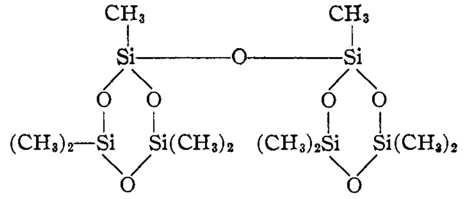
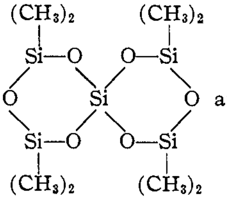
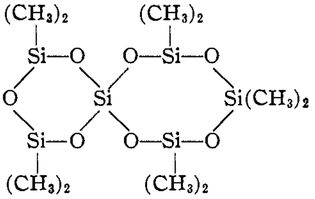


No attempt was made to determine which of several isomeric structures corresponded to the compounds actually obtained, since at present no simple straightforward means is available by which this might be done. Compound F had too low a solubility in any of numerous solvents tried to permit determination of its molecular weight by the cryoscopic method. Hence it was not completely characterized. The analytical data show that it is $[CH_3SiO_{3/2}]_{2n}$, where n is some integer. Thus each of its silicon atoms is bonded to only one methyl group. Its solubility behavior and the fact that it sublimes without melting, is indicative of a structure which can fit very compactly into the crystal lattice.

Methylpolysiloxanes resulting from co-hydrolysis of dimethyldichlorosilane and silicon tetrachloride have some silicon atoms which are bonded to two methyl groups and two oxygen atoms and some which are bonded to four oxygen atoms. If the methyl groups remain attached to the silicon atoms during thermal rearrangement, the products will likewise have silicon atoms bonded either to two methyl groups and two oxygen atoms or to four oxygen atoms. On this basis, compounds G and H, $(CH_3)_8Si_5O_6$ and $(CH_3)_{10}Si_6O_7$, respectively, are octamethylspiro[5.5]pentasiloxane and decamethylspiro[5.7]hexasiloxane



and



Compounds I and J cannot be assigned definite structural formulas because in each case two isomeric structures correspond to the empirical formula found. As before, no attempt was made to establish which of the two possible isomeric structures corresponded to the compound actually obtained.

Acknowledgment.—The analytical data listed in Tables I and II were obtained by Mr. L. B. Bronk of this Laboratory.

Summary

1. Six methylpolycyclopolysiloxanes have been prepared by thermal rearrangement of a co-hydrolysis product of dimethyldichlorosilane and methyltrichlorosilane.

2. Four methylspiropolysiloxanes have been prepared by thermal rearrangement of a co-hydrolysis product of dimethyldichlorosilane and silicon tetrachloride.

SCHENECTADY, N. Y. RECEIVED SEPTEMBER 11, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Methylpolysiloxanes[1]

BY WINTON PATNODE AND DONALD F. WILCOCK

The availability of the three methylchlorosilanes, $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$ and CH_3SiCl_3,[2] has prompted a further study of their products of hydrolysis, the methylpolysiloxanes and the methylchloropolysiloxanes. Sauer[3] has already described trimethyl silanol and its dehydration product, hexamethyldisiloxane, both derived from trimethylchlorosilane. Hyde and Delong[4] obtained a complex mixture of compounds by the hydrolysis of dimethyldichlorosilane, but did not report the isolation and purification of the compounds present, aside from an apparently cyclic trimer, $((CH_3)_2SiO)_3$. Rochow and Gilliam[5] described the resinous products produced by the co-hydrolysis of dimethyldichlorosilane and methyltrichlorosilane.

We have now studied more fully the methylpolysiloxanes derived from the methylchlorosilanes, as well as some of the reactions by which the polymers may be rearranged. The methylchlorosilanes used in this work were prepared by the reaction of methyl chloride on silicon according to the method of Rochow.[6] They were isolated from the reaction mixture by fractional distillation.

Hydrolysis of Dimethyldichlorosilane

When dimethyldichlorosilane is mixed with a large volume of water, hydrolysis occurs exothermally to form hydrochloric acid and an immiscible, colorless oil having an empirical composition close to $(CH_3)_2SiO$. Examination of this oil reveals that it contains cyclic polymers of the

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[1] The nomenclature used throughout this paper follows the system proposed by R. O. Sauer, *J. Chem. Ed.*, **21**, 303 (1944).

[2] W. F. Gilliam, H. A. Liebhafsky and A. F. Winslow, THIS JOURNAL, **63**, 801 (1941); A. G. Taylor and B. V. deG. Walden, *ibid.*, **66**, 842 (1944); W. F. Gilliam and R. O. Sauer, *ibid.*, **66**, 1793 (1944).

