method for studying adsorption. Although the interpretation of results is complicated as mentioned above, it has one definite advantage over conventional methods for investigating adsorption in that only a relatively small amount of surface (a few square centimeters) is required.

The authors are grateful to Professor Malcolm Dole for discussions of various aspects of this work.

## Summary

The change of surface electrical potential of various surfaces as caused by the adsorption of vapors of inorganic and organic substances has been observed by two different methods. The first apparatus, making use of a vacuum tube electrometer, gives direct qualitative observations of the effect. The second apparatus using a vibrating electrode, potentiometer, amplifier setup yields quantitative observations of the change of potential with pressure of vapor. The observed potential changes vary from 5 to 500 millivolts. It is believed that the technique will be useful as a method for studying adsorption.

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[Contributions from the Departments of Chemistry at Purdue and The Ohio State University]

# Chlorofluoropropanes

By E. T. McBee, Albert L. Henne, H. B. Hass and Norman Elmore[1]

The origin of this work was a desire to prepare $CH_2ClCF_2CF_2Cl$, a new compound wanted for further investigation. The sequence of reactions permitted the preparation of additional fluorinated compounds, some of which are new while the others gave improvements in previously reported data. The research also confirmed the uniquely asymmetrical course followed by the chlorination of $CH_3CF_2CH_3$[1a]; this reaction proceeds stepwise to yield $CH_3CF_2CH_2Cl$, $CH_3CF_2CHCl_2$, $CH_3CF_2CCl_3$, $CH_2ClCF_2CCl_3$, $CHCl_2CF_2CCl_3$ and finally $CCl_3CF_2CCl_3$, instead of a mixture of symmetrical and unsymmetrical compounds at each stage.

The starting compound was $CH_3CCl_2CH_3$, obtained from chlorinated propane[2]; its fluorination to $CH_3CF_2CH_3$ followed previous directions.[1a]

This difluoride was chlorinated at low temperature in sunlight or artificial light, and also at high temperature in the dark; asymmetrical chlorination prevailed in all cases. The resulting chlorofluorides were fluorinated with a strong fluorinating agent, as shown in the experimental part, after repeated failure of milder agents and conditions. The fluorination did not proceed further than indicated.

(1) This work was presented for the degree of Master of Sciences at Purdue University, by Mr. Elmore, whose present address is Standard Oil Development Co., Linden, New Jersey. The fluorination work was carried out in Dr. Henne's laboratory at The Ohio State University.

(1a) Henne and Renoll, This Journal, **59**, 2434 (1937).

(2) Hass, McBee, Hinds and Gluesen Kamp, *Ind. Eng. Chem.*, **28**, 1178 (1936).

## Experimental Results

The table lists the properties of three compounds (1, 2, and 3) which were obtained in a better state of purity than previously reported, and four (4 to 7) which are new. The latter were analyzed for chlorine by the method reported by McNevin,[3] but this was done while the method was still under investigation, and the deficiency is known to be due mostly to incorrect combustion. Only the last compound (no. 7) seems still impure, as indicated by the low molecular refraction and the low atomic refraction for fluorine (0.96 instead of an expected 1.15).

## Experimental

**Preparation of $CH_3CF_2CH_3$.**—2,2-Dichloropropane was obtained from by-product dichlorides from the chlorination of propane.[2] It was converted to $CH_3CF_2CH_3$ by the procedure already reported.[1a]

**Chlorination of $CH_3CF_2CH_3$. Liquid Phase Chlorination.**—The $CH_3CF_2CH_3$ was liquefied in a flask maintained at $-10°$ to $-5°$ and fitted with a reflux condenser and a chlorine inlet tube. Chlorine was added to the liquid and chlorination occurred in the presence of light. The temperature was maintained below 0° until all the $CH_3CF_2CH_3$ had been chlorinated and then it was allowed to increase gradually to 102°, the boiling point of $CH_3CF_2CCl_3$. This procedure yields about 10.4% $CH_3CF_2CHCl_2$, 61.7% $CH_3CF_2CCl_3$, and 28% of more highly chlorinated material consisting of $CH_2ClCF_2CCl_3$, $CHCl_2CF_2CCl_3$, and $CCl_3CF_2CCl_3$.

**Vapor Phase Chlorination.**—Chlorine was added to $CH_3CF_2CH_3$ in a large bottle, over water at room tempera-

(3) McNevin and Baxley, *Ind. Eng. Chem., Anal. Ed.*, **12**, 299 (1940).

