[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Fluorination of Trichlorosilane[1]

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Introduction

Recently Booth and Swinehart[2] reported that antimony trifluoride (with antimony pentachloride as catalyst), acts generally as a fluorinating agent for non-polar chlorides, bromides and iodides, to yield fluorohalides and fluorides. The object of this investigation was to study this reaction on trichlorosilane,[2a] "silicochloroform," ($SiHCl_3$). The stepwise fluorination of trichlorosilane should yield the following compounds: $SiHCl_2F$, $SiHClF_2$ and $SiHF_3$. Of these trifluorosilane[3] alone has been prepared.

Experimental

When trichlorosilane was condensed on antimony trifluoride and antimony pentachloride and the mixture allowed to warm, gas was generated so rapidly that it could not be removed and condensed fast enough, to prevent bursting the generator. Even the application of liquid air direct to the generator did not cool it sufficiently to control the reaction. As a result of many trials the apparatus shown in Fig. 1 was finally found suitable. Fluorination of trichlorosilane was carried out as follows: In place of the side-arm (B) a "dead end" standard interchangeable joint was placed at (C). Purified trichlorosilane[4] was condensed into the 150-cc. reaction bulb (A), by means of liquid air, and then the trichlorosilane was allowed to warm to room temperature. Five to ten cc. of antimony pentachloride was then let into (A) from the graduated tube (F). (A) was then gently warmed until the pressure in the system was slightly above atmospheric. The "dead end" at (C) was then removed and the side-arm (B) containing 50–60 g. of powdered antimony trifluoride was placed as shown by the dotted lines. By tilting this side-arm, and twisting the stirrers, (D) and (E), small amounts of antimony trifluoride could be dropped into the trichlorosilane, causing a steady evolution of gas. The white powdery antimony trifluoride soon became black and caked by the action of gaseous trichlorosilane; a "mirror of antimony" was deposited on the glass walls, and vigorous action of the stirrers was necessary to cause the solid to drop into the cell. This blackening action of gaseous trichlorosilane on antimony trifluoride was first noted by Ruff and Albert. Liquid trichlorosilane does not seem to react in the same way. The blackening appears not to affect materially the fluorinating action of antimony trifluoride.

The gases liberated by the action passed through the ice-cooled spiral (H) and were then condensed in the trap (I) by means of liquid air. The manometer (G) was so constructed that when the pressure in the system rose above atmospheric pressure, the gas flow was automatically by-passed around the condensing spiral through the side-arm (J). Rather than to chance the destruction of the apparatus, it was found advantageous to hang the section (B) by a wire, and allow it to blow out if the pressure became too great. This tended to happen toward the end of the reaction when the solid phases antimony trifluoride and antimony trichloride were in excess. The heat evolved from the strongly exothermic reaction could not be carried away fast enough through the solid, and gases were so rapidly evolved that the liquid air could not completely condense them. To eliminate this difficulty stopcocks (L) and (M) were added to the manometer (G). Toward the end of the reaction, when the pressure was steadily increasing in the system, stopcock (L) was closed and the mercury was drained from the upper half of the manometer through stopcock (M). This connected the reaction cell directly to the trap (I) through (J) and (K). Stopcock (N) was then closed and suction was applied to the system. The gases condensed rapidly in the trap (I). The gases evolved at the end of the reaction seemed to be more volatile than those obtained by the smooth action in excess of trichlorosilane. Trifluorosilane and probably silicon hydride were then produced.

Purification of Gases.—The gases evolved from the fluorination could be separated roughly into constituent parts by a few simple ampoule to ampoule fractionations in the usual gas system. Fluorination yields were poor, however, and a large percentage of the product was always found to be unused trichlorosilane. The gaseous products fell into fractions boiling roughly at -10, -40 and $-90°$. Traces of a still more volatile compound were found, but as it had a high vapor pressure at liquid air temperatures and would not freeze, it was pumped away as an "air-block" in the system.

