On the Lower Boiling Product of Silicon-methylchloride Reaction

By Rokuro ŌKAWARA and Minoru SAKIYAMA

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Among the products obtained from the reaction of silicon and methylchloride, methyltrichlorosilane, dimethyldichlorosilane and trimethylchlorosilane were well known since the finding of the "direct method of synthesis" by Rochow. These three main chlorosilanes have a close boiling point centering around 65°C and have been used for the starting materials of "silicones".

Now we wish to report on the presence of tetramethylsilane $(CH_3)_4Si$ (I′), dimethylchlorosilane $(CH_3)_2SiHCl$ (II′) and methyldichlorosilane CH_3SiHCl_2 (III′) and a small amount of trichlorosilane $HSiCl_3$ (IV′) in the lower boiling product centering around 35°C of the direct synthesis. The compounds (I′)[1,2], (III′)[3] and (IV′)[4,5] have already been characterized, but on the compound (II′) only the boiling point has been assumed by calculation to be 35.5°C[6] and 39.1°C[7].

To obtain pure (II′), the starting material was twice distilled through a modified large Stedman column of about 15 theoretical plates and divided into many fractions. These fractions may be roughly included into three main fractions A (b. p. 26°–34°C), B (b. p. 34°–36°C) and C (b. p. 36°–41°C). As the fraction B was supposed to be a plateau of impure (II′), B was repeatedly fractionated through a more efficient column. Finally a constant boiling fraction was obtained, but its chlorine content was found to be lower than the calculated value. The reason may be explained by assuming the contamination of a hydrocarbon by-product having the boiling point close to (II′). In fact, the presence of such a hydrocarbon in the starting material has been found by hydrolysis. Referring to the case of trimethylchlorosilane[8], it may be considered that an azeotrope of (II′) and the hydrocarbon is formed at the constant boiling plateau at 34.5°–35°C, but it could not be verified in this experiment.

As it was difficult to separate (II′) from the contaminating hydrocarbon by distillation, B was ethanolyzed in excess ethanol and dimethylaniline, and the dimethylethoxysilane thus formed was reacted in a bomb with benzoylchloride. From the product the freaction boiling at 36°C was confirmed to be (II′).

Ethanolysis of the fraction B in excess dimethylaniline and ethanol, liberated dimethylethoxysilane, methyldiethoxysilane and a small amount of dimethyldiethoxysilane and ill-defined triethoxysilane. It was supposed that dimethyldiethoxysilane was produced by the fission of Si-H during the course of ethanolysis. The presence of triethoxysilane reveals the presence of (IV′) in the redistilled product, this assumption was further supported by the fact that on repeated fractionation of B, the fraction B′ having a higher chlorine content was found in front of the plateau B″ as shown in Fig. 1.

By hydrolysis, methylhydropolysiloxanes were obtained as the main product. In this paper, to denote various methylpolysiloxanes, shorthand notation is used which is based on that of Wilcock[9], in which **M**, **D** and **T** represent mono-, di- and tri- functional units. Prime is used to indicate the hydrogen atom directly attached to silicon atom.

Unit	Formula
M′	$(CH_3)_2HSiO_{1/2}$
D′	CH_3HSiO
D	$(CH_3)_2SiO$
T	$CH_3SiO_{3/2}$

The following compounds were made by hydrolyzing the starting material and rigorously distilling the resultant oil.

$\mathbf{M'D'_nM'}$ $(n=0\text{–}6)$

$\mathbf{M'D_nM'}$ $(n=1\text{–}2)$

$\mathbf{D'_n}$ $(n=4\text{– })$

$\mathbf{M'D'DM'}$

The main components of the resultant oil were a series of linear copolymers $\mathbf{M'D'_nM'}$,

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[1] J. G. Aston, R. M. Kennedy and G. H. Messerly, *J. Am. Chem. Soc.*, **63**, 2343 (1941).

[2] A. P. Mills and C. A. MacKenzie, ibid., **76**, 2672 (1954).

