Fluorochloroethylenes

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During an extended search for new non-combustible anesthetics a large number of fluorine gases were studied. This paper describes the preparation and properties of the fluorine substituted chloroethylenes, CF_2=CFCl, CFCl=CFCl, CFCl=CCl$_2$ and attempts to prepare C_2F_4.

Trifluoro-monochloroethylene.—If the $C_2F_3Cl_3$ obtained by Booth, Mong and Burchfield[3] has the formula $CF_2ClCFCl_2$, reduction with zinc dust and alcohol should yield CF_2=CFCl, since Swarts[4] has found that in such reductions chlorine is always removed in preference to fluorine.

Accordingly 102 g. of $C_2F_3Cl_3$ was slowly refluxed with 300 g. of zinc dust in 500 cc. of absolute alcohol for two hours and the evolved gas collected by refrigeration. Forty-seven grams of a gas (equivalent to a 70% yield) was obtained. After repeated fractional distillation[5] the gas boiled at approximately $-28°$. The purified gas gave positive tests for both fluorine and chlorine. It had a slight odor like ethylene. It decolorized alkaline permanganate solution and added bromine to form an oily liquid insoluble in water, which indicated its unsaturated character.

Analysis.—An attempt to establish its formula by determination of the density of the gas proved fruitless. The gas has a molecular weight much higher than the formula would require, probably indicating considerable association just above its boiling point.

A sample was carefully fractionally distilled a number of times, until no difference could be detected in the vapor pressure of different fractions. The method of Chablay modified,[6] was used to decompose the gas, instead of the Carius method. In the original Chablay method the gas is not weighed, but the weight calculated from its volume assuming the perfect gas laws. Our attempts to determine its molecular weight showed the necessity of weighing the gas. The pure gas was condensed by means of liquid air into a previously weighed small bulb fitted with a stopcock and a flat joint.[7] The sample bulb was reweighed and attached to the apparatus. The gas was then allowed to pass in small portions, to condense in the reaction flask (kept at $-78°$) and to mix with the solution of sodium in liquid ammonia. When the pressure in the sample bulb no longer fell, the reaction bulb was cooled with liquid air to bring over as much as possible of the sample, which on warming reacted. Ammonia gas was condensed in the sample bulb and then transferred by refrigeration to the reaction flask thus rinsing out all the sample into the reaction flask. The procedure from this point on is the same as described by Booth, Mong and Burchfield.[8] The gas gave on analysis 30.41% chlorine. Calcd. for C_2F_3Cl, 30.51%.

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(3) Booth, Mong and Burchfield, *Ind. Eng. Chem.*, **24**, 328 (1932).

(4) Swarts, *Acad. Roy. Belgique*, 728 (1909); *Chem. Centr.*, II, 1098 (1897); et seq.

(5) Booth, *J. Chem. Ed.*, **7**, 1250 (1930).

(6) Chablay, *Ann. chim.*, **9**, 469 (1914).

(7) Wourtzel, *J. chim. phys.*, **11**, 57 (1913).

(8) Booth, Mong and Burchfield, *Ind. Eng. Chem.*, **24**, 329 (1932).

Swarts[9] has found that by reduction with alcoholic zinc dust the chlorine is removed first in preference to the fluorine unless the carbon atom has no chlorine atom attached to it to be removed, in which case a fluorine atom is removed. For example, the reduction of $CHCl_2CHClF$ by alcoholic zinc dust yields $CHCl=CHF$ while the reduction of CHF_2CHCl_2 also yields $CHCl=CHF$ due to the removal of an atom of fluorine since that carbon had no chlorine available for removal. The alcohol solution left after the generation of the gas, C_2F_3Cl, was found to contain only chlorine. It seems certain then that the starting material has the structure, $CF_2ClCFCl_2$.

