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

III. Methyl Trichlorosilane and Its Fluorination Products[1]

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Introduction

Although compounds of the general formula $RSiX_3$, where R may be any aliphatic or aromatic radical and X may be either a halogen or other aliphatic or aromatic group or both, have been known for a long time, it has only been recently that enough attention has been focused on them to warrant a careful study of the properties of these compounds and their fluorination products.[3,4]

The purpose of the present investigation was to study the alkyl halogeno silanes containing one methyl group and three halogen atoms.

Experimental

Preparation.—Methyl trichlorosilane is best prepared by the slow addition of 2 moles of the methyl Grignard reagent in one liter of ether to 1000 ml. of silicon tetrachloride in 500 ml. of ether.

After the removal of the ether and silicon tetrachloride in a liquid type column the methyl chlorosilane is purified further by distillation at reduced pressure as if it were a gas. It has been discovered that it is difficult to separate slight amounts of dimethyl dichlorosilane from the main portion of methyl trichlorosilane since they boil about four degrees apart.

Fluorination.—There are three fluorination products of CH_3SiCl_3 possible, two being gases and the third a liquid at ordinary temperatures. As shown by the work of Booth and Carnell[3] and Booth and Halbedel[4] in this Laboratory, the substitution of a fluorine atom for a chlorine atom in an alkyl chlorosilane molecule lowers the boiling point of the compound approximately 33°. Therefore, the three fluorination products from methyl trichlorosilane should boil at +33, 0 and −33°. All of these as well as the trichloride itself were handled very easily as gases in the usual all-glass vacuum-tight apparatus developed in this Laboratory.[5,6]

Finely powdered antimony trifluoride was charged into the reservoir of the fluorinating flask and the system was evacuated. 100–200 g. of methyl trichlorosilane and about 15–20 g. of antimony pentachloride was added, and the pressure was allowed to rise to 760 mm. and the temperature to 45°, at which temperature antimony fluoride was added. The fluorination products were removed at such a rate that the pressure was maintained constant. At atmospheric pressure and at 45°, the products obtained were mostly the completely fluorinated compound, with a small amount of the methyl dichlorofluorosilane and only traces of methyl chlorodifluorosilane.

Upon successively lowering the operating pressure the temperature at which fluorination would take place was correspondingly lowered so that at 150–200 mm. the reaction would proceed although the generator flask and contents was immersed in an ice-bath. Reaction proceeded more rapidly and at a lower temperature in the presence of a catalyst, although the catalyst had little effect on the amounts of products obtained.

The first fluorination product, methyl dichlorofluorosilane, was reasonably easy to obtain in amounts large enough to study its properties. However, the rate of reaction of the second stage of fluorination was sufficiently high to cause the replacement of both residual chlorine atoms at once with the result that the second fluorination product was extremely difficult to obtain.

Fluorination with high speed stirring and dilution of the trichloride in the generator flask with an inert material, tetrachloroethylene at as low a pressure as possible (50 mm.) by having the flask and contents open directly through a large bore stopcock to five ampules cooled in liquid nitrogen, yielded only a trace of material corresponding to the methyl chlorodifluorosilane.

Twenty ml. of methyl dichlorofluorosilane was fluorinated with antimony fluoride. With the high speed stirring, low pressure and volatility of the methyl dichlorofluorosilane, most of it was carried over before fluorination could occur. The portion which had not been further fluorinated was again treated with antimony trifluoride, this time in the presence of a small amount of antimony pentachloride and at 600–650 mm. pressure.

The results in both cases were very much the same. Only traces of the desired product were obtained in each experiment. However, as expected, more of the completely fluorinated product was obtained when the higher pressure was employed.

The best yields of methyl chlorodifluorosilane by fluorination with antimony trifluoride were obtained under the following conditions. A pure sample of methyl trichlorosilane was fluorinated at atmospheric pressure in the presence of a catalyst. A water condenser was used to return higher boiling products to the flask for further fluorination and the flask and its contents were heated to 45° for a vigorous but smooth reaction. Although these were apparently the best conditions employed, the yields of the monochlorodifluoride were still so small as to be unprofitable.