[3] R. O. Sauer, *ibid.*, **66**, 1707 (1944).

[4] J. F. Hyde and R. C. Delong, *ibid.*, **63**, 1194 (1941).

[5] E. G. Rochow and W. F. Gilliam, *ibid.*, **63**, 798 (1941).

[6] E. G. Rochow, *ibid.*, **67**, 963 (1945).

composition $[(CH_3)_2SiO]_x$ where x is an integer greater than 2. The diol $(CH_3)_2Si(OH)_2$ has not been found although there are indications of polymeric diols of the type $HO[(CH_3)_2SiO]_xSi(CH_3)_2OH$ where x is large, and which tend to condense by dehydration with the passage of time, thus forming still larger polymers and droplets of water. The monomer $(CH_3)_2SiO$ has not been encountered nor has the dimer $[(CH_3)_2SiO]_2$ been found. But beginning with the trimer $[(CH_3)_2SiO]_3$, a series of cyclic polymers increasing by units of $(CH_3)_2SiO$ have been isolated up to the decamer and, no doubt, still higher members of the series may be isolated.

The relative proportions of the compounds formed by hydrolysis of dimethyldichlorosilane depend upon the conditions of hydrolysis. There is a very strong tendency toward the formation of the tetramer, $[(CH_3)_2SiO]_4$, which is generally produced in the greatest amount. As the molecular weights of the polymers increase, the proportion of any one compound decreases rapidly, thus making the isolation of such compounds laborious. The boiling points also increase rapidly and fractional distillation of the mixture as a means of separation becomes impractical. The proportion of relatively volatile compounds may be changed between limits at will, however, by hydrolysis in the presence of solvents and by the choice of hydrolysis media. In general it may be said that hydrolysis in strongly acid media increases the proportion of material of low molecular weight, as does the use of a water-miscible solvent, while hydrolysis in alkaline media has the opposite effect although there are exceptions to the general rule.

A. Complete Hydrolysis.—The hydrolysis of approximately 4 liters of dimethyldichlorosilane by adding it slowly to 12 liters of vigorously stirred water at a temperature of 15–20° yielded something over 2 liters of an immiscible, colorless, oily liquid. On fractional distillation at atmospheric pressure and at 20 mm., polymers of $(CH_3)_2SiO$ were isolated in the following proportions: trimer, 0.5%; tetramer, 42.0%; pentamer, 6.7%; hexamer, 1.6%; and still-pot residue, 49.2%. The heptamer, octamer and nonamer also listed in Table I were isolated by fractionating high-boiling still-pot residues combined from several preparations. The compounds were identified by the method of preparation, by the constant boiling points, by cryoscopic measurement of molecular weight in cyclohexane, and in a few cases by chemical analysis.

Anal. Calcd. for $(CH_3)_2SiO$: C, 32.38; H, 8.16; Si, 37.86; mol. wts. for trimer to nonamer, 222, 296, 371, 444, 519, 593, 667. Found: for trimer, C, 32.39; H, 8.03; Si, 37.87; for tetramer, C, 32.32; H, 7.90; Si, 37.90; for heptamer, C, 32.06; H, 7.96; Si, 37.45; mol. wts. for trimer to nonamer, 219, 304, 368, 438, 518, 617, 656.

TABLE I

CYCLIC METHYLPOLYSILOXANES

Compound	B. p., °C. 760 mm.	B. p., °C. 20 mm.	M. p., °C.	$d^{20°}$, g./cc.	n^{D}_{20}
$[(CH_3)_2SiO]_3$	134	...	64	....	....
$[\quad]_4$	175	74	17.5	0.9558	1.3968
$[\quad]_5$	210	101	−38	.9593	1.3982
$[\quad]_6$	245	128	− 3	.9672	1.4015
$[\quad]_7$	...	154	−26	.9730	1.4040
$[\quad]_8$	...	175	*ca.* 30	....	1.4060
$[\quad]_9$	...	*ca.* 188	..	....	1.4070

B. Complete Hydrolysis in Different Media.—In order to observe the effect of the hydrolysis medium on the nature of the products of hydrolysis, 200 cc. of dimethyldichlorosilane, with or without a solvent as listed in Table II, was introduced below the surface of cooled, vigorously stirred hydrolysis medium held between 10 and 20°. The immiscible reaction product was separated from the hydrolysis medium and distilled out of a Claisen flask, gradually lowering the pressure to 1 mm. and increasing the still-pot temperature to 200°. After distillation had ceased under these final conditions, the volume of distillate, exclusive of the solvent, was measured and calculated as per cent. of the total polymer.

