rectness of the linear model with anti-parallel units which he adopted for the polymer structure. The existence of but one equilibrium, $6HF \rightleftarrows (HF)_6$, with the hexamer a ring, which was found[4] capable of representing the vapor density data, is quite inconsistent with the dipole moment results. The infinitely extended zig-zag chain shown by X-ray analysis[9] to exist in the crystal would, of course, be broken into fragments in the vapor. In the molecular beam indicated by electron diffraction[8] as consisting of these fragments, an appreciable proportion of cyclic structures might have escaped detection and the proportion may actually have been much lower than that existing under the conditions of the dielectric measurements. It is interesting to note that the zig-zag structure indicated for the polymeric chain as compared to a rectilinear structure involves an attractive force between the proton of one hydrogen fluoride unit and negative charge localized as by an orbital in the fluorine of the adjacent hydrogen fluoride unit. In other words, the hydrogen bonding, in this case, though electrostatic, is not merely the undirected electrostatic attraction between the charges of a proton and an anion, as often implied in hydrogen bonding. The existence of both linear and cyclic structures in hydrogen fluoride is consistent with the belief of Bernal and Fowler[19] that both should exist in the liquid and with the conclusion of Pauling[10] that the additional bond obtained by ring formation should increase the stabilities of ring structures over open-chain structures when the degree of polymerization is greater than 5.

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Summary

The dielectric polarization of hydrogen fluoride vapor has been measured as a function of pressure at various temperatures above the normal boiling point of 19.4°. The apparatus employed has been described, and the errors due to adsorption of the hydrogen fluoride on the condenser walls have been shown to be unimportant. In the region of temperature and pressure where no molecular association occurs, a dipole moment value identical with that previously found in this laboratory has been obtained. At lower temperatures and higher pressures the experimental results show conclusively that a very considerable fraction of the associated molecules in the vapor state exists in various linear structures of large dipole moment, and that the average degree of association increases rapidly with increasing pressure or decreasing temperature. Further analysis of the data indicates that cyclic structures also exist in equilibrium with the chains, and that the former tend to increase in relative proportion with increase in pressure and decrease in temperature.

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[19] Bernal and Fowler, *J. Chem. Phys.*, 1, 515 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Perfluorinated Olefins

BY ALBERT L. HENNE AND THOS. H. NEWBY

The synthesis of perfluorinated ethylene and its polymerization to commercial TEFLON, $(CF_2)_n$, have become industrial processes; efforts are now directed at the synthesis of other fully fluorinated olefins in order to study their polymerization characteristics and their ability to copolymerize with $CF_2{=}CF_2$. We report here experiments toward the preparation of $CF_3CF{=}CF_2$, $CF_3CF{=}CFCF_3$, and $CF_3CF_2CF{=}CF_2$.

Synthesis of $CF_3CF{=}CF_2$

Perfluorinated propylene has been prepared by us before, but by a sequence which has too many steps for industrialization.[1] To simplify, we have subjected the easily available[2] $CCl_3CClFCCl_3$ to fluorination with antimony fluoride in the standard way, and have obtained in one step a 70% yield of $CF_2ClCFClCF_2Cl$, from which zinc in alcohol yielded $CF_2ClCF{=}CF_2$ almost quantitatively. From this olefin, it was expected that "allylic" fluorination[3] would easily yield the desired perfluorinated propylene, but this did not appreciably succeed because an allylic rearrangement took place which gave $CF_3CF{=}CClF$ instead of the desired product. The course of the rearrangement was evident from the facts that the rearranged olefin differed from the known[3] $CF_3CCl{=}CF_2$, and that its alkaline oxidation[4] yielded nothing but trifluoroacetic acid.

The desired synthesis was, however, completed as follows. The rearranged compound accepted a mole of chlorine to give the known[1] $CF_3CFClCFCl_2$, which antimony fluoride transformed into the known[1] $CF_3CFClCF_2Cl$. Dechlorination with zinc gave the desired perfluorinated propylene. The sequence is thus a simplified laboratory preparation, but is still too complex for industrial application.

The rearrangement reminded us of a similar case which could not be explained at the time. A

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[1] Henne and Waalkes, THIS JOURNAL, 68, 496 (1946).

[2] Henne and Haeckl, *ibid.*, 63, 2692 (1941).

[3] Henne, Whaley and Stevenson, *ibid.*, 63, 3478 (1941).