[3] R. O. Sauer, W. J. Scheiber and S. D. Brewer, ibid., **68**, 962 (1946).

[4] H. S. Booth and W. D. Stillwell, ibid., **56**, 1529 (1934).

[5] A. Stock and F. Zeidler, *Ber.*, **56 B**, 986 (1923).

[6] C. A. MacKenzie, A. P. Mills and J. M. Scott, *J. Am. Chem. Soc.*, **72**, 2032 (1950).

[7] R. N. Lewis and A. E. Newkirk, ibid., **69**, 701 (1947).

[8] R. O. Sauer, W. J. Scheiber and E. M. Hadsell, ibid., **70**, 4254 (1948).

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

which were formed from (II′) and (III′). A small amount of $\mathbf{M'D_nM'}$, in which only $\mathbf{M'DM'}$ was accurately characterized, may be assumed to be formed by the fission of Si-H bond during the hydrolysis in the concentrated hydrogen chloride solution.

$$3H(CH_3)_2SiCl+2H_2O$$
$$=H(CH_3)_2SiOSi(CH_3)_2OSi(CH_3)_2H+3HCl+H_2$$
$$(\mathbf{M'DM'})$$

Such a reaction may occur also with Si-H of methyldichlorosilane to form $\mathbf{M_3'T}$, an isomer of $\mathbf{M'D'DM'}$. But in this experiment, the presence of this compound could not be detected accurately. The presence of $\mathbf{D_n'}$, which has already been characterized by Sauer[3] by hydrolyzing (III′), was found between the plateaus of $\mathbf{M'D_n'M'}$.

The distribution of these polymers, tetramethylsilane (I′) and hydrocarbon by-product in the hydrolyzates with regard to the chlorine content of the redistilled chlorosilane, is shown in Fig. 2. The properties of these polymers are given in Table II.

Experimental

Starting Materials.—The industrial low boiling methylchlorosilane, having the boiling point between 26°C to 40°C (hydrolyzable chlorine, 40%) obtained from the reaction of silicon and methylchloride was supplied from the Shin-etsu Chem. Ind. Co.

A. Chlorosilane and Its Ethanolysis

Distillation.—The starting material (4 Kg.) was fractionated through a modified Stedman column of about 15 theoretical plates (38 mm. inner diameter, packed length 30 cm.). From the boiling point and the chlorine content, the distillates were roughly separated into three main fractions as follows.

Main fraction	Boiling point (°C)	Hydrolyzable chlorine (%)	Weight (%)
A	26–34	–36	25
B	34–36	36–43	25
C	36–41	43–60	50

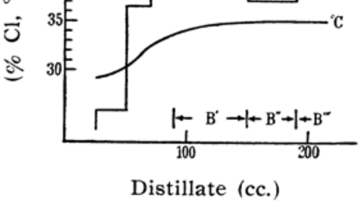

Fig. 1. Redistillation of fraction B through a 30 plates column.

As the fraction B was supposed to be an incomplete plateau, a part of which was fractionated through a Stedman column of about 30 theoretical plates (inner diameter 18 mm. and packed length 40 cm.). The result are shown in Fig. 1.

The distillation curve obtained was similar to that of the starting material, but the chlorine content of the distillate was somewhat different. The fraction B″ having a slightly lower chlorine content than the neighbouring fractions, B′ and B′″, was found. The higher values in B′ and B′″ were supposed to be caused by the contamination of a asmall amount of trichlorosilane (IV′) (b.p. 31.5°C[4], 31.8°C[5] Calcd. Cl, 78.5%) and methyldichlorosilane (III′) (b.p. 41.0°C[3] Calcd. Cl, 61.5%), respectively. The fraction B″ (Found Cl, 37.1%) was distilled through the same column and the constant boiling frection of 34.5° to 35°C was obtained, but the chlorine contents of 39.4, 35.1 and 36.4% were found with the amount of each 10 cc. of the distillate. If the fraction B″ was (II′) contaminated only by a small amount of (IV′) and (III′), the redistilled fraction having the minimum chlorine content would become closer to the chlorine content calculated for (II′) (37.4%). In this experiment, the second fraction having the minimum chlorine content (35.1%) did not close to the calculated value, but too small a value resulted.