TABLE II

Solvent	Hydrolysis medium	Per cent. distilled
None	600 cc. Water	57
None	600 cc. 6 *N* HCl	71
None	600 cc. 6 *N* NH_4OH	37
400 cc. Ether	400 cc. Water	98
200 cc. Ether	400 cc. Water	97
100 cc. Ether	500 cc. Water	77
200 cc. *n*-Heptane	400 cc. Water	52
400 cc. Ether	200 cc. 28% NH_4OH 800 g. Ice	20

C. Partial Hydrolysis.—Dimethyldichlorosilane may be partially hydrolyzed to form methylchloropolysiloxanes of the type $Cl[Si(CH_3)_2O]_xSi(CH_3)_2Cl$ where x is an integer equal to or greater than 1. Although such compounds are formed when less than the stoichiometric quantity of water is added dimethyldichlorosilane, the yields are poor. Much better yields result when the reaction is carried out in a 1-phase system through the use of mutual solvents for the starting materials and products. The methylchloropolysiloxanes of low molecular weight may be separated from the reaction mixture by fractional distillation, but those of high molecular weight are very difficult to isolate. The first five members of the series have been isolated and are listed in Table III.

The partial hydrolysis of dimethyldichlorosilane to form the methylchloropolysiloxanes was carried out as follows: A mixture of 2 liters (16.6 moles) of dimethyldichlorosilane and 2 liters of ether was placed in a 3-necked flask of 5-liter capacity which was fitted with a high-speed stirrer, a reflux condenser cooled with solid carbon dioxide and acetone, and a dropping funnel whose capillary tip dipped below the surface of the liquid close to the blades of stirrer. One hundred fifty cc. (8.3 moles) of water mixed with an equal volume of dioxane was slowly added through the dropping funnel to the vigorously stirred mixture of ether and dimethyldichlorosilane. The temperature of the mixture rose slightly at first, but as it became saturated with hydrogen chloride the temperature fell below that of the room and hydrogen chloride boiled out, carrying some condensable vapor which was returned to the flask by the reflux condenser. The aqueous solution emerging from the dropping funnel apparently dissolved instantly, since two liquid phases were not observed. After all of the water and dioxane had been added, the reaction mixture was fractionally distilled. Besides the ether and dioxane, which were discarded the liquid yielded the following products in the proportions noted: $(CH_3)_2SiCl_2$ (22%), $Cl(CH_3)_2SiOSi(CH_3)_2Cl$ (28%), $Cl[(CH_3)_2SiO]_2Si(CH_3)_2Cl$ (24%), $Cl[(CH_3)_2SiO]_3Si(CH_3)_2Cl$ (15%), $Cl[(CH_3)_2SiO]_4Si(CH_3)_2Cl$ (6%), $Cl[(CH_3)_2SiO]_5Si(CH_3)_2Cl$ (3%), and still-pot residue (2%). No cyclic dimethylpolysiloxanes were found. The products were identified by the method of preparation, by the constancy and regularity of boiling points, and by analysis for hydrolyzable chlorine. The analyses were carried out by dissolving weighed samples in ether, shaking with water, and titrating the liberated hydrochloric acid with sodium hydroxide. The per cent. chlorine calculated and found for the first five compounds of the series are: Calcd. 34.93, 25.59, 20.19, 16.67, 14.20. Found, 34.89, 25.45, 20.12, 16.69, 14.38. Analyses for the other elements and measurement of mol. wt. were deemed unnecessary for identification.

TABLE III

METHYLCHLOROPOLYSILOXANES

Compound	B. p., °C. 760 mm.	B. p., °C. 20 mm.	M. p., °C.	$d^{20°}$ g./cc.
$Cl[(CH_3)_2SiO]_1Si(CH_3)_2Cl$	138	41	−37	1.038
$[\quad]_2$	184	79	−53	1.018
$[\quad]_3$	222	111	−62	1.011
$[\quad]_4$	...	138	*ca.* −80	1.005
$[\quad]_5$	...	161	*ca.* −80	1.003