Mr. M. J. Bahnsen, of this Laboratory, using an accurately calibrated multiple thermocouple, by means of warming curves, has very kindly determined the melting point of $CF_2=CFCl$ to be $-157.5°$. This gas in contact with water slowly hydrolyzes, a fact which definitely negatives its use as an anesthetic.

Determination of Vapor Pressure.—The vapor pressure of these fluoro-chloroethylenes was measured on a simplified Germann type manometer,[10] to be described later by Booth and Swinehart. The temperature of the bath surrounding the 5-cc. vapor pressure bulb containing the fluoro-chloroethylene, was controlled by adding manually small amounts of carbon dioxide snow or liquid air as needed and could easily be maintained sufficiently constant for our purpose. The temperature was measured by means of an accurately calibrated Anschütz thermometer or a resistance thermometer for the lower temperatures. The temperatures with corresponding vapor pressure readings, for C_2ClF_3, after the necessary corrections were made, are recorded in Table I.

TABLE I

VAPOR PRESSURE OF C_2ClF_3

T, °K.	Pressure, mm.	T, °K.	Pressure, mm.
194.6	45.2	246.7	815.0
239.6	593.4	247.8	853.7
244.7	742.1	249.7	920.7
245.4	767.3		

Substituting the values of Table I in the Rankine equation and evaluating the constants in the usual manner, the equation for the vapor pressure of C_2ClF_3 takes the form

$$\log P = -1044/T + 1.191 \log T + 4.292$$

when P is expressed in millimeters.

The heat of vaporization, ΔH, obtained by differentiating the log P equation, converting to natural logarithms, and equating this result to the Clausius–Clapeyron equation, is 5400 cal./mole at 245.2 K. Log P was plotted against $1/T$ and the resulting straight line established the constancy of ΔH at different temperatures. By plotting P against T the boiling point of C_2ClF_3 is found to be $-27.9°$ at 760.0 mm.

Symmetrical Difluoro-dichloroethylene.—After some preliminary tests, 200 g. of $C_2F_2Cl_4$ was dissolved in 300 cc. of absolute alcohol and gradually dropped into the generating flask upon 400–500 g. of zinc dust. Gentle warming was required to start the reaction which then proceeded smoothly until the $C_2F_2Cl_4$ was consumed. A clear low-boiling liquid collected in the receiver, which was cooled with carbon dioxide snow. Fractionation in an efficient Vigreux column with still head yielded 125 g. of a liquid which boiled at approximately 21° (equivalent to a yield of 96%).

(9) Swarts, *Chem. Centr.*, I, 13 (1903).
(10) Germann, This Journal, **36**, 2456 (1914).

The liquid had a musty, not unpleasant, odor, closely resembling ethylene. The liquid decolorizes alkaline permanganate and adds bromine easily to form a mushy solid or heavy oil, indicating its unsaturated character. The ready hydrolysis of this compound negatives its possible use as an anesthetic.

Analysis.—Qualitative tests showed that the compound contained both fluorine and chlorine. For the quantitative determination the technique using glass bulblets better suited to a low boiling liquid was used, as previously described.[8] Found, chlorine, 53.49. Calcd. for $C_2F_2Cl_2$, 53.36.

Mr. Bahnsen, of this Laboratory, as described, found the melting point of $C_2F_2Cl_2$ to be −112°.

Vapor Pressure.—The corrected vapor pressures of $C_2F_2Cl_2$, are recorded in Table II.

TABLE II

VAPOR PRESSURES OF $C_2F_2Cl_2$

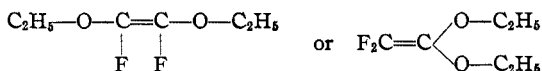| T, °K.	Pressure, mm.	T, °K.	Pressure, mm.
239.9	59.05	288.1	609.9
251.2	113.0	291.1	685.5
258.2	161.8	293.0	738.3
263.2	206.6	293.5	750.8
267.2	249.8	294.0	765.2
273.1	330.2	295.0	793.6
283.1	502.3		

Substituting the values in Table II in the Rankine equation and evaluating the constants in the usual manner, the equation for the vapor pressure of $C_2Cl_2F_2$ takes the form

$$\log P = -2004/T - 4.829 \log T + 21.62$$

where P is expressed in millimeters.