Ethanolysis.—A fraction of B (150 g., b.p. 35°–36°C, Anal. Cl, 42.5%) was added to the mixture of excess of ethanol (120 g.) and dimethylaniline (250 g.) in a three-necked flask equipped with an efficient stirrer, a dropping funnel and a condenser with a calcium chloride tube. During the reaction, the mixture was cooled with an ice-bath below 5°C. After the addition of the chlorosilane, the reaction mixture was refluxed over a period of two hours with vigorous stirring, followed by the separation of dimethylanilinehydrochloride through a separating funnel and the fractional distillation of the organic layer. The fraction boiling at 53°–57°C (39 g.) thus obtained, was rigorously fractionated by a Stedman column of about 50 theoretical plates. The fraction boiling at 54°C was found to be dimethylethoxysilane $H(CH_3)_2SiOC_2H_5$ from the analysis of H(-Si). n_D^{20} 1.3683, d_4^{20} 0.7572, MR_D Found: 31.00, Calcd.[10]: 31.30.

Anal. Found: H(-Si), 0.94%. Calcd. for $H(CH_3)_2SiOC_2H_5$: H(-Si), 0.97%.

This compound contained a trace of chlorine compound detectable by the Beilstein test and gradually decomposed by evolving a gas from the bottom of the receiver. Even after repeated distillation, the chlorine compound and evolution of the gas did not completely disappear.

The higher boiling fraction collected from several ethanolysis reactions, was fractionally distilled through a Stedman column of about 30 plates. The following three ethoxysilanes were obtained.

Methyldiethoxysilane, $HCH_3Si\ (OC_2H_5)_2$.

b.p. 97.5°C, n_D^{20} 1.3772

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[10] Calculated from bond refractivities by E. L. Warrick, *J. Am. Chem. Soc.*, 68, 2455 (1946).

Reported[11]: b.p. 97.5°C, n_D^{25} 1.3738, d_{25}^{25} 0.8295

Dimethyldiethoxysilane, $(CH_3)_2Si(OC_2H_5)_2$.

b.p. 112°C, n_D^{20} 1.3821, d_4^{20} 0.8398

MR_D Found: 41.09, Calcd.[10]: 41.06

Reported[12]: b.p. 114°C, n_D^{20} 1.3805, d_4^{20} 0.8395

Triethoxysilane, $HSi(OC_2H_5)_3$.

b. p. 134°–5°C, n_D^{20} 1.3840

Anal. Found: H(-Si), 0.43%, Calcd. 0.61%

Reported[6]: b.p. 131.5°C, n_D^{20} 1.3767

The data of triethoxysilane did not accord well with the reported value. On account of the small amount (1 cc.) of this fraction, the satisfactory separation from the neighbouring compounds could not be achieved. By the alcoholysis reaction carried out as above, cyclocompound $\mathbf{D'_4}$ (Reported[3]: b.p. 134.5°C, n_D^{20} 1.3873) having the boiling point close to that of triethoxysilane might not be formed. The active hydrogen content of this fraction lower than the calculated value also reveals the absence of $\mathbf{D'_4}$ (Calcd. H(-Si), 1.68%).

Chlorination of Dimethylethoxysilane.—Dimethylethoxysilane (28 g., 0.27 mol.) was reacted with benzoylchloride (38 g., 0.27 mol.) in an iron bomb at 200°C over a period of four hours. The reaction mixture was rigorously fractionated through a Stedman column of about 50 theoretiplates. The constant boiling fraction at 36°C (2 cc.) was obtained. From its chlorine content, it was found to be dimethylchlorosilane (II′). n_D^{20} 1.3820

Anal. Found: Cl, 37.6%. Calcd. for (II′): Cl. 37.4%.

