products formed in the oxidation–reduction process, and are also absolutely free from any drift throughout, such small deviations from the theoretical as encountered here cannot be accorded any significance. The latter requirement is especially important when dealing with compounds such as reduced phthiocol which is extremely susceptible to traces of oxygen at alkaline *p*H values. Since, however, the data here analyzed have met these requirements rigidly, I am inclined in agreement with Hill to consider the deviations from the theoretical encountered in the unpoised region of the curve as an indication that a change in slope of the curve has begun at least in the region of *p*H 10.5.

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The Action of Elementary Fluorine on Organic Compounds. IV. The Vapor Phase Fluorination of Ethane[1]

BY JOHN D. CALFEE AND LUCIUS A. BIGELOW

In the third paper of this series[2] we have described the vapor phase fluorination of hexachloroethane over a copper gauze catalyst, with the production of *sym*-difluorotetrachloroethane. Since then this type of catalyst, originally suggested by Fredenhagen and Cadenbach,[3] has been patented abroad;[4] but neither the above-mentioned writers nor the patent specifications have described the substitution of chlorine or hydrogen by fluorine with the formation of definite products of known constitution. Also Ruff[5] has found that fluorine reacts vigorously with fluoroform, with the formation of carbon tetrafluoride and hexafluoroethane, and this observation has been confirmed in part, very recently, by Henne,[6] although details were not given in either case. In view of these considerations, it seemed a logical development to attempt the vapor phase fluorination of a simple saturated hydrocarbon, using a procedure similar to that which we had developed before.

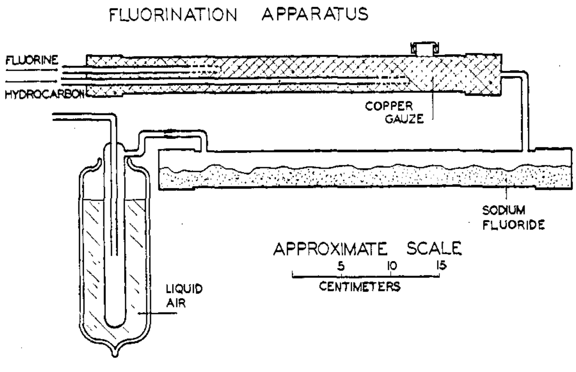

Fig. 1.—Apparatus for the vapor phase fluorination of ethane.

Accordingly, we permitted ethane and fluorine to mingle within the meshes of a copper gauze coil, when a perfectly quiet, continuous reaction occurred. The gaseous products were freed from hydrogen fluoride, and condensed by means of liquid air. After preliminary purification, the material was distilled through a low temperature Podbielniak still at atmospheric pressure, making use of a simplified form of the excellent technique recently described by Booth and Bozarth.[7] At first there came over a considerable fore fraction (4–5 cc.) boiling at about −125° and remaining liquid at −183°, which was clearly carbon tetrafluoride (b. p. −128°). This was followed by two minor fractions, the first (1 cc.) at −88° (ethane, b. p. −89°) and the second at −84° (fluoroform, b. p. −84.4°,[5] −82.2°).[6] Then came the main product (5–6 cc.) boiling at −78° and melting at −101°, which constituted roughly a third of the material fractionated. This was unquestionably hexafluoroethane, C_2F_6 (b. p. −78.3°, m. p. −101° according to Ruff).[8] Finally a small but definite fraction (1.0–1.5 cc.) was obtained at −48 to −50°, which we believe probably consisted of methylfluoroform, CH_3CF_3 (b. p. −46.7° according to Henne and Renoll),[9] although it could possibly have been methylene fluoride CH_2F_2 (b. p. −51.6° according to Henne).[10] Both are resistant to hydrolysis. A more complete discussion of these, and the other substances which were formed at the same time, will be reserved for later papers in this series.

From these results it appears to be established definitely that simple aliphatic hydrocarbons containing more than one carbon atom can be fluorinated directly in the vapor phase, with the formation of chemical individuals of known constitution, other than carbon tetrafluoride.

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[1] Presented in part before the Organic Division at the Chapel Hill Meeting of the American Chemical Society on April 13, 1937.

[2] Miller, Calfee and Bigelow, THIS JOURNAL, **59**, 198 (1937).

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

[4] British Patent 452,656; *C. A.*, **31**, 1042 (1937).

[5] Ruff, *Ber.*, **69**, 299 (1936).

[6] Henne, THIS JOURNAL, **59**, 1200 (1937).

[7] Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

[8] Ruff, *Z. angew. Chem.*, **46**, 739 (1933).

[9] Henne and Renoll, THIS JOURNAL, **58**, 889 (1936).