Separation and purification of the gas samples was performed in a fractionating column (Fig. 1) similar to that previously described.[4]

The still-pot (P) containing the liquefied gas was surrounded by a cold Dewar flask, provided with a small heating coil of nichrome wire, by which a constant current, and thus a constant heating effect, was applied to the liquefied gas.

The still-head (Q) was filled with copper shot cooled by means of liquid air. The influx of liquid air, and hence the temperature of the still-head, was automatically controlled through the action of a relay and sounder operated by contacts in the manometer. The contacts were so arranged that when the pressure in the system was at one

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[1] From a part of a thesis submitted by Wm. D. Stillwell to the Graduate Faculty of Western Reserve University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Booth and Swinehart, THIS JOURNAL, **54**, 4750 and 4751 (1932).

[2a] This nomenclature will be used throughout this paper because of the ease in naming the fluorochlorides as derivatives of trichlorosilane.

[3] Ruff and Albert, *Ber.*, **38**, 53, 2222 (1905).

[4] For preparation and properties, see Booth and Stillwell, THIS JOURNAL, **56**, 1529 (1934).

atmosphere, the sounder and relay would close, automatically closing the vent on a liquid air reservoir not shown in the diagram. This would cause pressure to build up in the reservoir, and liquid air would be forced into the still-head. This action cooled the still-head, causing the gas to condense and the pressure to drop, thus breaking the relay contacts and stopping the flow of liquid air. After equilibrium in the system had been established and reflux action was progressing, the pressure would vary less than 2 mm. Thermocouples between the glass walls of the still-head recorded the temperature of the condensing gas through the medium of a special high-speed Leeds and Northrup "Micromax" recording potentiometer. The gas was then distilled into an ampoule such as (R). As long as one gas fraction continued to distil over, the still-head temperature remained constant. The graph on the recording potentiometer was a straight line. When this dropped off, *i. e.*, when the still-head temperature became higher, a new fraction of gas was indicated and the distillate would then be condensed into another ampoule.

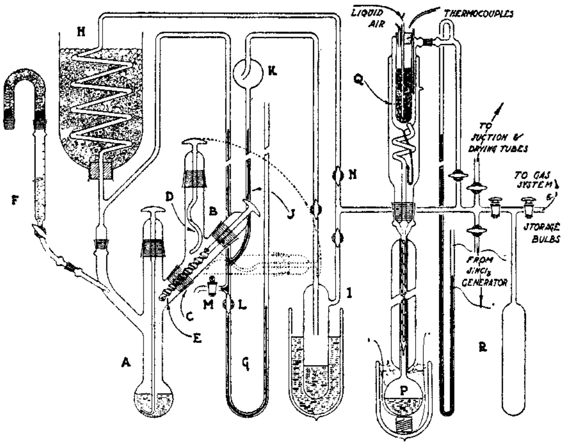

Fig. 1.

Identification of Fluorination Products.—The identification of the gaseous compounds prepared by the fluorination of trichlorosilane, was accomplished through analysis and the determination of melting point, vapor density and vapor pressure.

The Measurement of Vapor Pressures.—The vapor pressures of these gases were measured on a simplified Germann type barometer,[5] to be described later by Booth and Swinehart. The liquefied gas was contained in a small 5-cc. vapor pressure bulb immersed in a four-liter Dewar full of petroleum ether, maintained at constant temperature by stirring during the attainment of equilibria. The temperature was automatically regulated by a device similar to that described for the still-head, in which the vapor pressure of a second sample of the gas operated adjustable manometer contacts which made and broke an electrical current with a relay and sounder, thus regulating the addition of liquid air to the bath and so controlled its temperature. Equilibrium was considered to be attained, and readings were recorded, only when the vapor pressure was constant for some time. The purity of the samples was further checked by boiling off small amounts and remeasuring the vapor pressure of the residue. The temperature of the bath was determined by means of a platinum resistance thermometer.[6]

The Measurement of Melting Points.—The melting points of the gas samples under their own vapor pressure were determined by means of accurately calibrated multiple thermocouples in conjunction with the specially sensitive recording potentiometer. The liquefied gas samples were well stirred by an electromagnetic stirrer during the cooling process. The first formation of crystals was simultaneous with a sharp break in the cooling curve.

