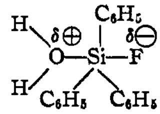
results which are identical within experimental error demonstrates that the rate of reaction of trityl fluoride is independent of *p*H.

Summary

The hydrolysis of triphenylmethyl fluoride in 50% water–50% acetone is insensitive to *p*H, is aided by *p*-alkyl substituents, and is strongly accelerated by increasing the per cent. of water. This indicates an intermediate with a more positive charge on the central carbon atom than the starting material and only three groups attached to it by predominantly covalent bonds.

The hydrolysis of triphenylsilyl fluoride in 50% water–50% acetone is more than a million times faster with hydroxide ion than with water, is retarded by *p*-alkyl substituents, and is weakly accelerated by increasing concentration of inert salt or per cent. of water. These observations are not consistent with the idea of a siliconium ion intermediate with a positive charge on silicon analogous to the "carbonium ion" intermediate in the hydrolysis of triphenylmethyl fluoride above. They indicate instead that the intermediate in the reaction with water has a less positive charge on the silicon atom than the starting material and is more closely represented by the following structure with pentacovalent silicon.



It appears that many reactions of organosilicon compounds may proceed through similar pentacovalent silicon intermediates. This constitutes an easy reaction path for displacements on silicon which is not available to displacements on carbon, since carbon lacks the ability to expand its valence shell to include more than eight electrons.

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

Methyldichlorosilane and its Fluorination Products[1]

BY HAROLD SIMMONS BOOTH AND ROGER LUCIEN JARRY

This investigation is a continuation of the work done in this Laboratory on the alkyl chloro silanes.[2–7] To the best of our knowledge no mention of the fluorination products, methylchlorofluorosilane and methyldifluorosilane, is made in the literature.

Experimental

Fluorination of Methyldichlorosilane.—Purification of the methyldichlorosilane[7a] prior to fluorination was accomplished by fractional distillation in a column having a total condensation head, and take-off of the design used by Whitmore and Lux. The fluorination was carried out by the Swarts reaction using antimony trifluoride as the fluorination agent, but without the use of a catalyst. The decision not to use a catalyst was made after preliminary tests indicated the possibility of chlorination of the methyldichlorosilane by antimony pentachloride; the yields of the two products without the usual catalyst were in sufficient quantity for purification and study. The apparatus and procedure for the fluorination were essentially the same as those described in previous papers from this Laboratory[8,9] with the modification of the direct condensation described by Booth and Spessard.[2] This modification entailed direct condensation in liquid-nitrogen-cooled ampules instead of the previous procedure of passing the fluorination products through a stripping column and refluxing. Since the problem of producing the intermediate fluorination product in this case was not considered difficult, as subsequent fluorinations proved, the fluorination was carried out at room temperature and atmospheric pressure. The average yields were about fifty per cent. fluorinated products, of which methyldifluorosilane comprised 70% and methyl chlorofluorosilane comprised 30%. The unfluorinated methyl dichlorosilane was repurified and refluorinated. The threshold fluorination temperature is below 20°.

Purification of the Fluorination Products.—The products of fluorination, methylchlorofluorosilane and methyldifluorosilane, were fractionally distilled in a low temperature distillation column of the type previously described[8] with the exception that the packing was a single Podbielniak Heligrid. The pressure control was a modification of the anticipator previously described[10] and will be given in a future publication. The cooling agent used in the column head was acetone cooled by a Dry Ice–acetone-bath. The methylchlorofluorosilane was distilled at pressures of 740 mm. and 300 mm. approximately; the methyl difluorosilane at 740 mm. and 250 mm. approximately.

Analysis.—Samples for analysis were taken in small sealed-glass bulbs.[11] Chlorine was determined by the Volhard method and fluorine by hydrolysis with standard base and back-titrating with standard acid with correction for the hydrochloric acid produced in the hydrolysis. The analysis of the methyldichlorosilane by the Volhard method, after hydrolysis with sodium hydroxide, gave consistently low results. To avoid this a modified Chablay method[12] was used. The results are shown in Table I.

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[1] From a thesis presented by Roger L. Jarry to the Graduate School of Western Reserve University, September, 1948, in partial fulfillment of the requirements for the degree of Master of Science, and based upon work done in connection with a research project sponsored by the Office of Naval Research.

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

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

[4] H. S. Booth and W. F. Martin, *ibid.*, **68**, 2655 (1946).

[5] H. S. Booth and J. F. Suttle, *ibid.*, **68**, 2658 (1946).

[6] H. S. Booth and D. R. Spessard, *ibid.*, **68**, 2660 (1946).

[7] H. S. Booth and A. A. Schwartz, *ibid.*, **68**, 2662 (1946).

[7a] Procured from the General Electric Company.

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

[9] H. S. Booth and W. C. Morris, THIS JOURNAL, **58**, 90 (1936).

[10] H. S. Booth and R. McNabney, *Ind. Eng. Chem., Anal. Ed.*, **16**, 131 (1944).

[11] H. S. Booth and W. D. Stillwell, THIS JOURNAL, **56**, 1531 (1934).