The calculated latent heat of vaporization is 6600 cal./mole at 293.8°K., which value varies but slightly with change in temperature. From a pressure–temperature curve the boiling point is found to be 20.9° at 760 mm.

$C_2F_2Cl_2$ reacts with finely divided sodium to give gaseous products. Sodium in alcohol reacts vigorously with it if warmed. When the product is poured into water a heavy oil separates, which by analogy with Swarts' results should be either

$$C_2H_5\!-\!O\!-\!\underset{\underset{F}{|}}{C}\!=\!\underset{\underset{F}{|}}{C}\!-\!O\!-\!C_2H_5 \qquad \text{or} \qquad F_2C\!=\!C\!\!\diagdown\!\!\!\!\!\diagup\!\!\!\begin{array}{l} O\!-\!C_2H_5 \\ O\!-\!C_2H_5 \end{array}$$

These products were not investigated further. Booth, Mong and Burchfield[3] concluded that $C_2F_2Cl_4$ had the symmetrical structure $CFCl_2CFCl_2$. On this basis the structure of $C_2F_2Cl_2$ must be $CFCl\!=\!CFCl$.

Monofluoro-trichloroethylene.—Monofluoropentachloroethane[3] reacted vigorously with zinc in ethyl alcohol. The reaction was found to be sufficiently exothermic that it was necessary to control the speed of the reaction with a refrigerant. The product was a liquid with an odor resembling ethylene, which reduced alkaline permanganate solution and added bromine to yield a water-insoluble, heavy oil or mushy solid. However, the boiling point of this unsaturated product was so close to that of the ethyl alcohol that it was impractical to purify it sufficiently by fractional distillation.

Accordingly C_2FCl_5 was reduced by granular zinc in benzyl alcohol and the products from two experiments fractionated. The boiling point of the product was 70.0° at 740.8 mm.; and calculated to be 71.0° at 760 mm. by the law of Ramsay and Young.[11] The compound was further purified by vacuum distillation in a small gas-fractionating apparatus, in which the fractionating bulbs contained solid barium oxide[12] to remove any moisture from the liquid and any acid which may have been formed by hydrolysis during previous treatment.

Mr. Bahnsen again kindly determined the melting point of this purified liquid to be −82°.

The specific gravity of this compound was found to be 1.5304 at 25°.

Analysis.—Samples of the freshly distilled liquid were immediately sealed into weighed bulblets and determined as described. Found: 71.04 chlorine; calcd. for C_2FCl_5 71.20.

The compound was found to be stable over long periods in the absence of moisture. However, if a few drops of the liquid are placed in a small tube containing several cubic centimeters of water plus a drop of methyl orange, the mixture acquires a red tinge in seven minutes, and at the end of several hours is deep red, indicating hydrolysis. The ready hydrolysis of this compound negatives its use as an anesthetic.

Tetrafluoroethylene.—According to Chabrie[13] tetrafluoroethylene may be prepared by the double decomposition of tetrachloroethylene and silver fluoride at 220° in a sealed tube for two hours. Humiston[14] claims to have prepared it by the direct action of fluorine on filtchar at −80°, and reported its boiling point as −32°.