B. Hydrlyzates

Hydrolysis.—Hydrolysis was carried out by adding a sufficient amount of cracked ice to the ice-cooled chlorosilane. The oily layer was vigorously shaken with fresh ice-water repeatedly, but it was found to be difficult to complete the hydrolysis, for the red color of methylorange, which was added as an indicator, appeared gradually on standing. To complete the hydrolysis the hydrolyzate and water were vigorously stirred at room temperature with an efficient stirrer. When the red color of methylorange appeared, the mixture was titrated back to the orange color with a dilute sodium bicarbonate solution until the orange color remained unchanged. Then useing chlorophenolred (pH 5.0–6.6) as an indicator, the same treatment was repeated. The hydrolysis reaction was very slow and it required twenty to thirty hours' stirring with 200 to 250 g. of the hydrolyzate. The hydrolyzates of the starting material and fraction A, which contain volatile tetramethylsilane (I′), were twice washed with fresh ice-water, followed by the dehydration on sodium sulfate and the fractionation to distil off (I′). And the residue was neutralized as above.

In spite of these careful treatments, a trace of chlorine compound was sometimes found in the distillate. Accordingly, on each fractionation, the distillate and the residue were tested by the Beilstein test and a trace of chlorine compound was again hydrolyzed off.

Composition of the Hydrolyzate.—As it was very difficult to separate the starting material into its components through distillation, the hydrolysis was carried out with the representative fractions which were obtained by redistillation through the 15 plate large Stedman column. The results are given in Table I (Expt. 1 to 8).

TABLE I

HYDROLYSIS OF REDISTILLED AND STARTING MATERIAL

	Sample				Hydrolyzate
Expt. No.	Boiling range °C	Hydrolyzable chlorine %	Classed to the Main fraction	Weight g.	Yield %
1	28.5–29.0	22.9	A	30	78
2	30.1	28.7	A	195	68
3	30.1–33.5	34.6	A	250	71
4	34.0–34.5	39.8	B	135	69
5	34.8–35.4	40.0	B	210	77
6	35.4–35.9	42.7	B	140	81
7	36.0–37.0	46.7	C	120	73
8	37.5–38.1	49.5	C	100	68
9*	38.8–	53.7	C	290	76
10**	26 –40	40	—	870	79

* Residue of the distillation of Expt. 1 to 8.

** Starting material.

The results obtained with the residue of redistillation and the starting material are also given in Expt. 9 and 10, respectively. By the hydrolysis, the formation of gelatinous mass was found in Expt. 3 and 4 which may be contaminated by (IV′). In Expt. 9 some gelatinous mass and viscous oil resulted.

Throughout this experiment, the distillation of the hydrolyzate was carried out through a semimicro Stedman column of about 50 theretical plates. By distillation, tetramethylsilane (I′) distilled out at first, then a small amount of hydrocarbon boiling at 33°–37°C and the succeeding plateaus of $\mathbf{M'_2}$, $\mathbf{M'D'M'}$, $\mathbf{M'DM'}$, $\mathbf{D'_4}$ and $\mathbf{M'D'_2M'}$ were obtained at 70°, 117°, 128°, 133° and 154°C, respectively. The small plateau $\mathbf{M'DM'}$ appeared in the fraction A and B and its amount was found to be about 5% of $\mathbf{M'_2}$. The presence of $\mathbf{D'_4}$ was assumed by its higher refractive index at its boiling point in the hydrolyzates of the fraction C, while in Expt. 8 and 9 the small plateau of $\mathbf{D'_4}$ was found.

In calculating the percentage composition, $\mathbf{M'DM'}$ and $\mathbf{D'_4}$ were included into the trimer

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[11] Dow-corning Silicone Notes.

[12] H. J. Fletcher and M. J. Hunter, *J. Am. Chem. Soc.*, **71**, 2918 (1949).

fraction and the intermittent fraction between the succeeding plateaus was assigned to both sides fractions by cutting on the distillation curve. The percentage composition of the hydrolyzate plotted against the chlorine content of the samples (Expt. 1-9) is shown in Fig. 2.