Booth and Bozarth[5] and Booth and Dutton[6] were able to increase the yields of chlorofluoride obtained by passing the vapors of the halide over heated calcium fluoride pellets. Accordingly the vapors of methyl trichlorosilane were passed over calcium fluoride powder heated to 200°, at 700–750 mm. in a rotating copper tube, and the products were collected in the usual manner. Equal amounts of all three fluorination products were obtained from this experiment, but this amounted to less than one ml. in each case.

Purification.—The products obtained from fluorination were separated in a low temperature distillation column into rough fractions which were later redistilled at several different pressures to obtain the pure compounds, according to the usual technique in this Laboratory.

Purification of Methyl Trichlorosilane.—Due to the difficulty of obtaining methyl trichlorosilane free from dimethyl dichlorosilane, the material used for fluorination usually contained a small amount of dimethyl dichlorosilane. Upon fluorination this small amount of impurity would also fluorinate to give a product with a boiling point very near that of methyl chlorodifluorosilane. It was difficult to separate these two compounds, methyl chlorodifluorosilane and di-methyl difluorosilane, by distillation.

It was found that samples of pure methyl trichlorosilane could be prepared by preliminary fluorination at low pressures. A portion of the methyl trichlorosilane would be fluorinated and the small amount of dimethyl dichloro-

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[3] I, H. S. Booth and P. H. Carnell, THIS JOURNAL, **68**, 2650 (1946).

[4] II, H. S. Booth and H. S. Halbedel, *ibid.*, **68**, 2652 (1946).

[5] H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937); THIS JOURNAL, **61**, 2927 (1939).

[6] H. S. Booth and F. B. Dutton, *ibid.*, **61**, 2937 (1939).

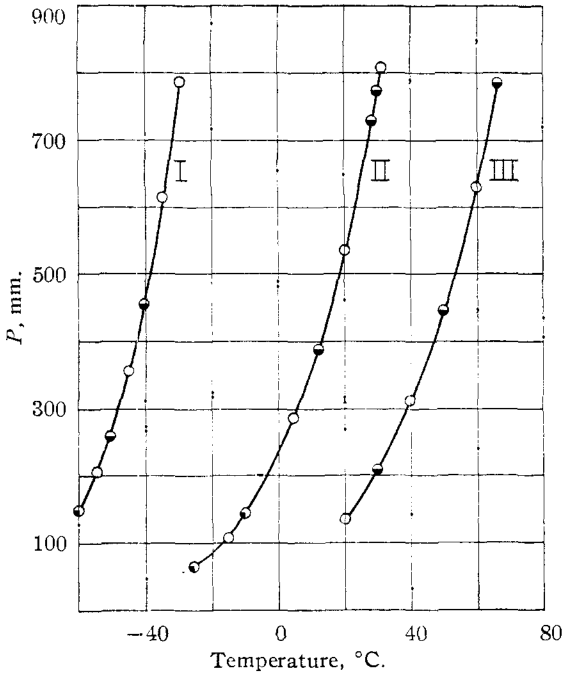

Fig. 1.—Vapor pressure of: I, CH_3SiF_3; II, CH_3SiFCl_2; III, CH_3SiCl_3: sample A, ○; sample B, ◒; coincident points, ◐.

silane was fluorinated also, but at the low pressures employed (50 mm.) the majority of the methyl trichlorosilane would be transferred over to the receiving section of the system unchanged. Analysis of this product after distillation showed that the methyl trichlorosilane so obtained was quite pure. The material so treated was then collected and used in subsequent fluorinations, and for study of its properties.

Analysis.—Samples for analysis were sealed off in thin-walled bulbs, weighed and then dropped into a standard flask containing a dilute solution of sodium hydroxide, and the flask and its contents were shaken until the bulb broke and the sample was completely hydrolyzed by the caustic solution. Chlorine was determined by the Volhard method[7] while fluorine was determined volumetrically by the lead chlorofluoride method.[8]

The presence of both carbon and silicon was demonstrated qualitatively.

