trope, b. p. 56.5–56.8° at 760.5 mm., $n^{25}D$ 1.4030, found by comparison with a plot of $n^{25}D$/% composition for known mixtures to contain 75 weight % of lower boiling 1,2-dichloropropene.

Ozonization of the above 1,2-dichloropropene-1 in carbon tetrachloride solution at −15° followed by treatment with boiling water gave a mixture of hydrochloric, formic and acetic acids. Treatment with silver hydroxide precipitated silver chloride, oxidized the formic to carbonic acid, and thus permitted identification by the Duclaux method of the acetate in the filtrate.

The structure of the 1,2-dichloropropene-1 was confirmed by addition of chlorine at 0° in light from a 200-watt clear glass lamp, giving the saturated 1,1,2,2-tetrachloropropane, b. p. 153–155° at 774 mm., $n^{25}D$ 1.4850.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 16, 1948

The Structure of C_3F_6

BY EDMOND G. YOUNG AND WILLIAM S. MURRAY

Studies in this Laboratory involving methods of commercial feasibility for the synthesis of $CF_3CF{=}CF_2$ brought to the fore the question of the proper structure of C_3F_6 as prepared by several methods. In particular, Benning, Downing and Park[1] reported the structure of the C_3F_6 obtained from pyrolysis of "Teflon" tetrafluoroethylene polymer as being a cyclic compound. It is to be noted that Lewis and Naylor[2] report the difficult oxidation of this product to acidic substances which also suggests the cyclic structure.

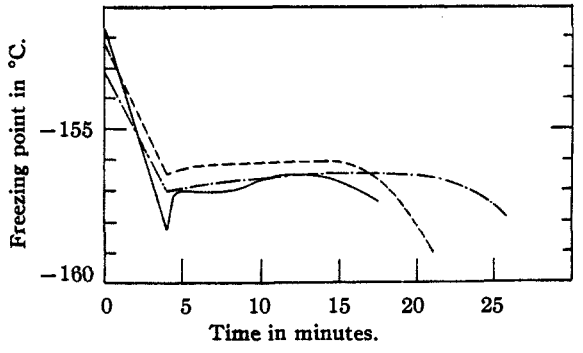

Fig. 1.—C_3F_6 products: ---, pyrolysis product; —·—, dechlorination product; ——, mixed.

It has been the purpose of this work now being reported, to establish the structure of C_3F_6 firmly and to correct any errors which have appeared in the literature.

A sample of C_3F_6 prepared by pyrolysis of tetrafluoroethylene polymer was compared with a sample of C_3F_6 prepared by the dechlorination of $CF_3CFClCF_2Cl$ with zinc and alcohol.[3] The marked similarity of these products is shown in Table I.

TABLE I

Product source	"Teflon" pyrolysis	$CF_3CFClCF_2Cl$ dechlorination
Molecular weight from vapor density	151	153
Boiling point, °C.	− 29.8	− 29.6
Freezing point, °C.	−156.2	−156.5
Mixed freezing point, °C.	156.6	

Not only is the mixed freezing point datum excellent evidence for the identity of these products (see Fig. 1), but also the infrared absorption curves of these two preparations were found to be identical. The curve for C_3F_6 is given in Fig. 2. The maximum at 5.55 microns is a positive indication of the existence of a double bond in the molecule.

Chlorination in light of the two C_3F_6 products (A) from polymer and (B) from $CF_3CFClCF_2Cl$ gave the corresponding dichlorides which were identical to each other and different from the dichloride obtained (C) by chlorination of $H(CF_2)_3$-

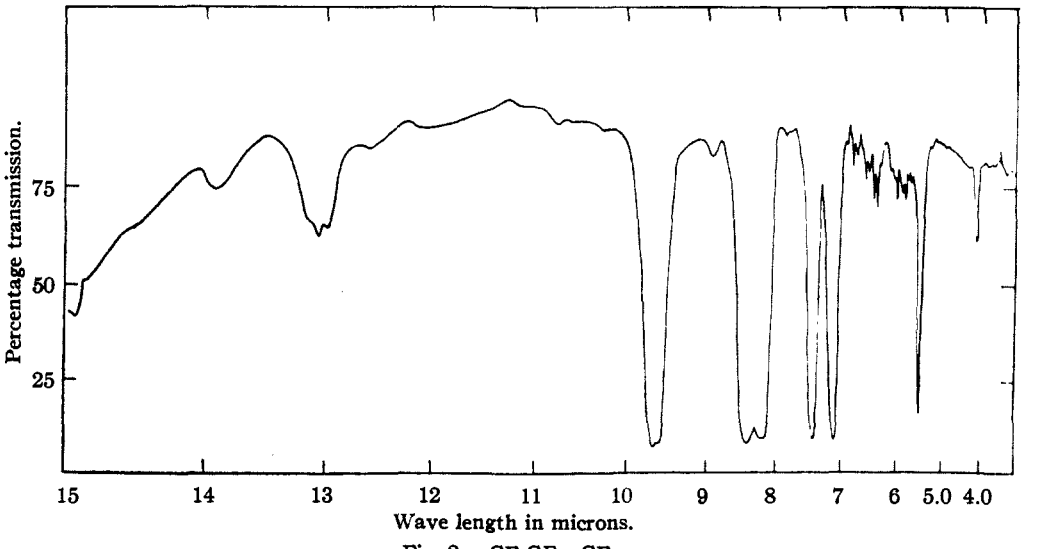

Fig. 2.—$CF_3CF{=}CF_2$.

(1) Benning, Downing and Park, U. S. Patent 2,394,581.
(2) Lewis and Naylor, THIS JOURNAL, **69**, 1968 (1947).
(3) Henne and Waalkes, *ibid.*, **68**, 496 (1946).