When 1130 cc. (9.38 moles) of dimethyldichlorosilane was partially hydrolyzed by the addition of 84.5 cc. (4.69 moles) of water in the same manner as the previous hydrolysis, but without the use of mutual solvents, the reaction mixture remained transparent except for haziness in the neighborhood of the tip of the funnel and continuing a few inches away in the swirling liquid. Fractional distillation of the reaction mixture yielded 48% (540 cc.) of the original quantity of dimethyldichlorosilane which had not reacted. The remainder of the reaction product (388 cc.) yielded approximately 50 cc. of $Cl(CH_3)_2SiOSi(CH_3)_2Cl$, 15 cc. of $Cl[(CH_3)_2SiO]_2Si(CH_3)_2Cl$, 100 cc. of $[(CH_3)_2SiO]_4$, 20 cc. of $[(CH_3)_2SiO]_5$, 10 cc. of $Cl[(CH_3)_2SiO]_3Si(CH_3)_2Cl$ and other high-boiling materials containing chlorine attached to silicon. It is to be noted that although nearly half of the starting material did not react with the water, a considerable quantity of the remainder was completely hydrolyzed to dimethylpolysiloxanes. This preparation and the preceding one illustrate the difference between the single-phase and 2-phase reaction, and the influence of mutual solvents in controlling the course of the hydrolysis.

Hydrolysis of Methyltrichlorosilane

The hydrolysis of methyltrichlorosilane by adding it to a large volume of water yields hydrochloric acid and a highly condensed, insoluble and infusible white powder. This is to be expected since the functionality of three permits the formation of compounds of very high molecular weight by the process of cross-linking. However, the degree of condensation and cross-linking may be controlled by dilution of the methyltrichlorosilane with a water-miscible solvent before hydrolysis. Hydrolysis in a large volume of ether, for example, yields a product of sufficiently low molecular weight to be soluble in the ether. But this soluble polymer still bears reactive silanol groups so that condensation proceeds to produce an insoluble polymer under the action of dehydrating agents, heat, evaporation of the solvent, or under some circumstances, merely with the passage of time. Neither the monomeric triol, $CH_3Si(OH)_3$, nor its intramolecular dehydration product, CH_3SiOOH, has been isolated, and presumably does not exist.

Co-hydrolysis of Mixtures of the Methylchlorosilanes

The products resulting from the co-hydrolysis of the methylchlorosilanes are characterized by the nature of the mixtures. As noted above,[5] mixtures of methyltrichlorosilane and dimethyldichlorosilane yield resins. Mixtures of dimethyldichlorosilane and trimethylchlorosilane yield linear polysiloxanes of the type $CH_3((CH_3)_2SiO)_x\text{-}Si(CH_3)_3$ in which the monofunctional trimethylchlorosilane acts as a growth terminating agent or "chain-stopper." And similarly, mixtures of methyltrichlorosilane and trimethylchlorosilane yield branched compounds. These latter two classes of compounds may be prepared in better yields by a process of catalytic rearrangement which is described a little later in this paper.

Thus, it is seen that the methylchlorosilanes are characterized by the ease with which the chlorine atoms are hydrolyzed and by the high stability of the methyl to silicon bonds toward hydrolytic agents. The resulting products, therefore, are siloxanes or silanols containing all of the methyl groups originally present in the silanes. When less than the stoichiometric quantity of water is used for hydrolysis, the ensuing partial hydrolysis yields methylchloropolysiloxanes. The methylchlorosilanes are further characterized by yielding on hydrolysis a preponderant proportion of polysiloxanes rather than the simple silanols. Apparently the methyl silanols lack the stability exhibited by the aryl silanols, which are readily isolated in crystalline form.

Rearrangement of Cyclic Methylpolysiloxanes

A. Thermal Rearrangement.—As described in a previous section the product of complete hydrolysis of dimethyldichlorosilane consisted of a mixture of polymers of composition $[(CH_3)_2\text{-}SiO]_x$, part of which was distillable.

The residue was a viscous oil which was then heated in a Claisen flask at atmospheric pressure while a slow stream of nitrogen was passed through the flask and condenser. Up to a liquid temperature of 350° a distillate of 3 to 4 drops of water and 3 to 4 cc. of a liquid immiscible with the water was obtained. The water presumably came from condensation of polymers of the type $HO[Si(CH_3)_2O]_xSi\text{-}(CH_3)_2OH$ where x is very large, and which are believed to be present in the product in small quantity. Beginning at about 350° and continuing up to 400° the heated liquid in the flask boiled and yielded a distillate at the rate of 3 to 4 drops per second. The vapor temperature of the distillate varied between 135 and 210°. The cooled condensate was a mixture of colorless liquid and crystals. Continued heating at about 400° maintained the steady rate of distillation until the liquid in the flask was reduced to small volume, when the rate decreased. At the end of the heating period there remained in the flask only 2 to 3 cc. of a very soft gel adhering to the bulb of the thermometer. The condensate was then fractionally distilled and was found to have the composition noted in column (b) of Table IV. Column (a) lists the proportions of the compounds present in the volatile portion of the original product of hydrolysis.