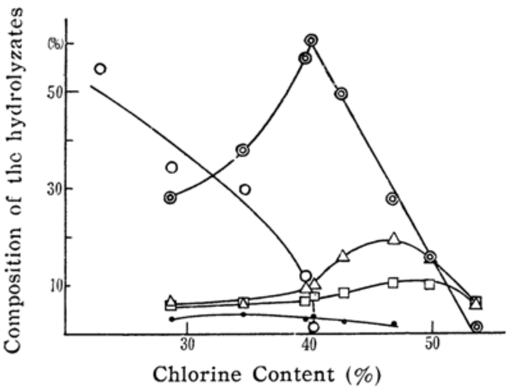

Fig. 2. Composition of the hydrolyzates with regard to the chlorine content of the redistillates.

● Hydrocarbon by-product
○ Tetramethylsilane ◎ Disiloxane
△ Trisiloxane □ Tetrasiloxane

From Fig. 2, the distribution of the components of the starting materials will be assumed.

Tetramethylsilane and Hydrocarbon By-product.—Crude tetramethylsilane (I') was shaken with a dilute sodium hydroxide solution and redistilled. A small amount of fore-run and then the constant boiling fraction having the constant refractive index was obtained.

b.p. 26.5°-26.6°C, n_D^{10} 1.3649, d_4^{10} 0.6495.

MR_D Found: 30.34, Calcd.[10] for (I'): 30.28.

(Reported: n_D^{20} 1.3588[2], d_4^{20} 0.6399[2] and 0.646[1]
b.p. 26.64°[1] and 25.5°C[2])

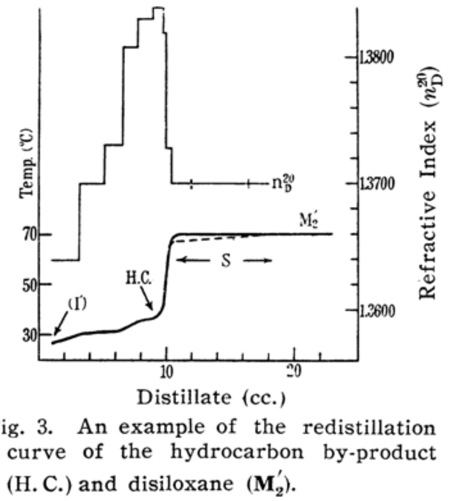

Fig. 3. An example of the redistillation curve of the hydrocarbon by-product (H. C.) and disiloxane ($\mathbf{M}_2'$).

Dotted line ---- shows the curve when the silanol is present.

As described above, a small plateau was found at 33°-37°C by the distillation of A and B. In some experiments, the fractionation was carefully carried out at the reflux ratio of 40-50 and the distillate was divided into many small fractions. The stepwise rise of the refractive index was observed as shown in Fig. 3.

The qualitative test, by taking a sample in a capillary and burning it slowly on a flame, gave a whit silicious smoke or white residue stuck at the end of the capillary with the samples of lower refractive index, but with the samples of higher refractive index this characteristic of the silicon compound was not found. The analysis for the fraction (n_D^{20} 1.3785) gave a high carbon content (Found: C, 80.96%; H. 14.18%).

From these data, the rigorous separation from the contaminating silicon compound, probably (I'), may be questionable and the determination by what kind of hydrocarbon the hydrolyzate is contaminated was not successful.

Isolation and Characterization of the Methylhydropolysiloxanes

Disiloxane ($\mathbf{M}_2'$).—As shown by the dotted line on Fig. 3, the gradually rising plateau (S) at 68°-70.5°C was obtained after the hydrocarbon by-product had distilled out. It was found usually that the refractive index of (S) decreased gradually from n_D^{20} 1.3715 to that of $\mathbf{M}_2'$ (n_D^{20} 1.3700). During the course of distillation in this temperature range, droplets of water were observed to accumulate gradually in the outlet tube of the column. The formation of water may be assumed to be caused by the condensation of unstable silanol to disiloxane.

$$2H(CH_3)_2SiOH = H(CH_3)_2SiOSi(CH_3)_2H + H_2O$$

By redistillation, the formation of water and the range indicated in the dotted line rapidly decreased. On repeated distillation three or four times, the formation of water has not been observed and the rigorously constant plateau of $\mathbf{M}_2'$ at 70.5°C, which was indicated by full line in Fig. 3, resulted.