The Measurement of Vapor Densities.—The densities of the gases were determined by the globe method.[7]

Method of Analysis.—Samples were first dissolved in measured volumes of standard sodium hydroxide solution as follows. Small bulbs of very thick glass, provided with a long neck of thick-walled capillary tubing, joined to the inner cone of a standard interchangeable conical joint, as shown at (A), Fig. 2, were dried and weighed empty. These were then attached to the gas system, and a gas sample was condensed in the bulb by means of liquid nitrogen. The gas was liquefied, a portion pumped off and the contents again frozen.

The bulbs were then sealed off at the capillary, as shown at (B), Fig. 2, while connected to the apparatus and the confined gas was allowed to warm to room temperature. The bulb and conical joint were then removed, washed, dried and weighed. By difference, the weight of the sample was obtained. This was corrected for the buoyant effect of air after sealing. The pressure in the bulbs was considerable, but only once during this work did one burst, even though trifluorosilane boiling at −97.5° was above its critical point at room temperature. $SiHCl_2F$, boiling at −18.4°, was a colorless, very mobile liquid at room temperature.

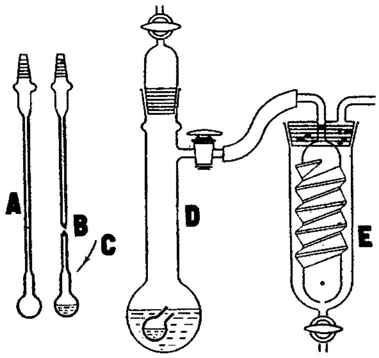

Fig. 2.

The bulbs were again placed in liquid nitrogen and the contents solidified. The neck-like capillary was then marked with a file at (C), Fig. 2, broken off and the bulb was quickly dropped into a flask (D) containing a known amount of standard 0.5 *N* sodium hydroxide. There the gas reacted to yield hydrogen, the sodium halides and a precipitate which dissolved on standing. The liberated hydrogen was passed through several wash bottles, such as (E), Fig. 2, of water containing a known amount of stand-

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[5] A. F. O. Germann, This Journal, **36**, 2456 (1914).

[6] For details see *J. Phys. Chem.*, **34**, 2810 (1930).

[7] Germann and Booth, *ibid.*, **21**, 81 (1917).

ard caustic to completely remove the acid. The alkaline solutions were combined and then made up to definite volume in a volumetric flask.

The reactions involved are probably

$$SiHCl_2F + 7NaOH = NaF + 2NaCl + 3H_2O + H_2 + Si(ONa)_4$$

or

$$SiHF_3 + 7NaOH = 3NaF + 3H_2O + H_2 + Si(ONa)_4$$

or more simply

$$SiHF_3 + 3NaOH + H_2O = 3NaF + Si(OH)_4 + H_2$$

The quantitative determination of chlorine in the sample was effected by acidifying an aliquot portion of the alkaline solution and titrating by the usual Volhard method.

For the quantitative determination of fluorine a method was evolved which was essentially a determination of the excess base over that required to react with the sample. To eliminate the poor end-point, caused by hydrolysis of the sodium fluoride, the F^- ion was removed according to the following procedure.

An aliquot portion of the alkaline solution was made just acid to methyl red indicator in the cold with a known amount of standard hydrochloric acid. To this acid solution was added slightly more than the calculated amount of neutral 20% calcium chloride solution, forming calcium fluoride as an opalescent suspension in the liquid. With the interfering sodium fluoride now removed from the solution, the excess hydrochloric acid was then titrated to methyl red end-point with standard sodium hydroxide.