TABLE IV

Compound	Per cent. by volume (a) Volatile portion	(b) Pyrolyzed portion
$[(CH_3)_2SiO]_3$	1	44
$[\quad]_4$	82	24
$[\quad]_5$	12	9
$[\quad]_6$	3	10
Above hexamer	2	13

It is evident that pyrolysis serves not only as a means of converting the non-volatile polymers of $(CH_3)_2SiO$ into cyclic polymers of low molecular weight, but also provides a convenient method of preparing the trimer in good yield. Whereas the products of such pyrolysis are identical with those separated by distillation from the original product of hydrolysis of dimethyldichlorosilane, they are produced in different proportions.

No monomer of composition $(CH_3)_2SiO$ has been observed, nor has the dimer $[(CH_3)_2SiO]_2$ been encountered, lending further evidence that these two compounds probably do not exist. The fact that a practically theoretical yield of volatile products may be produced from a non-volatile polymeric mixture indicates that the pyrolysis proceeds without fission of methyl groups, and that the rearrangement takes place by an opening and closing of Si–O–Si bonds.

The yield of medium-boiling compounds may be increased at the expense of the lower-boiling materials by carrying out the rearrangement under reduced pressure, for example by heating at 360–400° in an atmosphere of nitrogen at 20 mm. pressure. Under such conditions the less volatile products are more rapidly removed from the heated zone, thus preserving them from further pyrolysis.

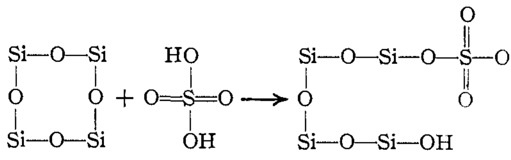
B. **Catalytic Rearrangement.**—It has been shown above that polymers of the type $[(CH_3)_2SiO]_x$ where x is large may be rearranged by pyrolysis into polymers where x is small. It will now be shown how polymers where x is small may be transformed into polymers where x is large.

When a small quantity of concentrated sulfuric acid is agitated with a larger quantity of the oily liquid resulting from the hydrolysis of dimethyldichlorosilane, the mixture increases in viscosity and may develop into a rubbery gel. Removal of the acid by washing with water does not convert the viscous mass back to the original liquid, but there remains a polymeric mixture of the same chemical composition, but of much higher average molecular weight.

A superficial explanation of this phenomenon is based upon the well-known dehydrating properties of concentrated sulfuric acid and its known catalytic effect on the condensation of alcohols. But this explanation presupposes the presence of polymers of the type $HO[(CH_3)_2SiO]_xSi(CH_3)_2OH$, and the increase in average molecular weight is ascribed to the condensation of molecules of this type by dehydration between the hydroxyl end-groups. No doubt such an explanation would suffice were it not for another reaction which predominates, and which does not require the presence of hydroxyl end-groups. This reaction involves the breaking and rejoining of Si–O–Si linkages under the action of sulfuric acid and results in an over-all increase in average molecular weight of the polymeric mixture.

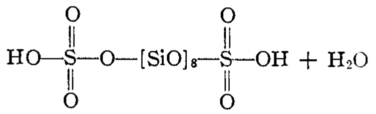
When a few drops of concentrated sulfuric acid are added to a quantity, say 10 cc., of octamethyl*cyclo*tetrasiloxane, $[(CH_3)_2SiO]_4$, there is no marked change in appearance or temperature. Two phases persist, even on agitation, but the viscosity of the mixture gradually increases until it attains a very high value, sometimes so high as to form an elastic gel. In contrast, when a few drops of the tetramer are added to a larger quantity of concentrated sulfuric acid, they dissolve on gentle agitation and there is no further observable change in the appearance of the solution. If, however, this solution be diluted with water, a second phase appears which may be a viscous liquid or a gel, depending upon the conditions and procedure. Examination of the washed, acid-free, product resulting from either of these two procedures shows that it is a mixture of polymers of $(CH_3)_2SiO$ units of high average molecular weight. The methyl groups have not been removed, but fission and recombination of Si–O–Si linkages has occurred, leading to a rearrangement of the $(CH_3)_2SiO$ units.

Since it is known that the Si–O–Si linkage may be broken by sulfuric acid with the formation of easily hydrolyzable sulfates, such as $[(CH_3)_3SiO]_2SO_2$,[7] a possible mechanism of the rearrangement may be formulated as follows: (For simplification of the formulas used below, the two methyl groups attached to each silicon atom have been deleted.)