TABLE I

| No. | | M. p., °C. | B. p. 760 mm., °C. | $d^{20}_4$ | $n^{20}_4$ | $MR_D$ | ARF | Cl, % Found | Cl, % Calcd. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $CH_3CF_2CCl_3$ | 52.8–53.3 | 101–102 | | | | | | |
| 2 | $CH_2ClCF_2CCl_3$ | | 150.8–150.9 | 1.6404 | 1.4459 | 35.41 | 1.04 | | |
| 3 | $CH_3CF_2CFCl_2$ | | 60.0–60.5 | 1.4175 | 1.3534 | 25.58 | 1.03 | | |
| 4 | $CH_2ClCF_2CFCl_2$ | | 108.3 | 1.5813 | 1.3954 | 30.63 | 1.09 | 52.0 | 52.6 |
| 5 | $CH_2ClCF_2CF_2Cl$ | | 67.9 | 1.5225 | 1.3464 | 25.91 | 1.13 | 37.9 | 38.3 |
| 6 | $CHCl_2CF_2CF_2Cl$ | | 91.7–91.9 | 1.5877 | 1.3750 | 30.90 | 1.15 | 47.3 | 48.4 |
| 7 | $CCl_3CF_2CF_2Cl$ | | 112.0–112.5 | 1.6992 | 1.3961 | 34.96 | 0.96 | 54.7 | 56.4 |

ture. The reaction was accelerated by means of artificial light provided by three 200-watt light bulbs around the five-gallon glass carboy. Heat from the reaction and lights gave a temperature of 60–70°. The chlorinated product condensed and sank to the bottom of the bottle; the hydrogen chloride dissolved in the water. If a suitable water displacement device is used, the pressure in the bottle remains substantially the same and the water rises and falls in the bottle as the $CH_3CF_2CH_3$ is used up and more is added to the flask. The process can be operated in a semi-continuous manner. The ratio of products varies with conditions; in a typical run the yields were 3% $CH_3CF_2CH_2Cl$, 24% $CH_3CF_2CHCl_2$, 64% $CH_3CF_2Cl_3$, and 9% of the more highly chlorinated products.

**Chlorination of $CH_3CF_2CCl_3$.**—Chlorine was passed into 1900 g. of $CH_3CF_2CCl_3$ maintained at 55°. Light to accelerate the reaction was provided by three 200-watt light bulbs. After sixteen hours the reaction was discontinued and the unreacted $CH_3CF_2CCl_3$ removed by rectification for further chlorination experiments. The residue of chlorinated material amounting to 368 g. was rectified to yield 168 g. (45.7%) of $CH_2ClCF_2CCl_3$ and 200 g. of $CHCl_2CF_2CCl_3$ and $CCl_3CF_2CCl_3$.

**Fluorination of $CH_2ClCF_2CCl_3$.**—One mole of antimony trifluoride was placed in a steel container, and one-half mole of chlorine was allowed to be absorbed, to make equimolar amounts of $SbF_3$ and $SbF_3Cl_2$. One gram mole of $CH_2ClCF_2CCl_3$ was added, and the container, which was equipped with pressure gage and needle valve, was closed, placed in an oil-bath and heated progressively to 160°. The pressure rose to about ten atmospheres, where it was maintained by allowing gas to be discharged through the needle valve. The discharged gas was passed into cracked ice where hydrogen fluoride and hydrogen chloride dissolved, and the fluorinated products condensed. After a few hours, the remainder of the organic material was allowed to distill into the cracked ice. The organic layer was washed, dried and ultimately separated by rectification. The product consisted of a mixture of $CH_2ClCF_2CFCl_2$ and $CH_2ClCF_2CF_2Cl$; the former compound was further refluorinated to give more of the desired $CH_2ClCF_2CF_2Cl$.

**Chlorination of $CH_2ClCF_2CF_2Cl$.**—1,3-Dichloro-1,1,2,2-tetrafluoropropane was chlorinated by passing chlorine gas into the liquid at room temperature in the presence of light. Substantially quantitative yields of $CHCl_2CF_2CF_2Cl$ and $CCl_3CF_2CF_2Cl$ were obtained. The ratio of these two chlorinated products depends upon the degree of chlorination.

## Summary

1. Chlorination of $CH_3CF_2CH_3$ has been conducted in both liquid and vapor phase to give successively, $CH_3CF_2CH_2Cl$, $CH_3CF_2CHCl_2$, $CH_3CF_2CCl_3$, $CH_2ClCF_2CCl_3$, $CHCl_2CF_2CCl_3$, and $CCl_3CF_2CCl_3$.

2. Fluorination of $CH_2ClCF_2CCl_3$ gave two new compounds, $CH_2ClCF_2CFCl_2$ and $CH_2ClCF_2CF_2Cl$.

3. Chlorination of $CH_2ClCF_2CF_2Cl$ gave two new compounds, $CHCl_2CF_2CF_2Cl$ and $CCl_3CF_2CF_2Cl$.

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