Products of Fluorination.—After preliminary separations, the various fractions were rigorously distilled in a fractionating column as previously described. The products $SiHCl_2F$, $SiHClF_2$ and $SiHF_3$ were gases condensable to clear, colorless liquids which solidified to clear, colorless solids on further cooling. They hydrolyzed readily to yield hydrogen, halogen hydride, hydrated silica and probably silicoformic anhydride.

In Tables I and II are presented data establishing the identity of these gases. $SiHClF_2$ was obtained only in small quantities; about 20% of the fluorinated gases was $SiHCl_2F$, the larger portion being $SiHF_3$.

TABLE I

ANALYSES

Compound	Vapor density, 0° and 760 mm. Obs.	Calcd.	Cl, % Obs.	Calcd.	F, % Obs.	Calcd.
$SiHCl_2F$ Av.	119.17	119.06	59.53	59.55	16.12	15.98
$SiHClF_2$[a]	100.2	102.53				
$SiHF_3$	84.38	86.06			66.45	66.23

[a] Approximate value only. Too small amounts of this gas were obtained to purify it and to determine its physical properties and analysis precisely.

TABLE II

PHYSICAL PROPERTIES

Compound	M. p., °C.	B. p., °C.	ΔH cal. at b. p.	v. p. $\log p =$
$SiHCl_2F$	-149.5 ± 0.1	-18.4 ± 0.1	4838	$(-912.871/T) - 1.30853 \log T + 3.3170$
$SiHClF_2$[a]	above -144	approx. -50		
$SiHF_3$	-131.2 ± 0.1	-97.5 ± 0.1	3859	$(-1561.87/T) - 9.4206 \log T + 32.834$

In Tables III and IV are shown the vapor pressure measurements of $SiHCl_2F$ and $SiHF_3$ at various temperatures from which the boiling points, ΔH, and v. p. equations were determined.

TABLE III

VAPOR PRESSURES OF $SiHCl_2F$

T, °K.	Vapor pressure, mm.	T, °K.	Vapor pressure, mm.
177.3	13.3	241.9	464.4
181.3	17.3	247.2	575.0
189.8	30.8	251.5	673.7
212.0	111.6	253.8	748.4
223.2	197.0	257.5	855.5
229.4	267.0	260.4	944.2
235.3	347.6		

Samples of trifluorosilane were very carefully purified by repeated fractional distillation in the column, but reproducible measurements of its physical properties when it had been stored as a gas for any length of time could not be made. Hence the data shown in Tables I, II and IV were found on samples of the gas *freshly* distilled in the fractionating column as described.

TABLE IV

VAPOR PRESSURES OF $SiHF_3$ (MAY 4)

T, °K.	Vapor pressure, mm.	T, °K.	Vapor pressure, mm.
160.7	166.2	176.5	661.1
165.5	289.1	179.0	776.1
167.6	363.7	180.6	850.5
173.0	529.0	182.3	939.5

The vapor density of trifluorosilane was determined eight times and every determination was lower than the theoretical value of 86.06. Two consecutive samples in two different globes yielded the values 84.35 and 84.41.

To check the seemingly unstable character of trifluorosilane, the purified sample of gas from which the data in Table IV were obtained was allowed to remain in the vapor pressure apparatus for a period of days, and then a few vapor pressures were again measured. These data are shown in Table V (see Fig. 3). During the first eight days (from May 4 to May 12) the gas was kept solid in liquid nitrogen, except for twelve hours when it was liquefied under pressure in a carbon dioxide snow–acetone mixture. The sample was kept in liquid nitrogen from May 12 to June 6.