[4] Henne, Alderson and Newman, *ibid.*, 67, 918 (1945).

sample of $CF_2=CFCFCl_2$ had been supplied by Dr. W. T. Miller of Cornell University with a request that it be "allylically" fluorinated to $CF_2=CFCF_3$. The operation failed to go further than C_3F_7Cl. The physical properties of this heptafluoride were the same as those of $CFCl=CFCF_3$ made by chlorine removal from $CFCl_2CFClCF_3$, as well as those of the rearranged product mentioned above.

Preparation of $CCl_3CFClCCl_3$.—Chlorine was bubbled through 250 ml. of $CH_3CFClCH_2Cl$ in ultraviolet light until the refractive index no longer increased (one week). After washing, neutralizing and drying, vacuum distillation gave 53% of good $CCl_3CFClCCl_3$, b. p. 95° at 9 mm., *n*D 1.5194 at 20°, and 47% of incompletely chlorinated material which was successfully rechlorinated.

Preparation of $CF_2ClCFClCF_2Cl$.—In a steel vessel, 216 g. (1.2 mole) of antimony trifluoride was combined under pressure with 44 g. (0.62 mole) of chlorine. This was then heated with 160 g. (0.53 mole) of $CCl_3CClFCCl_3$ at 225° for two hours, then at 150° overnight. The organic material was distilled from the bomb then steamed, to give 110 g. of material *n*D 1.358 at 20°. Fractional distillation gave 98 g. (70%) of $C_3F_5Cl_3$, b. p. 72–73°, *n*D 1.350 at 22° and a small amount of less fluorinated product.

Anal. Calcd.: Cl, 44.8; mol. wt., 238. Found: Cl, 44.9; mol. wt., 240.

Preparation of $CF_2ClCF=CF_2$.—$C_3F_5Cl_3$ (168 g. or 0.706 mole) in 150 ml. of absolute alcohol was refluxed with 65 g. (1 mole) of mossy zinc for two days. The reaction product which distilled through the reflux condenser was liquefied in an ampule cooled with Dry Ice. After washing through water and drying, fractional distillation gave 102 g. (86%) of $CF_2ClCF=CF_2$, b. p. 7.6°, and a small amount of unreacted material. Dilution of the reaction mixture with water precipitated an additional 6% of unreacted material. Titration of the chlorine ion in the solution indicated the correct molecular weight for the olefin.

Rearrangement to $CF_3CFC=FCl$.—In a steel vessel, 82 g. (0.46 mole) of antimony fluoride was combined with 13 g. (0.18 mole) of chlorine. After cooling, 102 g. (0.16 mole) of $CF_2ClCF=CF_2$ was added. The vessel was closed, heated in steam for eighteen hours, then at 125° for nine hours. Distillation gave a small amount of low boiling material, then 84 g. (82%) of a substance, b. p. 7.7 to 7.9° (uncor.), f. p. −156.8 to −159.6°. These properties come close to those reported[1] for the *cis-trans* mixture of $CF_3CF=CFCl$, b. p. 7.9°, f. p. −158°.

Synthesis of $CF_3CF=CFCF_3$

By means of the lead oxide–hydrogen fluoride procedure,[5] the previously reported[6] $CF_3CCl=CClCF_3$ was transformed into $CF_3CFClCFClCF_3$, from which zinc gave an excellent yield of the desired perfluorinated 2-butene. Later, the starting $CF_3CCl=CClCF_3$ was prepared in a single, standardized operation[7] from commercial C_4Cl_6, and this improvement made the sequence adaptable to commercial production.

Preparation of $CF_3CClFCClFCF_3$.—In a steel vessel cooled with Dry Ice were placed 239 g. (1 mole) of lead dioxide, 400 g. (20 moles) of liquefied hydrogen fluoride and 240 g. (1.03 mole) of $C_4H_6Cl_2$. After closing, the system was allowed to warm up, while being mechanically rocked. A reaction took place which temporarily raised the pressure to six atmospheres. The reaction mixture was poured onto ice, neutralized while cold, then steamed. The distillate contained 229 g. of a product *n*D 1.337 at 25°. This is a mixture of $C_4F_8Cl_2$, b. p. 63°, and $C_4F_6Cl_2$, b. p. 65°, which it is impractical to separate by distillation. In general this mixture accounted for 26% of the desired reaction product and 63% of recovered olefin. To prepare pure $C_4F_8Cl_2$, the mixture was fractionally distilled, and the head fractions treated with permanganate to destroy the olefin. *Anal.* Calcd.: Cl, 26.2. Found: Cl, 24.2.