Determination of Physical Properties.—The method used to determine the physical properties (Table I) of the various compounds was the same as previously described by workers in this Laboratory. All of the compounds obtained gave definite freezing points with sharp breaks in the time *vs.* temperature curve as recorded on a Leeds and Northrup recording potentiometer. This fact is of interest since the corresponding ethyl and propyl silicon compounds tended to form glasses instead of giving freezing points.

Some difficulty was encountered in the determination of the freezing point of methyl trifluorosilane. Extreme care had to be employed in liquefying this compound in the freezing point tube in order that the top portion would not become superheated before the bottom portion liquefied. If this took place, the pressure would build up rapidly from the warmer top material until it would be sufficient to blow out through the conical joint joining the top and bottom sections of the freezing point cell or else blow out through the escape manometer.

Of considerable interest is the fact that methyl trifluorosilane has an appreciable vapor pressure at its freezing point, −72.8°, amounting to about 84.6 mm. This phenomenon is rather rare, but is analogous to that with silicon tetrafluoride.[9]

The same general type of apparatus was used to measure the vapor pressure[9a] of the various pure samples as has been described previously. The temperature of the bath was measured by a five-junction copper-constantan thermocouple recorded on a Leeds-Northrup Speedomax recording controlling potentiometer which likewise controlled the bath temperature. With care temperatures could be maintained constant to within ±0.1°. Two samples were always run in order to obtain checks on purity. The two samples were always purified by distilling at two different pressures with freezing points run on each sample as a test of purity. Equations summarizing the vapor pressure data are given in Table I and shown graphically from data in Fig. 1.

Physical and Chemical Properties.—Methyl trichlorosilane and the products obtained from its fluorination with antimony fluoride, when pure, are colorless compounds and give easily reproducible physical constants.

While none of the compounds fume in moist air they hydrolyze very readily in moist air. The completely fluorinated product hydrolyzes so readily that the only distinguishable odor is that of hydrogen fluoride. The odor of the other compounds is irritating, pungent and disagreeable.

They are only slightly soluble in water but hydrolyze rapidly to give a gelatinous precipitate of so-called methyl siliconic acid. In the presence of alkali the hydrolysis proceeds rapidly forming the salt of the acid which is soluble in sodium hydroxide solution.

They are unreactive toward mercury and nichrome at temperatures up to the boiling points although the trichloro compound causes the usual "smutting" of mercury which is shown by many chlorides.

They all freeze to white crystalline solids. Methyl dichloromonofluorosilane exhibits a long range of supercooling, varying from 6 to 12°, depending upon the rate of cooling. Methyl trifluorosilane exhibits no supercooling, methyl trichlorosilane supercools about 2°.

An attempt was made to determine the possibility of coördination between sodium fluoride and methyl trifluorosilane. An ampule fitted with a stopcock and conical joint was partially filled with glass wool impregnated with sodium fluoride. This was evacuated and weighed, and about 10 ml. of methyl trifluorosilane condensed into the ampule. The ampule was set aside in an ice-bath for one week after which time the methyl trifluorosilane was pumped off and the ampule again weighed. A gain in weight would be an indication of coördination between the two compounds.

The gain in weight was very small in two different experiments so that unless the coördination compound which might be formed is quite unstable, it is doubtful if methyl trifluorosilane and sodium fluoride coördinate.

Discussion

While methyl trichlorosilane was first identified by G. Martin[10] in 1913, it was not until 1941 that Gilliam, Liebhafsky and Winslow[11] restudied this compound. They found a boiling point of 66.2–67° at 765.8 mm. and a freezing point of −90°, compared with 65.7° at 760 mm. and −77.8° found in this investigation. Their analysis and lower freezing point indicate the possible presence of a slight amount of impurity, probably, from

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[7] J. Volhard, *Ann.*, **190**, 1 (1878).

[8] F. P. Treadwell, and W. T. Hall, "Analytical Chemistry," Vol. II, 8th ed., John Wiley and Sons, New York, N. Y., 1935, p. 418.