In this Laboratory silver fluoride and tetrachloroethylene were refluxed for several hours at atmospheric pressure without formation of any gas. Likewise, 150 g. of anhydrous silver fluoride prepared as described by Moissan,[15] and 50 g. of C_2Cl_4 were heated in a small sealed steel bomb at 155° for seven hours without the generation of any gas. The experiment was repeated at 240° for three and one-half hours and also at 300° for three hours without any better success. Lebeau and Damiens[16] reinvestigated the action of silver fluoride and carbon tetrachloride, which Chabrie[13] claimed gave carbon tetrafluoride, and found that the product was a mixture chiefly of CCl_2F_2. However, one hesitates to question Chabrie's work without more thorough study. Reflection has suggested that the iron of the bomb may have interfered, though there was no sign of reaction between the iron and the silver fluoride. Perhaps in Chabrie's experiment the glass of the bomb exerted some favorable catalytic action. Booth and Bixby[17] also found a similar difficulty in preparing fluoroform by the action of silver fluoride on chloroform as described by Chabrie.[18] One of us has since repeatedly attempted to prepare fluoroform by Chabrie's original and also by modified methods without success.

Discussion

It is interesting to note (Table III) that the replacement of chlorine in C_2Cl_4 by fluorine as established in this work produces a regular drop in the boiling points of 50°. It will be noticed that the boiling point of C_2F_4 (−32°) as given by Humiston,[14] who claimed to prepare it by action of

(11) Ramsay and Young, *Phil. Mag.*, [V] **20**, 515 (1885); **21**, 33 (1886); **22**, 37 (1886).
(12) Booth and McIntyre, *Ind. Eng. Chem., Anal. Ed.*, **2**, 12 (1930).
(13) Chabrie, *Compt. rend.*, **110**, 281 (1890).
(14) Humiston, *J. Phys. Chem.*, **23**, 572 (1919).
(15) Moissan, *Ann. chim. phys.*, [6] **19**, 272 (1890).
(16) Lebeau and Damiens, *Compt. rend.*, **182**, 1340 (1926).
(17) Booth and Bixby, *Ind. Eng. Chem.*, **24**, 637 (1932).
(18) Chabrie, *Bull. soc. chim.*, [3] **7**, 24 (1892).

fluorine on charcoal at $-80°$, is only $4.1°$ below that of $CF_2 \!=\! CClF$. It is obviously out of line.

TABLE III

COMPARATIVE PROPERTIES OF THE FLUOROCHLOROETHYLENES

Compound	B. p., °C.	Differences	M. p., °C.	Liquidus range	Latent heat of vaporization
C_2Cl_4	121	50	-19	140	
C_2Cl_3F	71		-82	153	
$CClF \!=\! CClF$	20.9	50.1	-112	132.9	6600 cal./mole
C_2ClF_3	-27.9	48.8	-157.5	185.4	5400 cal./mole
C_2F_4	$-32?$	4.1	.....	...	

The boiling points of C_2Br_3F, $C_2Br_2F_2$ and C_2BrF_3 are, respectively, 147.2, 70.5 and $-2.5°$ with an average difference in boiling point of $75°$. Experience has shown that boiling points of fluorochloro compounds may be predicted by these differences. On this basis it would seem likely that the true boiling point of C_2F_4 would lie between -76 and $-82°$.[19]

It is also interesting to note that all the compounds prepared in this work contained the $\!=\!CFCl$ grouping and were readily hydrolyzed. It would be interesting to learn whether the isomer CF_2CCl_2 would be more stable.

C_2F_3Cl has a latent heat about equal to that of sulfur dioxide and a boiling point, $-27.9°$, considerably lower. It might be a satisfactory refrigerant save where its slow hydrolysis would interfere.

Summary

Monofluoro symmetrical difluoro, and trifluorochloroethylenes, boiling respectively at 71.0, 20.9 and $-27.9°$, have been prepared and their properties studied. None of these compounds are suitable for anesthetics because they all slowly hydrolyze. From the fact that the original preparation could not be duplicated and from the fact that the boiling point as published is so out of line with similar compounds, doubt is cast upon the published work on C_2F_4.

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(19) Since this article was set up O. Ruff and O. Bretschneider, Z. anorg. allgem. Chem., **210**, 173 (1933), have prepared C_2F_4 by thermally decomposing CF_4 in a carbon arc and have found its boiling point to be $-76.3°$, thus confirming our prediction.