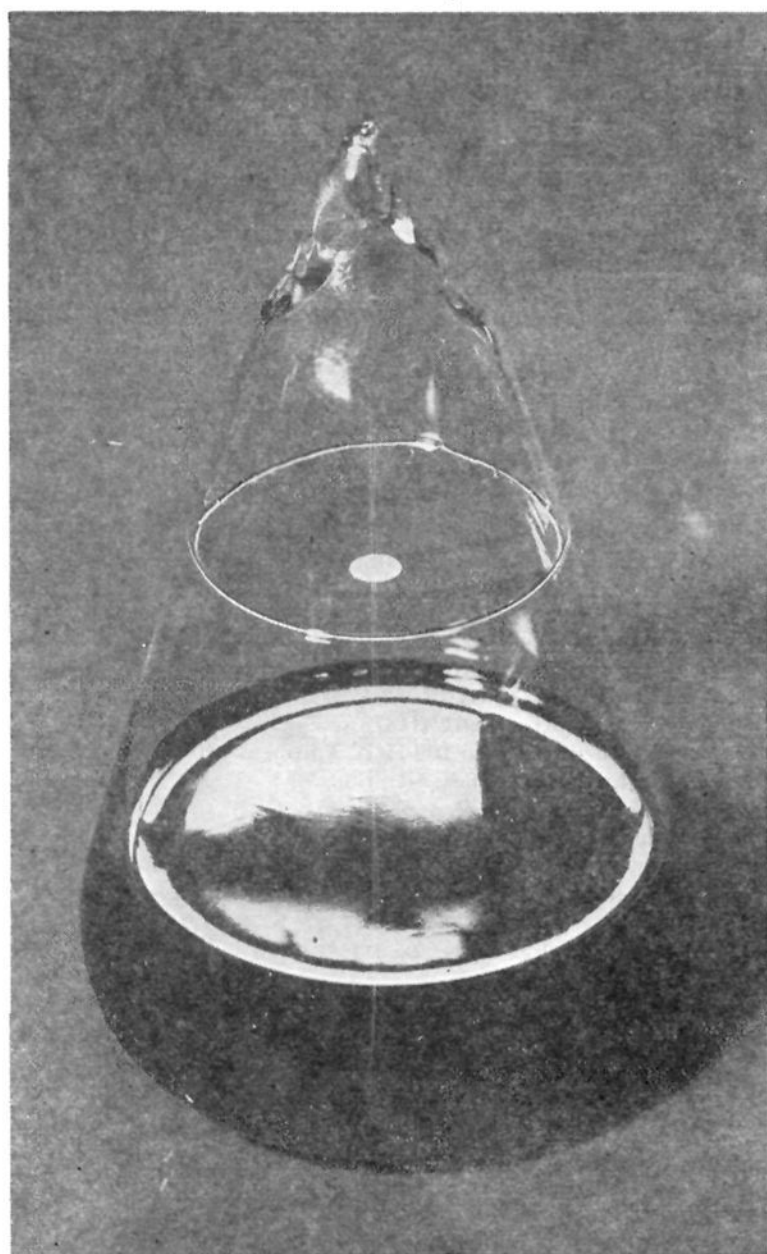


Fig. 1.—A black "soap" film of stearic acid in sulfuric acid and its suspended droplet.

Within a few minutes bands of interference colors appear arranged in rings. Soon the rings contract and there remains a colorless or "black" film, too thin to show interference color. The colored rings finally disappear at the center, into a disk-shaped droplet suspended by the colorless film. Such films within this flask may be about two inches in diameter. In the course of a few days a film may travel slowly upward because of the conical shape of the glass wall. The suspended liquid disk swings with great freedom when the flask is moved. If the glass at the edge of the film is warmed at one spot, as by contact of a finger, little iridescent "droplets" with streamers push out from the edge and pass to the center, where they become absorbed into the colorless droplet. These minute colored "droplets" move with great ease under the influence of gravity, showing the fluidity of these films. The color changes in these films are sharply discontinuous, as in bubbles of soap in water. These "black" films resemble the extremely stable black films of soap with glycerol prepared by Sir James Dewar, which showed the same movement of droplets. One of his black bubbles was 40 cm. in diameter and weighed about 50 milligrams, making the average thickness 150 Å. The minimum black bubble thickness has been estimated as 50 Å. or two molecular layers.¹

(1) Sir James Dewar, "Soap Bubbles of Long Duration," *J. Franklin Inst.*, **188**, 713-749 (1919); N. K. Adqm, "The Physics and Chemistry of Surfaces," 3rd ed., Oxford University Press, London, 1941.

WESTINGHOUSE RESEARCH LABORATORIES

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RECEIVED JULY 22, 1946

Preparation of the Methylfluorosilanes

BY ARTHUR E. NEWKIRK

The use of zinc fluoride to replace, by fluorine, a chlorine atom attached to silicon has been reported by Schumb and Gamble¹ who made hexafluorodisilane from hexachlorodisilane, and by Emeleus and Wilkins² who made ethyl and phenyl fluorosilanes from the corresponding chlorosilanes.

In connection with the investigations of organosilicon compounds in this Laboratory, the methylfluorosilanes have been prepared from the corresponding chloride and zinc fluoride. This method is of interest in view of the discovery by Rochow³ of a convenient method for the preparation of organohalosilanes. Although the fluorinated homologs may also be prepared by this direct method, it is not as convenient because of the difficulties in preparing the necessary organofluorine compounds.

Only the completely fluorinated compounds were obtained as products. Their boiling points were in good agreement with those reported by Pearlson, Brice and Simons,⁴ and by Booth and his

(1) Schumb and Gamble, *THIS JOURNAL*, **54**, 583 (1932).

(2) Emeleus and Wilkins, *J. Chem. Soc.*, 454 (1944).

(3) Rochow, *THIS JOURNAL*, **67**, 963 (1945).

(4) Pearlson, Brice and Simons, *ibid.*, **67**, 1769 (1945).