[12] H. S. Booth, W. L. Mong and P. E. Burchfield, *Ind. Eng. Chem.*, **24**, 328 (1932).

TABLE I

No.			1	2	3
Formula			CH_3HSiCl_2	$CH_3HSiClF$	CH_3HSiF_2
Composition, %	Cl	Calcd.	61.66	35.98	.....
		Found	61.30 61.60	35.80 35.80	....
	F	Calcd.	.....	19.27	46.29
		Found	....	19.28 19.29	45.80 45.94
Mol. wts.		Calcd.	115.02	98.56	82.10
		Found	......	99.2	83.2
Freezing pt., °C.			90.6 ± 0.5	−120.2 ± 0.5	−110.1 ± 0.5
Boiling pt., °C.			+40.4 ± 0.1	+1.2 ± 0.1	−35.6 ± 0.1
Liquid density, g./ml. at 0°C.			1.135	1.059	.....
Heat of vapn., cal.			6816	5933	5310
Trouton const., cal./deg.			21.7	21.6	22.3
Vapor pressure, log Pmm. =			(for 1) $-1489.4/T + 7.6304$ (for 2) $-1296.6/T + 7.6066$ (for 3) $-1160.4/T + 7.7655$		
Av. random dev., mm.			±4.3	±2.2	±3.1
Maximum dev., mm.			+8.7	+6.2	+5.5

Determination of Physical Constants.—Molecular weights of methylchlorofluorosilane and methyldifluorosilane were determined, during the course of distillation, by means of a gas density balance.[8]

The freezing points were determined as described by Booth and Martin.[13] Methyldichlorosilane supercooled about 3.6° the other two compounds showing no supercooling.

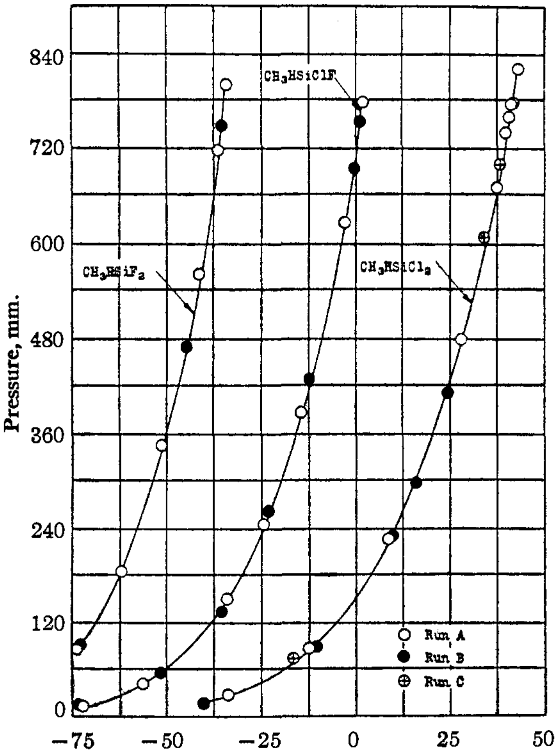

Fig. 1.—Plot of temperature *vs.* pressure for monomethyldichlorosilane and its fluorination products.

Liquid density of methyldichlorosilane and methylchlorofluorosilane were determined in a special type of pycnometer previously described.[14] The pycnometer was calibrated with freshly distilled mercury at 0° and the densities determined at the same temperature, allowance being made in the calculations for the free vapor space above the liquid.

Vapor pressures were determined as described by Booth, Elsey and Burchfield.[15]

The above determined physical properties are summarized in Table I. The vapor pressure data are given in the form of equations in Table I, and in Fig. 1 as a graph of the original data.[15a]

Physical and Chemical Properties.—These compounds fume in air and have sharp, irritating odors due to the hydrogen halides formed. They are readily hydrolyzed and dissolved by strong alkaline hydroxides with the evolution of hydrogen. They all smutted mercury, at room temperature, in time.

The lowering of the boiling point by the substitution of fluorine for chlorine followed the Swarts rule fairly closely; the substitution of the first fluorine lowered the boiling point by 39.3° while the substitution of the second fluorine lowered it 36.8°.

Trouton's constant showed an increase with increasing fluorine content which is to be expected with the more polar character of the fluorine.

Summary

Methyldichlorosilane has been fluorinated with antimony fluoride at room temperature and atmospheric pressure to yield the new compounds methyl chlorofluorosilane and methyldifluorosilane. Certain of the physical constants and chemical properties have been determined.

CLEVELAND 6, OHIO RECEIVED SEPTEMBER 7, 1948

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(13) H. S. Booth and D. R. Martin, *Chem. Rev.*, **33**, 2 (1943).

(14) H. S. Booth and C. Herrmann, THIS JOURNAL, **58**, 63 (1936).

(15) H. S. Booth, H. M. Elsey and P. E. Burchfield, *ibid.*, **57**, 2064 (1935).

(15a) For data for these vapor pressure curves consult original thesis at Western Reserve University Library.