In this range the density of the liquid and the vapor are almost identical and the deviations observed may be due to the fact that the reactor was in a mixture of the two phases. A summary of a series of computed values of the dielectric constant is given in Table I.

Acknowledgments.—We wish to express our thanks to Mr. Fred Denig, Vice President of Koppers Company, whose interest and support made the study possible, to R. C. Miller and J. W. Rex for their help in some of the experimental work.

Summary

The dielectric constant of water in equilibrium with its vapor has been determined in the temperature range from the normal boiling to the critical point. The data obtained may be expressed by the equation

$$D = 5321/T + 233.76 - 0.9297T + 0.001417T^2 - 0.0_68292T^3$$

where T represents absolute temperature ($273.1 + t$).

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

Cleavage of Silicones by Hydrogen Fluoride[1]

BY HAROLD SIMMONS BOOTH AND MEYER LOUIS FREEDMAN

The functional composition is a fundamental variable in silicone production. Empirical methods for estimating this functionality are limited to pure silicones.[2,3,4] Chemical methods, such as the determination of silicon–carbon ratios, may also fail when a variety of organic substituents are present or when the silicone is compounded with other materials. Studies made of reactions which produce silicone resins by hydrolysis[5] or oxidation[6] have been handicapped by the lack of a suitable analytical method for the products. This paper describes the reaction of silicones with anhydrous hydrogen fluoride and a new method of analysis of alkyl silicones based on this reaction.

The functional composition is fully expressed by a formulation of the monomeric siloxy units which would result, hypothetically, if every oxygen atom in the silicone molecule were split in two. Hydrofluorination effects such a depolymerization. Many organofluorosilanes have been synthesized and accurately characterized.[7–12] Table I gives the relationship for the methyl silicones. On a mole basis, the composition of a methylfluorosilane mixture is the same as the formulation, in equivalent siloxy units, of the hydrofluorinated methyl silicone. The weight of methyl silicone in a compounded sample is the sum of the siloxy unit weights. These can be calculated from the yield of methylfluorosilanes obtained by the new hydrofluorination method described in this paper.

TABLE I

METHYLFLUOROSILANES AND THEIR EQUIVALENT SILOXY UNITS

Methylfluorosilane	Conversion factor	Equivalent siloxy unit	Unit symbol	Unit weight	Unit silicon, %
Me_3SiF	0.881	$Me_3SiO_{1/2}$	M	81.16	34.5
Me_2SiF_2	.772	$Me_2SiO_{2/2}$	D	74.13	37.8
$MeSiF_3$	.671	$MeSiO_{3/2}$	T	67.09	41.8

The cleavage of silicones by hydrofluoric acid in sulfuric acid solution has occasionally been used to synthesize organofluorosilanes.[13,14,15] Yields and reaction rates were low. Liquid anhydrous hydrogen fluoride, as suggested by a theoretical study, was found to convert methyl silicones rapidly and quantitatively into the equivalent methylfluorosilanes. The reaction is one of solvolysis.

$$(Si—O—Si) + 3HF \longrightarrow 2(Si—F) + H_2O{\cdot}HF$$

Apparatus

The bar stock reactor valve (A of Fig. 1) is connected by Saran tubing and forged brass flare type fittings, either to the 10-g. capacity hydrogen fluoride ampule (B), to a vacuum pump, or to a nitrogen supply as needed. The doorknob shaped copper reactor (C) screws into the reactor head (D), seating on a Saran gasket. The reactor head was machined from a 3-inch length of hexagonal steel bar, 1 inch in diameter. A nickel induction tube extends from the upper chamber of the reactor head into the reactor. The Saran safety manometer (E) dips 10 cm. into a reservoir of mercury (not shown) in order to obtain pressure greater than atmospheric in the reaction. The absorption tube (F) is a 3 foot length of $^1/_2$ inch i. d. nickel tubing. Moisture and hydrogen fluoride are removed from the generated gases by a 35-g. charge of Drierite

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[1] From a thesis presented by Meyer Louis Freedman to the Graduate School of Western Reserve University, September, 1949, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, and based upon work done in connection with a research project sponsored by the Office of Naval Research.

[2] George F. Roedel, *Anal. Chem.*, **20**, 705 (1948).