Preparation of $CF_3CF=CFCF_3$.—The mixture of $C_4F_8Cl_2$ and $C_4F_6Cl_2$ was treated with zinc in alcohol. A heating period of sixty hours was needed to complete the reaction. The expected amount of C_4F_8 distilled through the reflux condenser and was received in a Dry Ice cooled ampule. It was purified by fractional distillation; its molecular weight was computed as 270 from the chlorine ion concentration in the reaction mixture (calcd. 271). Its boiling and freezing characteristics indicate a *cis–trans* mixture. From the reaction mixture, C_4F_6Cl was recovered by precipitation with water.

Attempted Synthesis of $C_2F_5CF=CF_2$

Several schemes were tried, all of which deviated from the expected paths for the reasons stated.

First Attempt.—$CF_3CCl_2CCl_2CCl_3$ was prepared by extensive chlorination of $CF_3CH=CCl-CCl_3$[6] for reaction with zinc, in the hope that $CF_3-CCl_2CCl=CCl_2$ would be preferentially obtained. From this derivative, the preparation of $C_2F_5CF=CF_2$ would have been the same problem as the synthesis of $CF_3CF=CF_2$ from $CCl_3CCl=CCl_2$. The zinc reaction could not be mastered, and only small amounts of $CF_3CCl_2CCl=CCl_2$ were obtained. This compound was transformed by a conventional fluorination into a pentafluoride presumed to be $C_2F_5CCl=CCl_2$ (calcd.: Cl, 42.8; found: 43). Oxidation of the latter gave a fluorinated acid which was not CF_3CO_2H, an indication that the double bond had not shifted to the center of the molecule. This fluorinated acid was not further identified.

Second Attempt.—The starting point was the easily obtained $CCl_3CF_2C_2Cl_5$.[8] Actuated by the observation that perchlorocyclopentene is easily transformed into a hexafluoride rather than a tetrafluoride,[9] we tried to transform the starting material with zinc into $CCl_3CF_2CCl=CCl_2$, in order to attempt fluorination of CCl_3 group located just beyond the allylic position. The zinc reaction could not be mastered, but this difficulty was skirted by subjecting the starting material to conventional fluorination, and obtaining thereby a tetra-, a penta- and a hexafluoride formulated as $CCl_3CF_2CCl_2CClF_2$, $CCl_2FCF_2CCl_2CClF_2$ and $CClF_2CF_2CCl_2CClF_2$ on the basis of the known[10] ease of fluorination. Dechlorination of the first two compounds with zinc proceeded quite well and gave the expected olefins $CCl_3CF_2CCl=CF_2$ and $CCl_2FCF_2CCl=CF_2$, respectively. Both were subjected to fluorination to see whether they would give $CF_3CF_2CCl=CF_2$. The reaction proceeded only at high temperature and gave a ma-

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[5] Henne and Waalkes, THIS JOURNAL, **67**, 1639 (1945).

[6] Henne, Zimmerschied and Hinkamp, *ibid.*, **68**, 1906 (1945).

[7] Henne and Trott, *ibid.*, **67**, 1820 (1947).

[8] Henne and Hinkamp, *ibid.*, **67**, 1195 (1945).

[9] Henne and Zimmerschied, *ibid.*, **67**, 1235 (1945).

[10] Henne in "Organic Reactions," Vol. II, John Wiley and Sons, New York, N. Y., p. 56.