Trisiloxanes (M'D'M' and M'DM').—Redistilled trisiloxanes having the constant boiling point and refractive index are given in Table II.

Tetrasiloxanes ($\mathbf{M'D_2'M'}$, M'D'DM' and $\mathbf{M'D_2M'}$).—The residues of the hydrolyzates of main fractions A and B, and starting material from which $\mathbf{M'D_2'M'}$ has been distilled out, were gathered and rigorously fractionated under reduced pressure. Between the plateaus of $\mathbf{M'D_2'M'}$ and $\mathbf{M'D_3'M'}$, two small plateaus appeared. The refractive index and the hydrogen evolved by aqueous sodium hydroxide were determined throughout the distillation and the results are shown in Fig. 4.

TABLE II

METHYLHYDROPOLYSILOXANES

Poly-siloxane	Boiling point °C/mmHg	Refractive index n_D^{20}	Density d_4^{20}	Molecular weight Found** (Calcd.)	Molar Refraction Found (Calcd.)10)	% H(-Si) Found***	% H(-Si) Found****	(Calcd.)
$\mathbf{M'_2}$	70.5/760	1.3700	0.7545	133 (134.33)	40.26 (40.18)	—	1.45	(1.50)
$\mathbf{M'D'M'}$*	117/760	1.3774	0.8245	192 (194.46)	54.37 (54.45)	—	1.54	(1.56)
$\mathbf{M'D'_2M'}$	154/760	1.3830	0.8613	254 (254.60)	68.89 (68.72)	—	1.57	(1.58)
$\mathbf{M'D'_3M'}$	82.5/21	1.3860	0.8897	309 (314.73)	83.06 (82.99)	1.60	1.58	(1.60)
$\mathbf{M'D'_4M'}$	104/21	1.3882	0.9081	368 (374.86)	97.46 (97.26)	1.58	1.54	(1.61)
$\mathbf{M'D'_5M'}$	122/21	1.3900	0.9218	425 (434.99)	111.84 (111.53)	1.61	1.51	(1.62)
$\mathbf{M'DM'}$	128/760	1.3811	0.8222	208 (208.49)	58.89 (58.82)	—	0.95	(0.97)

* $\mathbf{M'}=H(CH_3)_2SiO_{1/2}$, $\mathbf{D'}=H(CH_3)SiO$, $\mathbf{D}=(CH_3)_2SiO$.

** Cryoscopic measurements in benzene.

*** The sample in ethanol was reacted with aqueous sodium hydroxide.

**** The sample was reacted with butanol saturated with sodium hydroxide.

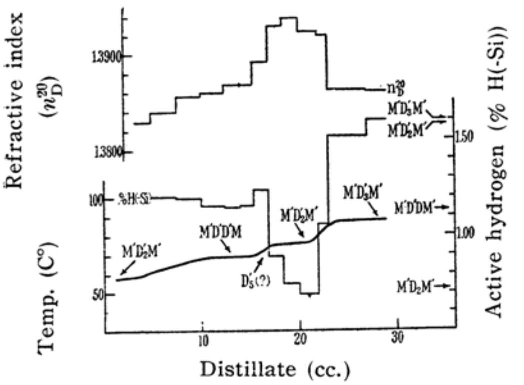

Fig. 4. Distillation curve of the intermittent fraction between $\mathbf{M'D'_2M'}$ and $\mathbf{M'D'_3M'}$ under reduced pressure (26 mm.).

Active hydrogen content was determined by adding aqueous sodium hydroxide to the sample in ethanol.

