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).

Chemical Laboratory
Duke University
Durham, N. C.

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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.

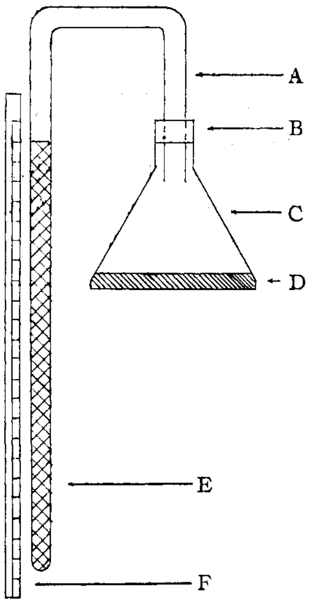

Fig. 1.— A, 5-mm. Pyrex tube; B, lacquered cork; C, 100 cc. flask; D, aluminum chloride; E, isoprene; F, graduated scale.

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).

into the reaction flask. This rate of reduction in volume is related definitely to the rate of polymerization of isoprene. Other experiments in which catalyst was omitted showed no change in the level of the meniscus; experiments in which the U-tube was open to the air showed complete evaporation of the isoprene outward in three and a half days. These facts show that the aluminum chloride determines the evaporation rate. The isoprene chamber and catalyst flask were maintained at 24–26° for a period of one thousand hours. Readings were taken at intervals, the percentage polymerized was calculated based on the original length of the liquid isoprene column, and the flask was shaken at intervals to keep the catalyst in a finely divided state. At the end of the reaction less than 3% remained as liquid isoprene polymer in the side arm. This was viscous, high boiling and smelled of terpenes. The catalyst mass was disintegrated, neutralized with ammonia and filtered. The clear filtrate was distilled at a temperature of 200° at 2 mm. This gave the soluble resin. The cake on the filter was completely soluble in dilute hydrochloric acid, indicating absence of insoluble polymer and the presence of inorganic material.

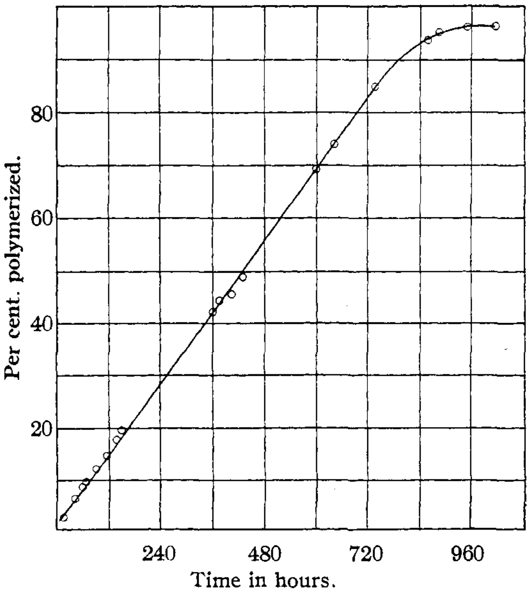

Fig. 2.

Figure 2 indicates the rate of polymerization and vaporization of isoprene. Table I is a relative comparison of the results obtained from both liquid[3] and vapor phase reaction.

TABLE I

Yields	Vapor phase	Liquid phase
Soluble polymer, %	98	12
Insoluble polymer, %	0	84
Molecular weight of soluble polymer in benzene	1300	600
Acid value	0.7	0.4
Iodine value	176	202

Summary.—Vapor phase polymerization of isoprene produces only soluble polymer; insoluble polymer is not formed. The molecular weight of this new polymer is approximately 1300. The molecular weight of the soluble polymer is approximately double that obtained by the usual liquid phase polymerization.

MT. LEBANON
PITTSBURGH, PENNA.

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

Preparation of *p*-Phenyltriphenylcarbinol, and the Existence of a Metastable Form

BY DANIEL B. CLAPP AND AVERY A. MORTON

p-Phenyltriphenylcarbinol was first prepared by Schlenk[1] from *p*-iododiphenyl, magnesium, and benzophenone. The preparation of this substance according to the method of Morton and Stevens,[2] using sodium instead of magnesium, has proved to be simpler and more economical. The yield of the carbinol is excellent, and *p*-chlorodiphenyl is substituted for the more expensive *p*-iododiphenyl.

In the first experiment, the carbinol was isolated, after three recrystallizations from ligroin, as white, prismatic needles; m. p. 112–113°. The carbinol prepared according to Schlenk melted at 136°. The form melting at 112–113° was shown to be pure by a cooling-curve determination on the melt, and to be a metastable form of *p*-phenyltriphenylcarbinol by its conversion into the higher melting form by heating at 100° for several hours, or by repeated crystallization from high boiling solvents. Also, the metastable form with acetyl chloride gave *p*-phenyltriphenylchloromethane,[1] m. p. 146–147°, and with phenol *p*-hydroxy-*p*′-phenyltetraphenylmethane,[3] m. p. 182°, both derivatives being identical, respectively, with those prepared from the carbinol melting at 136°.

In all subsequent preparations of the carbinol, only the stable high melting form was isolated,

[1] Schlenk, *Ann.*, **368**, 298 (1909).
[2] Morton and Stevens, THIS JOURNAL, **53**, 4028 (1931).
[3] Boyd and Hardy, *J. Chem. Soc.*, 1006 (1929).