[3] R. O. Sauer, THIS JOURNAL, **68**, 954 (1946).

[4] D. F. Wilcock, *ibid.*, **69**, 477 (1947).

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

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

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

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

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

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

[13] C. A. Burkhard, E. G. Rochow, H. S. Booth and J. Hartt, *Chem. Revs.*, **41**, 97 (1947).

[14] H. J. Emeléus and C. J. Wilkins, *J. Chem. Soc.*, 454 (1944).

[15] E. A. Flood, THIS JOURNAL, **55**, 1735 (1933).

granules in the front half of the tube. Residual hydrogen fluoride is removed by 40 g. of porous sodium fluoride pellets[16] in the rear section. The Drierite can be partially regenerated by evacuation so that one filling of the tube suffices for several runs. The glass trap (G) is sealed on with de Khotinsky wax. Its safety manometer (H) dips just below the surface of mercury in a wide bottle.

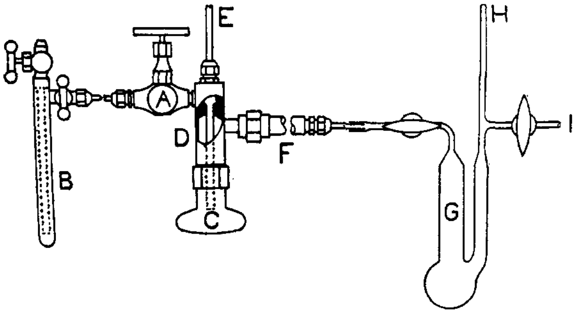

Fig. 1.

Reaction products are distilled from the trap into a fractionating column through (I) for analysis. Anhydrous conditions must be maintained as described in the procedures for working with fluoride gases.[17] The column used in this research was constructed of a 5-foot length of 2.5 mm. i. d. soft glass tubing containing a single spiral of 0.5 mm. nickel wire fitting tightly. This tube was enclosed in sections of strip-silvered vacuum jackets and capped by a Dewar cylinder at each end. Insulation was augmented by blowing dry chilled air down the annular space between the column and jackets. Construction and operation of the gas fractionating system followed, in general, the detailed descriptions given by Booth and Bozarth.[17] Any analytical gas fractionating column of low gas volume and low liquid hold-up and of moderate efficiency should be satisfactory for the separation.

Methyltrifluorosilane was distilled into an evacuated calibrated bulb contained in a thermostat for measurement, but the higher boiling components were condensed into weighing ampules.[18]

Procedure

Five grams of anhydrous copper sulfate is placed in the reactor (C) and the weighed silicone sample, approximately 5 g., is added. The apparatus is assembled, tested for leaks by partial evacuation, and the reactor cooled in a mixture of Dry-Ice and acetone while 10 g. of anhydrous hydrogen fluoride is distilled into the reactor from the measuring ampule (B). As the reactor warms to room temperature, gaseous products are evolved and pass through the absorption tube (F) and freeze out in the trap (G) cooled by liquid nitrogen. The rate of gas evolution is controlled by the rate at which the reactor is warmed. Too rapid generation of gases is evidenced by boiling of the liquid nitrogen and quick heating of the absorption tube. This may result in carry-over of hydrogen fluoride into the trap. Finally, a water-bath is placed around the reactor and slowly heated nearly to boiling. Dry nitrogen is then passed through the reactor for fifteen minutes at a rate of 4 to 5 l. per hour, to sweep residual gases through the trap. The nitrogen escapes through the manometer (H). The entire process requires about forty-five minutes.

The stopcock between trap and absorption tube is now closed and the liquid nitrogen cooled trap is evacuated through (I) to a pressure of 1 mm. This removes nitrogen and condensed air. Meanwhile, the reactor residue is dissolved in hot water and inspected for insoluble, unreacted silicone. The reaction products are transferred from the trap to the fractionating column for analysis. The final pressure in the trap is used to calculate a correction for residual vapor in the trap. Five ml. of dry acetone was used in the stillpot of the column as a chaser, to facilitate fractionation.