From the active hydrogen content, these two small plateaus were supposed to be those of $\mathbf{M'D'DM'}$ and $\mathbf{M'D_2M'}$. As the amounts of these compounds were small, it may be questionable whether or not the physical constants acquired here may be taken for those of pure compounds. Further, there is a possiblity of the appearance of isomerit $\mathbf{M'_3T}$ in front of the plateau of $\mathbf{M'D'DM'}$. This is because the branched chain polymer ($\mathbf{M_3T}$: b.p. 190°C) has been reported[13] to have a slightly lower boiling point than the isomeric linear polymer ($\mathbf{MD_2M}$: b.p. 194°C). Cyclopentamer $\mathbf{D'_5}$ (b.p. 168.7°C, n_D^{20} 1.3912)[3] will be expected to appear between the plateaus of $\mathbf{M'D'_2M'}$ and $\mathbf{M'D'_3M'}$. In this experiment, no proofs were found as to its presence except the higher active hydrogen content at the back part of the plateau of $\mathbf{M'D'DM'}$.

Polysiloxanes Higher than Tetrasiloxane.—Distillation was further continued and the succeeding plateaus of $\mathbf{M'D'_3M'}$, $\mathbf{M'D'_4M'}$, $\mathbf{M'D'_5M'}$ and $\mathbf{M'D'_6M'}$ were obtained at the temperature of 82.5°C/21 mm., 104°C/21 mm., 122°C/21 mm. and 87°C/2 mm. The portions having the refractive index higher than the neighbouring plateaus, a relation similar to that which is shown in Fig. 4, were found between the succeeding plateaus. The differences between the boiling points of the neighbouring plateaus became less with the distillate and it became difficult to differentiate the complete plateau from the intermittent fractions above $\mathbf{M'D'_6M'}$. Judging from the active hydrogen content and the increment of the refrcative index of the succeeding plateaus, the plateau of 87°C/2mm. (n_D^{20} 1.3940. Found: H(-Si), 1.53%. Calcd. for $\mathbf{M'D'_6M'}$: H(-Si), 1.63%.) was considered to be contaminated by the neighbouring compounds.

The properties of the polysiloxanes until $\mathbf{M'D'_5M'}$ are given in Table II.

Analysis of Active Hydrogen.—The determination of % H(-Si) was carried out by using Zerewitinoff apparatus. The values in the data obtained by adding butanol saturated with sodium hydroxide to the sample or its butanolic solution, were smaler than the calculated value with $\mathbf{M'D'_4M'}$ and $\mathbf{M'D'_5M'}$, the causes of which may be related to the formation of gelatinous mass[14] in the reaction mixture. Accordingly, aqueous sod-

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[13] W. I. Patnode and D. F. Wilcock, ibid., 68, 358 (1946).

[14] U. Takahashi, This Bulletin, 28, 443 (1955).

ium hydroxide was added to the sample in ethanol, as described by Sauer3), and the satisfactory results were obtained with the higher polymers without formation of gelatinous mass. Because of the closed value of % H(-Si) as the polymer size increased, it was necessary to characterize each compound practically by means of both % H(-Si) and molecular weight.

Summary

(1) Tetramethylsilane, dimethylchlorosilane and methyldichlorosilane and a small amounts of trichlorosilane and hydrocarbon by-product were found in the lower boiling product (b. p. 26°–40°C) of silicon methylchloride reaction.

(2) Dimethylethoxysilane and methyldiethoxysilane besides small amounts of dimethyldiethoxysilane and triethoxysilane were found in the ethanolysis product.

(3) Owing to the contamination of the hydrocarbon by-product, dimethylchlorosilane could not be isolated by repeated distillation. To characterize this substance, it was synthesized from dimethylethoxysilane and benzoylchloride.

(4) By hydrolysis, linear copolymers $\mathbf{M'D'_{n}M'}$ and $\mathbf{M'D_{n}M'}$ were found. Of these, copolymers $\mathbf{M'D'_{n}M'}$ having two to eight silicon atoms and $\mathbf{M'DM'}$ have been characterized.

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Department of Applied Chemistry
Faculty of Engineering, Osaka
University, Osaka