TABLE I

PHYSICAL CONSTANTS

Compound	B. p., °C. (760 mm.)	F. p., °C.	t, °C.	d^t_4	n^t_D	MR	AR_F
$CCl_2FCFClCFCl_2$	154.7	glass	20	1.7624	1.4387	40.4	1.0
$CF_2ClCFClCF_2Cl$	73.7	−72 ± 3	20	1.6631	1.3512	30.8	1.1
$CF_2{=}CFCF_2Cl$	7.5	glass	1.4	1.5116	1.3050	20.9	1.1
$CFCl{=}CFCF_3$	8.4	−156	(*cis–trans* mixture)				
$CF_3CCl{=}CClCF_3$[a]	.....	− 56 to −59	20	1.6203	1.3464	30.7	1.2
$CF_3CFClCFClCF_3$	62.9	− 73 to −75	20	1.6801	1 3100	31.1	1.0
$CF_3CF{=}CFCF_3$	0.4 to 3.0	−129 to −139	(*cis–trans* mixture)				
$CF_3CCl_2CCl_2CCl_3$		67–69					
$CF_3CF_2CCl{=}CCl_2$	140.7	.....	20	1.7421	1.4040	35.1	1.2
$CCl_3CF_2CCl_2CClF_2$	209	glass	20	1.8392	1.4551	49.3	1.0
$CCl_2FCF_2CCl_2CClF_2$	171.3	glass	20	1.8047	1.4211	45.0	1.1
$CF_2ClCF_2CCl_2CClF_2$	134.2	glass	20	1.7625	1.3856	40.5	1.2
$CCl_3CF_2CCl{=}CF_2$	142.4	glass	20	1.7084	1.4254	39.8	1.1
$CCl_2FCF_2CCl{=}CF_2$	104.1	glass	20	1.6671	1.3840	35.0	1.1
$CF_3CCl_2CClFCF_3$	97.5	glass	20	1.7494	1.3530	35.7	1.1
$CF_3CCl{=}CFCF_3$ (*cis-trans* mixt.)	32.2	glass	20	1.5482	1.2946	23.7	0.9

[a] Different *cis–trans* isomer ratio than that obtained by Henne, Hinkamp, and Zimmerschied[6] (m. p. −67.3°).

terial which analysis showed to be $C_4F_7Cl_3$ (calcd.: Cl, 37.2; found: Cl, 37.4). The first interpretation was that this was the dichloride of the desired $CF_3CF_2CCl{=}CF_2$. The two extra chlorine atoms were easily removed with zinc, and the olefin subjected to oxidation to ascertain whether it was the desired one. Instead of giving $C_2F_5CO_2H$, the oxidation yielded nothing but CF_3CO_2H, showing that the double bond had shifted to the center of the molecule. We were therefore forced to admit that an allylic shift had taken place, probably from $CClF_2CF_2CCl{=}CF_2$ to $CF_2ClCF{=}CClCF_3$ and that the latter had then been fluorinated to $CF_3CF{=}CClCF_3$.

Preparation of $CCl_3CF_2CCl{=}CCl_2$.—In a steel container were placed 211 g. (0.57 mole) of $CCl_3CF_2C_2Cl_5$, 40 g. (0.6 mole) of freshly cut zinc and 665 cc. of absolute alcohol. After closing, heating in a steam-bath was allowed for three days, which brought the pressure to about 4 atm. On pouring out after cooling, 126 g. of organic material and 70 g. of tar were obtained. Distillation at 2 to 3 mm. gave 92 g. of crude $C_4F_2Cl_6$, b. r. 44 to 50°, representing at 31% yield. Redistillation gave a pure material.

Fluorination of $CCl_3CF_2C_2Cl_5$.—The customary procedure was followed. With SbF_3Cl_2 as fluorinating agent, average yields were 6% of $C_4F_6Cl_4$, 23% of $C_4F_5Cl_5$, 40% of $C_4F_4Cl_6$ and 27% of a high polymer.

Dehalogenation of $C_4F_5Cl_5$ and $C_4F_4Cl_6$.—The customary zinc reaction in absolute alcohol proceeded very smoothly and quantitatively.

Fluorination of $C_4F_5Cl_3$ and $C_4F_4Cl_4$.—A mixture of these fluorides, (0.86 mole) was heated with SbF_3Cl_2 (1 mole) in a steel vessel at 200° for sixteen hours. The pressure reached 18 atmospheres. After bleeding off the gases, without obtaining $C_2F_5CCl{=}CF_2$, an additional heating period of twenty hours was permitted. On working up the reaction products, 143 g. of $C_4F_7Cl_3$ (53% yield) was found boiling at 97°. This material underwent the customary zinc dechlorination to yield C_4F_7Cl easily and quantitatively. The latter on standard oxidation gave exclusively trifluoroacetic acid, the sodium salt of which was analyzed to give 17.6% Na found (16.9 calcd.) and 41.8% F (41.9 calcd.). A search for a chlorofluoro acid gave negative results.

Summary

A synthesis sequence for $CF_3CF{=}CF_2$ was complicated by a rearrangement. A practical, simple sequence gave $CF_3CF{=}CFCF_3$. The preparation of $C_2F_5CF{=}CF_2$ was defeated by rearrangements.

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