Experimental

Preliminary experimentation developed the use of copper sulfate and Drierite to prevent plugging of the sodium fluoride absorption tube by moisture. A mixture of Dry Ice and acetone was used to cool the product trap in the first runs made on the samples of pure methylsiloxanes (Table II). Corrections were calculated for evaporation losses and vapor residues. The evaporation losses were later eliminated, and the trap residue corrections minimized, by using liquid nitrogen.

TABLE II

HYDROFLUORINATION OF PURE METHYLSILOXANES

Methylsiloxane sample	Sample weight, g.	Methylfluorosilanes obtained, g. F-1	F-2	F-3	Calcd. losses, g.	Theor. yield, g.	Recov., % calcd.
$(Me_3Si)_2O$	5.940	6.570			0.200	6.75	100.3
$(Me_2SiO)_4$	5.974		7.412		.268	7.70	99.8
$(Me_2SiO)_5$	5.211		6.529		.235	6.75	100.2
$(MeSiO_{1.5})$	2.90			4.27	.042	4.32	99.8

The hydrofluorination products were identified by analysis and by physical methods similar to those previously described.[12,13]

The composition of impure methyl silicones was determined by the final standard hydrofluorination procedure (Table IV). The calculated silicon contents were compared to the values found by chemical analysis using a Parr bomb.[19] The impure samples of linear polymers were obtained in amounts too small for purification. The resin solution residue was obtained by vacuum distillation from solution in a butanol–toluene mixture. It was estimated to contain 4% of residual solvent.

A silicone sample kit, distributed by the General Electric Co., was the source of many of the commercial samples. The silicone rubber samples (Table V) were prepared for hydrofluorination by cutting into pieces about 1 mm. thick. The glass cloth laminate (Table VI) was crushed to pulp with a pair of pliers. These compounded silicones reacted smoothly by the standard procedure, and the inert fillers were left completely dispersed in the reactor residues. Silicates and silica fillers were converted to the corresponding fluorides.

Application to Other Silicones

Samples of hexaethylcyclotrisiloxane and *n*-butyl silicone resin reacted with liquid hydrogen fluoride rapidly and completely. The standard hydrofluorination procedure was followed, except that dry nitrogen was passed through the reactor for several hours instead of fifteen minutes. The yields of the pure *n*-alkylfluorosilanes here were several per cent. below theoretical. The *n*-butyl silicone did not produce a detectable amount of butane, even when the reaction time was prolonged to twenty-four hours.

A tetramethylcyclotetrasiloxane sample required an excess of 10 g. of hydrogen fluoride per gram of sample for complete reaction. The silyl hydrogen was largely replaced by fluorine during the hydrofluorination. The chief products were hydrogen and methyltrifluorosilane. Copper sul-

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[16] Obtained through the courtesy of the Harshaw Chemical Co.

[17] H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

[18] H. S. Booth and C. V. Herrmann, THIS JOURNAL, **58**, 63 (1936).

[19] J. A. McHard, P. C. Servais and H. A. Clark, *Anal. Chem.*, **20**, 325 (1948).

TABLE III

IDENTIFICATION OF CLEAVAGE PRODUCTS

	Boiling pt., °C.		Freezing pt., °C.		Molecular wt.		Fluorine, %	
	Obsd.	Req.[5]	Obsd.	Req.[5]	Found	Calcd.	Found	Calcd.
Me_3SiF	16	16.4	−74	−74.3	92.2	92.18	20.6	20.61
Me_2SiF_2	3	2.7	−87	−87.5	96.4	96.14	39.3	39.52
$MeSiF_3$	−31	−30.2	−73	−72.8	..	100.01	57.0	56.97

TABLE IV

CLEAVAGE OF METHYL SILICONES

		Methyl silicone oil	Linear polymers MD_2M	Linear polymers MD_4M	Resin solution residue
Sample wt., g.		4.966	5.680	6.010	4.664
Methylfluorosilane yields, g.	$(CH_3)_3SiF$	0.178	2.854	2.232	
	$(CH_3)_2SiF_2$	6.148	4.103	5.243	0.812
	$(CH_3)SiF_3$				5.690
Composition mole %, calcd.	M	3.0	42.1	30.8	
	D	97.0	57.9	69.2	12.9
	T				87.1
R/Si ratic, calcd.		2.030	2.421	2.308	1.129
Recovery of silicone, %, calcd.		98.6	99.8	100.0	95.6
Composition wt. %, calcd.	M	3.3	44.3	32.6	
	D	96.7	55.7	67.4	14.0
	T				86.0
Silicon, %, calcd.		37.7	36.4	36.8	39.6
Silicon, %, found		37.7	36.4	36.9	39.6