TABLE V

VAPOR PRESSURE OF TRIFLUOROSILANE

May 12		June 6	
T, °K.	Vapor pressure, mm.	T, °K.	Vapor pressure, mm.
152.8	100.4	156.9	161.4
161.6	304.2	165.8	329.9
173.9	579.3	172.0	501.7
176.5	670.3	177.3	707.2
		182.1	937.1

Samples of impure trifluorosilane which were stored in gas balloons for some months gave indications of traces of a compound which gave a high vapor pressure in the solid state and melted only under pressure. The mixture melted to form a "mush" rather than a clear solution. This is in accord with the characteristics of silicon tetrafluoride, which liquefies at −75° only under two atmospheres of pressure. This solid exerts a vapor pressure of 760 mm. at −95°. This is very close to the boiling point of trifluorosilane, which is −97.5°.

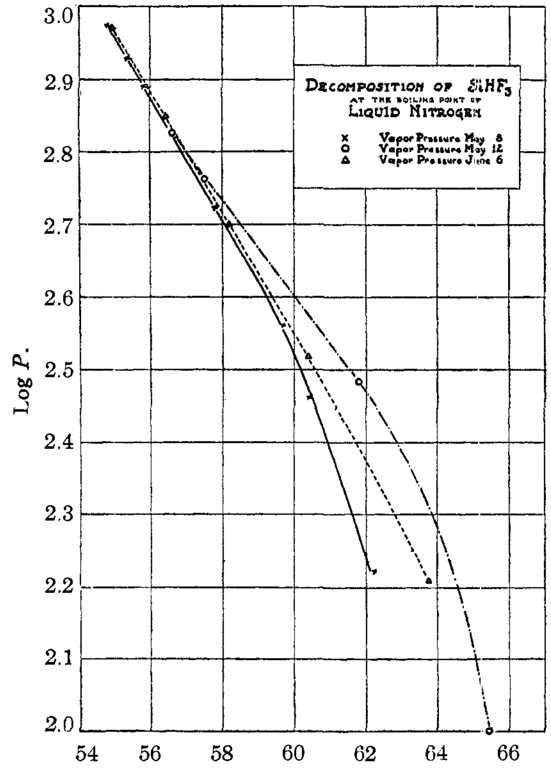

Fig. 3.

A small amount of gas was obtained which liquefied but did not freeze at liquid air temperature (−180 to −185°). Liquid nitrogen (−195°) solidified this gas. Silicon hydride boils at −112° and melts at −185°. The gas bubbled through mercury into the moist air of the room without giving a fog of hydrolytic products so characteristic of the chloro or fluoro gases of this series. Silane behaves in such a manner, indicating that silicon hydride was probably formed.

Discussion of Results

The action of antimony fluoride on trichlorosilane has been attempted by Ruff and Albert[3] as a means of preparation of trifluorosilane. They carried out the reaction in a closed tube with slight warming, reported the reaction to be

$$3SiHCl_3 + 4SbF_3 = 3SiF_4 + 3Sb + 3SbCl_3 + 3HCl$$

and so pursued the study no further.

The products of the reaction as carried out in this investigation, using antimony pentachloride as catalyst, yielded a larger proportion of trifluorosilane than of any other gaseous compound. As a slight trace of chlorine was found in the gases produced and traces of silicon tetrafluoride were also found, it might be assumed that the above reaction as found by Ruff and Albert may go to a slight extent under the conditions in this work. Ruff obtained no sign of $SiHCl_2F$ or $SiHClF_2$. While the latter was obtained in this investigation only in too small amounts to be isolated in a pure state, the former compound, $SiHCl_2F$, dichlorofluorosilane, was isolated and its physical properties were determined. The supercooling at the melting point, the vapor pressure curves, the analysis and a vapor density of the right order indicate that the compound was pure.

We first thought to identify trifluorosilane by checking the melting point and the boiling point of the gas with that obtained by Ruff and Albert. However, the values obtained were so at variance with their results that these constants were carefully redetermined.