[10] Henne, *ibid.*, **59**, 1400 (1937).

Experimental Part

The apparatus which we have used for the fluorination reaction was very simple and is illustrated to approximate scale in Fig. 1. The reaction tube was made from ordinary 2.5 cm. brass pipe, completely filled with 20-mesh copper wire gauze rolls, and fitted with a blow-off cap, which, in practice, was not required. The fluorine and the hydrocarbon entered through perforated 6.3-mm. copper tubes, each wrapped with strips of the gauze, and the halogen was introduced ahead of the other gas. In actual operation, two tubes filled with sodium fluoride were used instead of the one shown, as an added precaution. Also, the exit tube from the liquid air trap was provided with a T, through the side-arm of which a current of nitrogen was kept flowing, in order to prevent air from being sucked back into the apparatus. Any oxygen in the gas mixture was found to cause explosive reactions, and a similar result has been observed, with other substances, when the metal screen was omitted.[3]

In a typical run, the apparatus was first swept out with fluorine, which continued to flow at a rate corresponding to a current of 5 amperes through the generator,[11] or about 2 liters per hour. Then commercial ethane gas was introduced through a bubble-counter at a rate such that the estimated ratio by volume of halogen to hydrocarbon was 3:2. The products were passed over sodium fluoride, which absorbed quantitatively the hydrogen fluoride which had been formed, and finally condensed by means of liquid air.

The operation was continued for eighteen hours, and the condensate, which was a light yellow mixture of liquid and solid, was formed at the rate of nearly 1 cc. per hour. During this time the reaction tube warmed gradually to about 50°. The product was successively allowed to boil, frozen, and exhausted six times to remove dissolved fluorine, and then allowed to bubble through a 5% aqueous solution of potassium hydroxide, which dissolved approximately one-fourth of the sample. This procedure was carried out in order to minimize the attack on the mercury in the manometers. The gas was passed over Drierite, then over sodium fluoride, and finally distilled into the Podbielniak–Booth apparatus and fractionated, with the results which have been described in a preceding paragraph.

Summary.—Ethane has been fluorinated with elementary fluorine in the vapor phase over a copper gauze catalyst and by a continuous process. Hexafluoroethane was formed in good yield, together with carbon tetrafluoride, and a smaller amount of a product which was presumably methylfluoroform.

[11] Miller and Bigelow, THIS JOURNAL, **58**, 1585 (1936).

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Polymerization of Isoprene

BY WILLIAM H. CARMODY AND MARIE O. CARMODY

Earlier work has shown that when pure isoprene is polymerized with aluminum chloride two types of polymers are formed. The higher polymers occur in larger amounts and are insoluble; the lower polymers are soluble and occur in smaller quantity.[1] Prolonged standing of pure isoprene in contact with catalyst invariably gives the above products. Olefins, nitrobenzene, ethyl acetate, or in general a mutual solvent for both isoprene and catalyst were shown to be necessary to influence the formation of the two types of polymers.[2] The soluble isoprene polymer showed a molecular weight of 550–650 in 1% benzene solution; much higher values are probable for the insoluble polymer.

This article describes a new experimental procedure which forms all soluble polymer from pure isoprene, without the assistance of a mutual solvent as indicated above. It is now possible to polymerize isoprene and obtain distinctly new results.

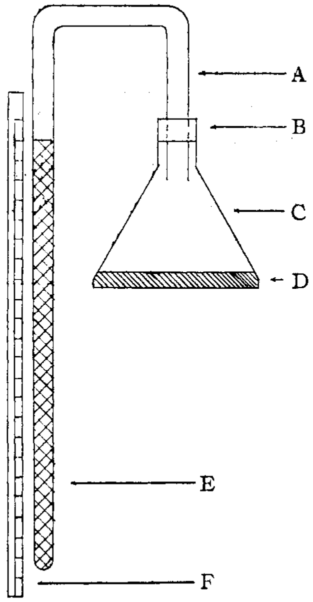

Fig. 1.— A, 5-mm. Pyrex tube; B, lacquered cork; C, 100 cc. flask; D, aluminum chloride; E, isoprene; F, graduated scale.

Figure 1 illustrates the apparatus for carrying out the polymerizations. One end of a sealed inverted U-tube is filled with isoprene; the other open end communicates with a container holding aluminum chloride. Isoprene vapor fills the system, impinges on the catalyst, is polymerized, and gradually the entire mass of isoprene vaporizes and is polymerized. A graduated scale indicates the rate at which liquid isoprene is vaporized

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[1] Thomas and Carmody, THIS JOURNAL, **54**, 2480 (1932).

[2] Thomas and Carmody, *ibid.*, **55**, 3854 (1933).