I

Two molecules of (I) may now condense intermolecularly by dehydration between the terminal hydroxyls, yielding

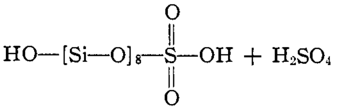


$$HO-\overset{O}{\underset{O}{S}}-O-[SiO]_8-\overset{O}{\underset{O}{S}}-OH + H_2O$$

II

thus giving rise to a chain of Si–O units of double the original length, and terminated by sulfate. But it is known that such terminal sulfates are readily hydrolyzed, and the water formed by dehydration may react with such a terminal sulfate producing another terminal Si–OH and regenerating the sulfuric acid. This molecule can then go through another doubling cycle, and by repetition can grow to considerable size.

Another possible reaction which (I) might undergo involves the intermolecular condensation between a terminal hydroxyl and a terminal sulfate to yield

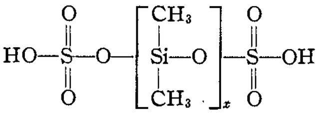


$$HO-[Si-O]_8-\overset{O}{\underset{O}{S}}-OH + H_2SO_4$$

III

in which case molecules of (III) can grow by further intermolecular condensation, leading again either to long chains or large rings.

Other similar mechanisms and numerous combinations of such mechanisms may be written involving the reaction and regeneration of sulfuric acid and Si–O–Si linkages. In all such proposed mechanisms, however, the reverse process also occurs, where the sulfuric acid breaks a long chain to produce shorter ones, and thus an equilibrium appears inevitable between sulfuric acid, water and polysiloxane chains and rings including sulfate radicals, and terminated by sulfates or hydroxyls. In the presence of a large quantity of sulfuric acid, the silicon is apt to be present largely in compounds of the type



$$HO-\overset{O}{\underset{O}{S}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_x-\overset{O}{\underset{O}{S}}-OH$$

where x is very small, whereas in the presence of only a small quantity of sulfuric acid, polysiloxanes of high molecular weight are apt to pre-

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(7) W. Patnode and F. C. Schmidt, THIS JOURNAL, **67**, 2272 (1945).

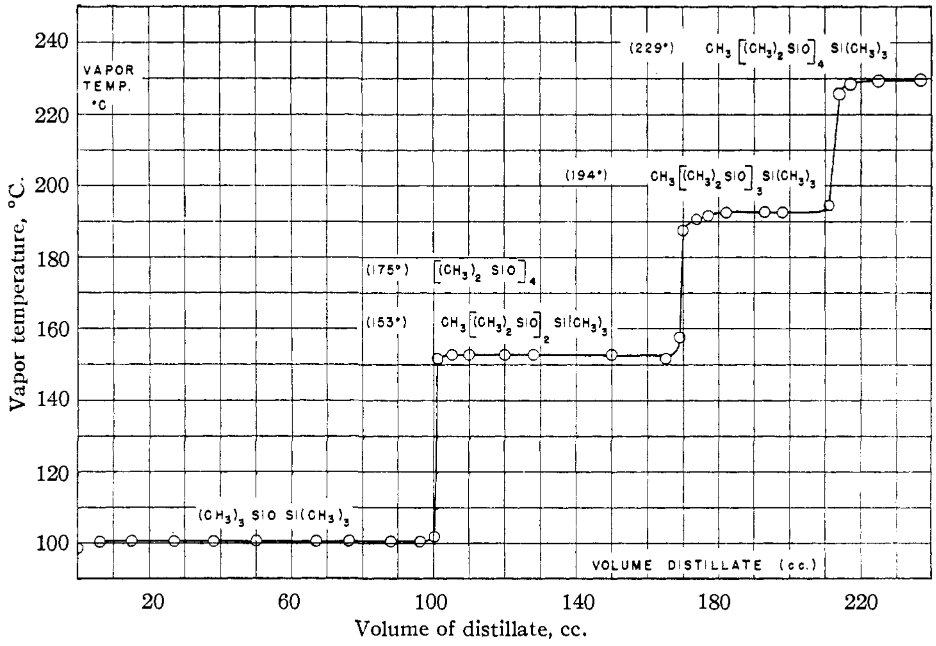

Fig. 1.

dominate. In the latter case it is doubtful whether equilibrium is ever attained, since the system gradually becomes immobile due to the increase in viscosity. Dilution of the system with a solvent such as ethyl ether, will maintain a sufficiently low viscosity so that equilibrium may be established in the liquid phase.