Ruff and Albert prepared trifluorosilane by the reaction of trichlorosilane on stannic fluoride or titanic fluoride, according to the equations

$$3SnF_4 + 4SiHCl_3 = 4SiHF_3 + 3SnCl_4$$
$$3TiF_4 + 4SiHCl_3 = 4SiHF_3 + 3TiCl_4$$

They report that the vapor density of the gas thus obtained was too high as compared to the theoretical value of 86.06. By repeated fractionations and vapor pressure determinations they lowered the value from 90.20 to 85.47 and 87.01. This value was then considered to be acceptable. It would be interesting to know just what value Ruff would have obtained had he fractionated his trifluorosilane to constant vapor density. In this work, samples of trifluorosilane were repeatedly fractionally distilled, with results checking one another but below the theoretical value. The final values of 84.35 and 84.41 at 0° and 760 mm. are thus low as compared with the theoretical.

This result might indicate the presence of gaseous impurities of lower molecular weight but the sharp melting point obtained negatives this suggestion. The percentage of silane or difluorosilane (an unknown gaseous compound) necessary to lower the vapor density by the amount found would surely affect the sharpness of the melting point. Analysis, on the other hand, gives the correct percentage of fluorine, which also negatives the presence of silane. It must be concluded that the impurities, if any, in the trifluorosilane were very small in amount.

Table VI compares the constants as determined by Ruff and Albert with those obtained in the present investigation.

TABLE VI

MELTING AND BOILING POINTS OF TRIFLUOROSILANE

	Ruff and Albert	This investigation
Boiling point, °C.	− 80	− 97.5
Melting point, °C.	−110	−131.2 ± 0.1

Ruff does not state the method by which he obtained the melting point; however, the boiling point, as recorded, was measured by means of a toluene thermometer. The accuracy of such a method is open to question.

The value of the boiling point of trifluorosilane should lie somewhere between the boiling point of silane (−112°) and the temperature at which silicon tetrafluoride gives a vapor pressure of 760 mm. (−95.0°).[8]

On this basis, the value obtained by Ruff and Albert is obviously quite out of order, and the present value is more in line with the predicted value.

The decomposition (or dissociation) of trifluorosilane at liquid nitrogen temperatures is evidenced by the difference in the vapor pressure over a period of eight days as shown by the data in Tables IV and V and graphically in Fig. 3. That this may be reversible is indicated by the vapor pressure after standing for a longer time entirely at liquid nitrogen temperatures. Ruff has found that at an elevated temperature trifluorosilane decomposes according to the equation

$$4SiHF_3 = 2H_2 + 3SiF_4 + Si$$

As no sign of amorphous silicon was found in this work, the above reaction probably does not occur at liquid nitrogen temperatures. However, as both silane and silicon tetrafluoride were noted, the following reaction is hypothesized

$$4SiHF_3 = SiH_4 + 3SiF_4$$

As one of these compounds boils at a lower temperature than trifluorosilane and the other yields a vapor pressure of 760 mm. at a temperature above that of trifluorosilane, the peculiar nature of the vapor pressure curve after a period of days in liquid nitrogen may be explained. If this change were due to hydrolysis, hydrogen (uncondensable in liquid nitrogen) would be obtained. The pressure of the system, however, remained zero at liquid nitrogen temperatures. No visible evidence of hydrolysis in the form of silica hydrate or silicoformic anhydride was observed.

Summary

The fluorination of trichlorosilane by antimony trifluoride in the presence of antimony pentachloride yields relatively large amounts of trifluorosilane, $SiHCl_2F$ and small amounts of $SiHClF_2$, the last two being new gases.

Trifluorosilane has been found to be unstable even at liquid nitrogen temperatures.

Certain of the physical properties of these gases have been determined.

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[8] Ruff and Ascher, *Z. anorg. allgem. Chem.*, **196**, 413 (1931); Boucher, Fischer and Biltz, *ibid.*, **207**, 64 (1932).