by McTaggart and by Lenard and his students. Since the cohesion, and therefore also the surface tension, of water is probably largely due to the electric forces between the dipoles, a disturbance of the normal electric distribution may cause a diminution of the surface tension.

As the solution becomes more concentrated (about 0.01 N or above), the mutual attraction between ions of opposite polarity becomes stronger than the forces between the ions and the water molecules and causes negative adsorption and an increase in surface tension in the manner discussed by Onsager and Samaras. We may conclude, therefore, that the treatment of Onsager and Samaras is over simplified and thus fails to give a complete and accurate result.

Summary

1. A modification of the capillary rise method of measuring the surface tension of solutions relative to that of the pure solvent, which makes it a differential method and substantially improves the accuracy of the results, is described.
2. The relative surface tension of aqueous solutions of potassium chloride, potassium sulfate, and cesium nitrates has been determined at 25° from 0.0001 N up to 3, 1 and 0.1 N, respectively, and of sucrose solutions from 0.0002 molar up to 0.005 molar.
3. These three salts all increase the surface tension of water from 0.01 N up to the highest concentration studied and give surface tension–concentration curves which are typical of strong electrolytes that are capillary inactive and negatively adsorbed in the surface layer.
4. At extreme dilutions (below about 0.006 N) all three salts cause a decrease in surface tension and are, therefore, positively adsorbed in the surface layer at concentrations below that giving the minimum (about 0.001 N) of the surface tension.
5. Sucrose gives a linear surface tension–concentration curve with no change in the sign of the slope at extreme dilutions.
6. The data are not in accord with the Onsager–Samaras equation for the surface tension as a function of the concentration.
7. The influence which causes diminished surface tension and positive adsorption at extreme dilution is ionic in character and probably due to an interaction between the ions and polarized water molecules.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. III. The Vapor Phase Fluorination of Hexachloroethane

BY WILLIAM T. MILLER, JR., JOHN D. CALFEE AND LUCIUS A. BIGELOW

Previous papers in this series[1] have described the fluorination of certain organic compounds dissolved in carbon tetrachloride, using, however, an open type of generator as the source of the halogen. This earlier procedure had two disadvantages, since the fluorine produced was contaminated with other gases, and also reacted to a considerable extent with the solvent. More recently, we have designed a new closed generator[2] capable of delivering fluorine 94–99% pure, and in addition have considered it desirable to avoid the use of solvents altogether. The present paper describes the vapor phase fluorination of hexachloroethane over a copper gauze catalyst. It is probable, of course, that the reaction took place at the surface of the metal, which acquired a thin coating of copper salts during the process, and cupric fluoride may have been the immediate fluorinating agent. However, the change did not occur rapidly at ordinary temperatures, and the gauze was not greatly attacked over a considerable period of time, even when heated. So far as the writers are aware, no similar, direct, vapor phase fluorination of an organic compound containing more than one carbon atom has as yet been reported, in which definite chemical individuals have been formed.

The procedure employed in this fluorination was exceedingly simple. The sample was placed in a horizontal tube, between two copper gauze rolls, suitably heated. The fluorine, diluted with nitrogen, was introduced at the center of one of

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(1) THIS JOURNAL, 55, 4614 (1933); 56, 2773 (1934).

(2) Miller and Bigelow, *ibid.*, 58, 1985 (1936).

these rolls, in a manner somewhat similar to that described by Fredenhagen and Cadenbach.[3] Under appropriate conditions, a perfectly quiet, continuous reaction occurred, and the products were condensed at reduced temperatures. After purification and rectification in a Podbielniak still, the main product, which was *sym*-difluorotetrachloroethane, boiled at 92°, and melted at 24–25°, corresponding closely to the values previously reported by Locke, Bride and Henne,[4] who obtained the compound by another method. The yield of the pure haloethane was approximately 20%. A further study of this and similar reactions is contemplated.

Experimental

The fluorination was carried out in a Pyrex glass tube, diameter 2.8 cm., length 75 cm. The gas was introduced through a 6.3-mm. copper tube, closed at the end, but perforated irregularly along the last 4 cm. of its length. The perforations were surrounded by a tight roll of clean 20-mesh copper gauze, 6 cm. in length, which fitted snugly into the glass tube. The charge was placed in the 10-cm. space immediately following the gauze, and the total distance occupied by both of these was surrounded, on the outside, by a sliding metal air bath. Beyond the charge, the reaction tube was filled for a length of 25 cm. with another roll of gauze, surrounded by a second, independent air-bath. In this very simple set up, connections were made with ordinary stoppers, wrapped with copper foil and painted with Ceresin wax.

In operation, the tube was first swept out with nitrogen, and the second gauze heated to 160°. Then the fluorine, diluted with nitrogen in the ratio of 1:1.6, was passed in at a rate corresponding to a current of 3.8 amp. through the generator (roughly 1.5 liters per hour). Finally the first gauze was heated gradually to 125°, when a continuous reaction took place, the fluorine being always in excess. The products were condensed as a mixture of liquid and solid in a trap at about −40°. On warming to room temperature there remained a clear liquid, which was formed at the rate of about 1.6 g. per hour. For each 10 g. of hexachloroethane utilized, approximately 7.4 g. of this liquid was produced. The crude material was dissolved in ether, washed with 5% sodium carbonate solution and dried over calcium chloride, during which process a considerable portion of it dissolved. The ether solution was then fractionated directly in a Podbielniak still. The pure product, b. p. 92°, m. p. 24–25°, was obtained in approximately 20% yield. According to Locke, Bride and Henne[4] *sym*-difluorotetrachloroethane boils at 92.8° and melts at 24.7°.

Anal. Calcd. for $C_2F_2Cl_4$: F, 18.6; Cl, 69.6; mol. wt., 204. *Found:* F, 18.5, 18.7; Cl, 69.3, 69.5; mol. wt., 209, 210.

The fluorine analyses were made by the Willard and Winter method, after decomposing the sample in a Parr bomb.

When tetrachloroethylene, b. p. 119°, was fluorinated in a similar manner, with both gauzes at 130°, and the haloethylene in excess, *sym*-difluorotetrachloroethane, boiling at 92°, was also produced, in about 20% yield, and further identified by means of a mixed melting point. Considerable substitution took place at the same time, however. In this case, the sample was introduced by passing nitrogen through the refluxing liquid, heated in a bath at 135°.

Summary

Hexachloroethane has been fluorinated directly, in the vapor phase over a copper gauze catalyst. A 20% yield of pure *sym*-difluorotetrachloroethane was obtained. Tetrachloroethylene, under similar conditions, yielded the same product.

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(3) Fredenhagen and Cadenbach, *Ber.*, **67**, 928 (1934).

(4) Locke, Bride and Henne, THIS JOURNAL, **56**, 1726 (1934).