Fifty-two cc. of octamethyl*cyclo*tetrasiloxane was placed in a stoppered bottle with 9.6 cc. of concentrated sulfuric acid and 25 cc. of ethyl ether. The two-phase system was shaken at room temperature for a day, whereupon the mixture became very viscous. After the further addition of 50 cc. of ether to reduce the viscosity, 25 cc. of water was added and the mixture was shaken. The lower aqueous layer (about 35 cc.) was then separated, and the ethereal solution was washed three times with 10-cc. portions of water, and was set aside to dry over anhydrous potassium carbonate. The following day the filtered ethereal solution was distilled. After the ether had distilled out of the oil, a further distillate of less than 3 cc. was obtained at a vapor temperature of about 190° and a still-pot temperature of over 300°. The clear viscous oil remaining in the still was examined. Its average molecular weight was measured cryoscopically in cyclohexane and was found to be 2740, corresponding to about 37 $(CH_3)_2SiO$ units.

Anal. Found: H, 8.28, 8.12; C, 31.37, 31.51; Si, 36.56, 36.67. Calcd. for $(CH_3)_2SiO$: H, 8.16; C, 32.38; Si, 37.86.

Conversion of Cyclic to Chain Polymers. The Effect of a Chain-Stopper

One of the most spectacular of these equilibration reactions is the catalytic rearrangement of a mixture of cyclic methylpolysiloxanes and hexamethyldisiloxane into linear methylpolysiloxanes, thus

$$[(CH_3)_2SiO]_x + [(CH_3)_3Si]_2O \xrightarrow{H_2SO_4} (CH_3)_3SiO\,[(CH_3)_2SiO]_xSi(CH_3)_3$$

This reaction is carried out merely by mixing the two ingredients, adding a small quantity of concentrated sulfuric acid and shaking the two-phase system at room temperature. The product is recovered by adding water to dilute the sulfuric acid, thus also hydrolyzing the sulfate esters present and discarding the aqueous layer.

One mole (162.3 g.) of hexamethyldisiloxane and 0.25 mole (74.1 g.) of $[(CH_3)_2SiO]_4$ were shaken together in a bottle with 10 cc. of concentrated (95.5%) sulfuric acid for four hours at room temperature. Then 25 cc. of water was added with shaking and the two-layer system allowed to stand. The lower aqueous layer (34 cc.) was separated and the upper layer was washed twice with 25-cc. portions of water. The oil was then dried overnight over anhydrous potassium carbonate. The filtered product (280 cc.) was then fractionally distilled, giving the distillation curve in Fig. 1. This curve shows that the tetramer (b. p. 175°) originally present in the reaction mixture has vanished, and that linear polymers of the type CH_3-$[(CH_3)_2SiO]_xSi(CH_3)_3$ have been formed. These compounds, listed in Table V, were identified by the method of preparation, by the constancy and regularity of the boiling points, by cryoscopic measurement of molecular weight in cyclohexane, and in some cases, by chemical analysis.

Anal. Calcd. for $CH_3[(CH_3)_2SiO]_2Si(CH_3)_2$: C, 40.63; H, 10.23; Si, 35.61. Found: C, 40.1; H, 10.6; Si, 35.8. Calcd. for $CH_3[(CH_3)_2SiO]_5Si(CH_3)_3$: C, 36.63; H, 9.23; Si, 36.70. Found: C, 36.2; H, 9.13; Si, 37.0. Mol. wt. calcd. for the first four compounds of the series: 236, 311, 385, 459. Found: 230, 302, 384, 462.

TABLE V

LINEAR METHYLPOLYSILOXANES

Compound	B. p., °C. 760 mm.	B. p., °C. 20 mm.	M. p., °C.	d^{20} g./cc.	$n^D{}_{20}$
$CH_3[(CH_3)_2SiO]_2Si(CH_3)_3$	153	...	*ca.* −80	0.8200	1.3848
$[\quad]_3$	194	...	*ca.* −70	.8536	1.3895
$[\quad]_4$	229	...	*ca.* −80	.8755	1.3925
$[\quad]_5$	...	142	< −100	.8910	1.3948
$CH_3Si[(CH_3)_3SiO]_3$	190	...	*ca.* −80	.8497	1.3880

It is apparent from a consideration of the overall reaction that fluids of almost any desired average molecular weight, and therefore viscosity, may be prepared by simply varying the proportions of the two ingredients. The hexamethyldisiloxane acts as a "chain-stopper" by providing mono-functional terminating groups.