[9] W. I. Patnode and J. Papish, *J. Phys. Chem.*, **34**, 1494 (1930).

[9a] For vapor pressure data consult original thesis at Western Reserve University Library.

[10] G. Martin, *Ber.*, **46**, 2442 (1913).

[11] W. F. Gilliam, H. A. Liebhafsky and A. F. Winslow, THIS JOURNAL, **63**, 801 (1941).

TABLE I

METHYL TRIHALOGENOSILANES

Formula	Percentage composition Chlorine Calcd.	Percentage composition Chlorine Found	Percentage composition Fluorine Calcd.	Percentage composition Fluorine Found	Mol. wt. Calcd.	Mol. wt. Found	F. p.,[a] °C.	B. p.,[b] °C.	Heat vap., cal.	Trouton's constant, cal./deg.	Vapor pressure, log(mm)	Random deviation Av.,[c] mm.	Random deviation Max., mm.
CH_3SiCl_3	71.19	71.16 71.19	...	...	149.4	152.7	−77.8	+65.7°	7240	21.3	$-1457/(T + 256) + 7410$	±2.6	−4.8
CH_3SiCl_2F	53.31	53.47	14.29	14.31	132.9	137.1	−98.7	+29.5	6740	22.3	$-1472.3/T + 7.7453$	±2.0	+5.8
CH_3SiClF_2	32.62	...	30.43	...	116.5	...	*ca.* −110	(−0.5°)[c]	..	..		...	...
CH_3SiF_3	...	...	56.97	56.80 57.02	100.0	101.0	−72.8	−30.2	5670	23.3	$-1238.1/T + 7.9752$	±1.8	−3.3

[a] ±0.2°. [b] ±0.1°. [c] Estimated.

their analysis, dimethyl dichlorosilane, which would not be surprising in view of the great difficulty of freeing methyl trichlorosilane completely from dimethyl dichlorosilane by distillation alone.

Methyl trichlorosilane cannot be prepared pure by the reaction of methylmagnesium bromide even with an excess of 5 moles of silicon tetrachloride to 1 mole of methylmagnesium bromide, inasmuch as small amounts of the dimethyl dichlorosilane are obtained and these cannot be separated from the monomethyl derivative by distillation in an ordinary column because the difference in boiling points for the two compounds is only 4°. Partial fluorination of the methyl trichlorosilane converts the trace of dimethyl dichlorosilane present, along with small amounts of the methyl trichlorosilane to fluorides which can be easily separated, yielding pure methyl trichlorosilane. While no difficulty was experienced in the preparation, purification and determination of physical constants of methyl trifluorosilane and methyl dichloromonofluorosilane, methyl monochlorodifluorosilane could not be obtained in large enough amounts free from contamination with dimethyl difluorosilane to enable a rigorous study of its physical properties to be made.

The smaller yields of the two chlorofluorides is in line with the results of the investigations of Booth and Carnell,[3] Booth and Halbedel[4] and Booth and Swinehart.[12] The increase of fluorine content of a molecule increases the rate of fluorination, so that the compound containing two fluorine atoms is much more difficult to isolate than is the compound containing only one fluorine atom, while the completely fluorinated product is very easily obtained.

The preferred method of obtaining optimum yields of methyl chlorodifluorosilane appears to lie in the use of calcium fluoride as the fluorinating agent at 200° or above. Approximately equal amounts of all three of the possible fluorination products can be obtained by this method.

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Summary

The fluorination of methyl trichlorosilane with antimony fluoride in the presence of a catalyst has been described. Identification of this compound as well as of two of its fluorination products previously unreported in the literature was also made. The vapor pressure, freezing point, boiling point, molecular weight, analysis, and a few chemical properties of these compounds were determined. An improved procedure for the purification of methyl trichlorosilane is described.

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(12) H. S. Booth and C. F. Swinehart, THIS JOURNAL, **57**, 1333 (1935).

(13) Original manuscript received July 18, 1945.