TABLE V

CLEAVAGE OF SILICONE RUBBER SAMPLES

	Crude gum rubber	Extruded channel gasket	Flat molded rubber	Molded rubber tube	Compression plug
Sample wt., g.	6.913	4.825	6.277	5.569	5.767
$(CH_3)_2SiF_2$ yield, g.	8.794	2.013	3.028	2.668	2.165
Methyl silicone in sample, % calcd.	98.2	32.1	37.3	36.9	28.9

TABLE VI

CLEAVAGE OF COMMERCIAL SILICONE SAMPLES

		Oil light	Oil heavy	Glass laminate	Grease lub.	Resin solution	Grease stopcock
Sample wt., g.		4.914	5.150	10.812	6.444	9.768	4.958
Methylfluorosilane yield, g.	$(CH_3)_3SiF$	0.600					
	$(CH_3)_2SiF_2$	5.315	6.500	0.250	5.973	2.144	5.750
	$(CH_3)SiF_3$	0.398	0.159	3.790	0.580	3.710	
Composition mole %, calcd.	M	9.9					
	D	84.1	97.7	6.4	91.5	37.5	100.0
	T	6.0	2.3	93.6	8.5	62.5	
R/Si ratio, calcd.		2.039	1.977	1.064	1.915	1.375	2.000
Methyl silicone in sample, %		99.8	99.7	25.2	77.7	42.5	89.5

fate could not be used because it is reduced to metallic copper.

A sample of pure silica yielded only 6% of the theoretical amount of silicon tetrafluoride, the rest having apparently been absorbed by the porous sodium fluoride pellets.

Silicon oxychloride did not react immediately when treated by the standard procedure. Unchanged sample was left in the reactor after evaporation of the hydrogen fluoride. However, hydrofluorination was complete when the reaction time was prolonged to twenty-four hours by cooling the reactor in an ice-bath. Since only a trace of liquid product was obtained, silicon tetrafluoride must have been the chief product. A similar slow reaction was obtained with octaphenylcyclotetrasiloxane. A reaction time of three days was needed for complete hydrofluorination. Only benzene, silicon tetrafluoride, and a little tar were produced. Phenylsilsesquisiloxane reacted with the hydrogen fluoride more rapidly and split off benzene less readily. A sample of 2,4,6,8-tetramethyltetraphenylcyclotetrasiloxane reacted rapidly, but gave large yields of methyltrifluorosilane and benzene. Some of the copper sulfate was reduced to metallic copper in all of these runs with phenyl silicones.

Discussion

The results given here are typical of the analyses obtained in one hundred and two runs, in which variables of materials and conditions were tested.

This hydrofluorination method was found to be primarily effective for the analysis of pure or compounded methyl silicones. It was also applied successfully to other *n*-alkyl silicones which yielded volatile alkylfluorosilanes. Hydrofluorination of mixed silicones, in which hydrogen or phenyl groups were substituted on the same silicon atom as a methyl group, produced methyltrifluorosilane by secondary reaction. Phenyl silicones could not be analyzed by this method. The phenylfluorosilanes which were formed by the initial cleavage underwent further solvolysis to give benzene and silicon tetrafluoride. The failure to determine silica due to absorption of silicon tetrafluoride on the sodium fluoride pellets is another restriction of the method.

Duplicate determinations on the pure methylsiloxane samples checked within 0.5%. Hydrofluorination of known mixtures of these pure siloxanes also gave results within 0.5% of the theoretical values. However, duplicate determinations made on more complex silicones varied by as much as 1.0%. The accuracy of this method would be expected to depend primarily on the efficiency of the fractionating column.

Precaution.—Liquid anhydrous hydrogen fluoride produces severe burns on contact with the skin. Proper protective measures should be employed in handling this material.