Mixtures of hexamethyldisiloxane and the cyclic tetramer of dimethyl silicone were prepared as listed in Table VI. To each mixture was added 2 cc. of concentrated sulfuric acid (35 *N*) and the mixtures were shaken for twenty-three hours. At the end of this period 10 cc. of water was added to each mixture and shaking was continued for one hour longer. The mixtures were then separated into two layers by centrifuging, and samples of the clear upper layers were taken for measurement of viscosity. The viscosities in centistokes at 100°F. (37.8°C.) and 210°F. (98.9°C.) are listed in Table VI. These data are plotted in Fig. 2, to give a straight line on log–log paper.

TABLE VI

$(CH_3)_3SiOSi(CH_3)_3$, cc.	$[(CH_3)_2SiO]_4$, cc.	H_2SO_4, cc.	Viscosity (centistokes), 100°F.	210°F.
1.0	49.0	2	137	59
1.2	48.8	2	111	46
1.6	48.4	2	76	31
2.0	48.0	2	58	25
3.0	47.0	2	33	14
4.0	46.0	2	25	10
5.24	44.76	2	17	7

The rearrangement of methylpolysiloxanes is in some respects similar to a polymerization reaction in that a cyclic compound of formula $[(CH_3)_2SiO]_4$ is converted into a mixture of the same composition but of much higher molecular weight. It differs from the ordinary polymerization reactions in that the monomer $(CH_3)_2SiO$ is unknown, and the nature of the original and final linkages is the same. There is nothing which corresponds to a double bond going to a single bond with a decrease of energy. There is no primary condensation such as takes place in polyester condensations, and the sulfuric acid plays a sort of catalytic role in that it is all recovered at the end of the reaction. Since the original and final Si–O–Si linkages are the same, they presumably have the same bond energy, except perhaps for minor changes due to strain in a small ring, and the entropy factor is likely the main driving force in the reaction.

Preparation of Branched Polymers.—A combination of co-hydrolysis of methyltrichlorosilane with trimethylchlorosilane, followed by catalytic rearrangement of the product, was used to prepare the branched compound $CH_3Si[(CH_3)_3SiO]_3$, isomeric with $CH_3[(CH_3)_2SiO]_3Si(CH_3)_3$, and which was separated from the final reaction mixture by fractional distillation. It was identified by the methods previously employed and is listed in Table V.

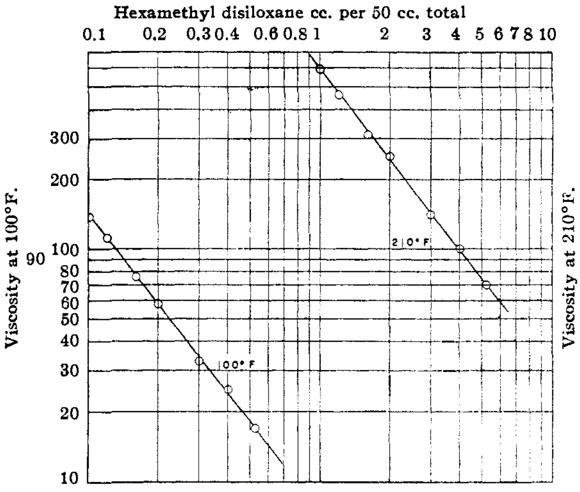

Fig. 2.

Anal. Calcd. for $CH_3Si[(CH_3)_3SiO]_3$: C, 38.66; H, 9.74; Si, 36.15, mol. wt., 311. Found: C, 38.4; H, 9.7; Si, 35.9; mol. wt., 316.

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Summary

1. The hydrolysis of dimethyldichlorosilane yields a series of cyclic polysiloxanes beginning with $[(CH_3)_2SiO]_3$ and increasing stepwise by 1 $(CH_3)_2SiO$ unit.

2. The partial hydrolysis of dimethyldichlorosilane yields a series of methylchloropolysiloxanes beginning with $Cl[(CH_3)_2SiO]Si(CH_3)_2Cl$ and increasing stepwise by 1 unit of $(CH_3)_2SiO$.

3. Polymers of composition $[(CH_3)_2SiO]_x$ where x is large may be rearranged to lower polymers by heating to 350–400° in the absence of air.

4. Contact with concentrated sulfuric acid converts polymers of $[(CH_3)_2SiO]_x$ where x is small to polymers where x is large.

5. Mixtures of $(CH_3)_3SiOSi(CH_3)_3$ and $[(CH_3)_2SiO]_4$ are converted to a mixture of compounds of the type $CH_3[(CH_3)_2SiO]_xSi(CH_3)_3$.

6. The viscosity of the fluids produced by treating methyl polysiloxanes with concentrated sulfuric acid may be controlled by the addition of chain-terminating groups derived from hexamethyldisiloxane.

7. The melting points, boiling points, densities and refractive indices of some of these compounds have been measured.

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