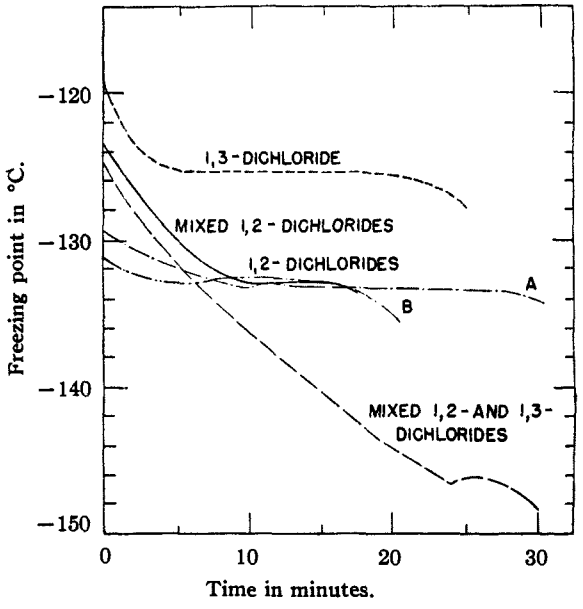

Fig. 3.—$C_3F_6Cl_2$ products.

in Fig. 4 where both A and B are represented by the single solid line.

TABLE II

COMPARISON OF $C_3F_6Cl_2$ PRODUCTS

Product	Molecular weight	Boiling point, °C.	Freezing point, °C.	Mixed freezing point, °C.
A	227.1	34.5	−132.7	−133.0
B	226.1	34.5	−133.3	
C	227.8	35.8	−125.4	−146.5
D	224.8	35.6	−126.3	−126.0

The reactions of the 1,2 and 1,3-dichlorohexafluoropropane with zinc in alcohol likewise differ in the products obtained. Although the 1,2-dichloride gave the original C_3F_6, the 1,3-dichloride gave a C_3F_6HCl which has identical infrared absorption with that of $CF_2HCF_2CF_2Cl$. The statement of Park, *et al.*,[5] that $CF_2ClCF_2CF_2Cl$ reacted with zinc to give a cyclic product must have been based upon the reaction of $CF_3CFClCF_2Cl$ obtained from pyrolysis of tetrafluoroethylene polymer, which at that time was thought to be the

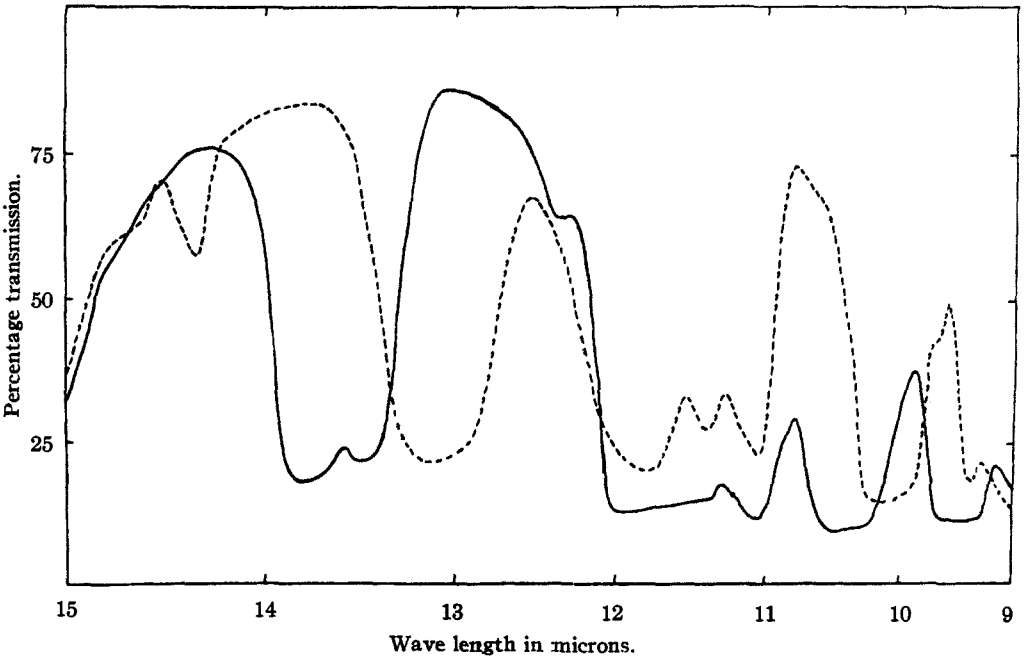

Fig. 4.— ---, 1,3-$C_3F_6Cl_2$; ——, 1,2-$C_3F_6Cl_2$.

Cl[4] and (D) by fluorination of $CFCl_2CF_2CFCl_2$. This is shown by the data given in Table II.

The freezing point curves shown in Fig. 3 not only verify the identity of A and B but also assure that the dichloride from the pyrolysis product of "Teflon" is not the same as the 1,3-dichloride. This is further corroborated by infrared absorption curves of the three $C_3F_6Cl_2$ molecules as shown

(4) Downing, Benning and McHarness, U. S. Patent 2,384,821.

1,3-dichloride, to give $CF_3CF{=}CF_2$ boiling at −30°.

There remains no doubt that C_3F_6 prepared by the pyrolysis of tetrafluoroethylene polymer is $CF_3CF{=}CF_2$ and not $\underline{CF_2CF_2CF_2}$.

JACKSON LABORATORY
E. I. DU PONT DE NEMOURS AND CO.
WILMINGTON, DEL.

RECEIVED APRIL 1, 1948

(5) Park, *et al.*, *Ind. Eng. Chem.*, **39**, 354 (1947).