Acknowledgment.—The samples of pure siloxanes and other silicones were made available for this research through the kindness of the Silicone Division, of the General Electric Co. and the Dow-Corning Company. The research was part of a project sponsored by the Office of Naval Research, U. S. Navy.

Summary

Methyl silicones, and other *n*-alkyl silicones were found to be rapidly and completely converted to their equivalent alkylfluorosilanes by reaction with liquid, anhydrous hydrogen fluoride in the presence of anhydrous copper sulfate at atmospheric pressure. The reaction was developed into an analytical method for determining the silicone content and functional composition of methyl silicone products. The gaseous methyl fluorosilanes are first contacted with Drierite granules, to remove moisture, and then with sodium fluoride pellets, to remove residual hydrogen fluoride. Finally, the gases are condensed and separated into pure methylfluorosilane components by quantitative fractional distillation.

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Isomerization Accompanying Alkylation. VI. Reaction of Isobutylene and 2-Butene with Benzene[1,2]

BY HERMAN PINES, J. D. LAZERTE[3,4] AND V. N. IPATIEFF

The catalytic alkylation of benzene with butylenes at elevated temperatures and pressures has heretofore not been investigated with the purpose of establishing the structure of the compounds produced. The object of the present study was to determine whether such an alkylation is accompanied by a skeletal isomerization of the alkyl group. For that reason 2-butene and isobutylene was treated with benzene in the presence of catalysts such as silico-phosphoric acid, alumina–zinc chloride and silica–alumina. The reaction was carried out in a flow type apparatus, at a temperature ranging from 200–380°, and at a pressure of 40 atmospheres using about 2.5 moles of benzene per mole of olefins.

Silico-phosphoric acid catalyzed the reaction between benzene and 2-butene; 62–75 mole per cent. of monobutylbenzene was obtained, based on olefins reacted. The remainder of the 2-butene was converted to octylenes, di-butylbenzene and higher boiling hydrocarbons. The monobutylbenzene fraction contained besides *s*-butylbenzene, 12–21% *t*-butylbenzene. The quantitative composition of the monobutylbenzenes was determined by means of infrared spectral analysis. The presence of *t*-butylbenzene was further substantiated by the isolation of *t*-butylbenzenesulfonamide, when the sulfonamides of monobutylated benzene were fractionally crystallized.

The reaction of benzene with isobutylene also yielded a mixture of *s*- and *t*-butylbenzene. In the experiment in which isobutylene was used, the degree of polymerization was more pronounced than in similar experiments carried out with 2-butene.

In the reaction between benzene and 2-butene, zinc chloride-alumina catalyst (25% by wt. zinc chloride and 75% aluminum oxide) caused only a small amount of isomerization to accompany alkylation, while silica–alumina catalyst produced a monobutylbenzene fraction free of *t*-butylbenzene. The experimental conditions and results obtained of the reaction of benzene with butylenes are summarized in Table I.

Since alkylation and dealkylation reactions are closely related, a study of the latter reaction was undertaken to ascertain if skeletal isomerization accompanied dealkylation. The dealkylation of di-*s*-butylbenzene or di-*t*-butylbenzene in the presence of benzene took place at temperatures of 300–350° to yield monobutylbenzenes consisting of both *s*- and *t*-butylbenzene. Catalysts used in these reactions were silicophosphoric acid and zinc chloride–alumina. The experimental data are summarized in Table II.

The use of orthophosphoric acid as a dealkylation catalyst was described previously by Ipatieff and Corson,[5] who reported that di-*t*-butylbenzene and benzene at 300–325° under pressure was con-

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[1] Presented before the Division of Petroleum Chemistry at the Meeting of the American Chemical Society, September, 1949, Atlantic City, N. J.

[2] For paper V of these series, see V. N. Ipatieff, E. E. Meisinger and H. Pines, THIS JOURNAL, **72**, 2772 (1950).

[3] Universal Oil Products Company Predoctorate Fellow 1946–1949.

[4] This paper has been constructed from a portion of the thesis submitted in March, 1949, in partial fulfillment of the requirements for the degree of Ph.D. in Chemistry.

[5] V. N. Ipatieff and B. B. Corson, THIS JOURNAL, **59**, 1417 (1937).