Alkylalkoxypolysiloxanes. VI[1]. *Lower Members of Cyclic Methyl-, and Ethyl-ethoxypolysiloxanes*

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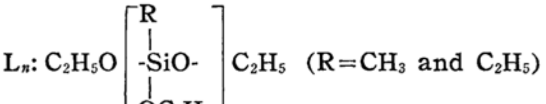
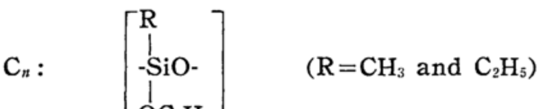
Lower members of linear methyl-, and ethyl-ethoxypolysiloxanes as indicated by formula L_n have been prepared by the partial hydrolysis of methyltriethoxysilane[2] and by the thermal reaction between ethyltriethoxysilane and partially ethanolyzed ethyltrichlorosilane[3], but of the cyclo-compounds as indicated by formula C_n no report has been presented.



$$L_n: C_2H_5O\left[\begin{array}{c}R\\ |\\ \text{-SiO-}\\ |\\ OC_2H_5\end{array}\right]_n C_2H_5 \quad (R=CH_3 \text{ and } C_2H_5)$$



$$C_n: \left[\begin{array}{c}R\\ |\\ \text{-SiO-}\\ |\\ OC_2H_5\end{array}\right]_n \quad (R=CH_3 \text{ and } C_2H_5)$$

Recently, diethoxycyclopolysiloxanes[4] having three to five silicon atoms were prepared by rapid hydrolysis of diethoxydichlorosilane using pyridine as an acid acceptor, and the liberated cyclotrimer, hexaethoxycyclotrisiloxane was found to be an unstable compound.

Here, this process was applied to methylethoxydichlorosilane (I) and ethylethoxydichlorosilane (II), and the first two members of cyclopolysiloxanes, C_3 and C_4

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[1] Part V of this series, R. Okawara and M. Sakiyama, This Bulletin, **28**, 367 (1955).

[2] H. J. Flether and M. J. Hunter, *J. Am. Chem. Soc.*, **71**, 2922 (1949).

[3] R. Okawara, This Bulletin, **27**, 428 (1954).

[4] R. Okawara, S. Hotta and T. Shimura, ibid., **28**, 541 (1955).

were obtained. As well as the case of diethoxydichlorosilane, these cyclotrimers were formed preferably by the hydrolysis carried out with considerable dropping rate. From the results of the fractionation of the hydrolyzate obtained from I, the boiling point of the cyclotetramer (129°C/10 mm.) was found to be very close to that of the linear trimer (126°C/10 mm.) which was obtained by treating the fractionation residue of the partially ethanolyzed product with sodium bicarbonate. The fractionation of the hydrolyzate of II gave succeeding plateaus of dimer, cyclotrimer, linear trimer and cyclotetramer. In this case, the amount of the cyclotrimer was not so small as in the case of hydrolysis of I, which was carried out under similar conditions. Further fractionation of the hydrolyzates I and II gave some plateaus, but their silicon content was not satisfactory enough to be taken as cyclo compounds.

The refractive index of cyclotrimer, $(CH_3Si(OC_2H_5)O)_3$ gradually increased during storage, but the change was not observed on the other three compounds given in Table II. A similar change has been reported with unstable cyclotrimers, $((CH_3)HSiO)_3$[5], $((C_2H_5O)_2SiO)_3$[4] and $((C_2H_5)HSiO)_3$[6].

Infrared spectra of two cyclotrimers obtained in these experiments showed an absorption band at 1023 cm^{-1}. Recently, the band appearing at 1023 cm^{-1} in the spectra of unstable triethylcyclotrisiloxane[6] was found to decrease in intensity with its increase in refractive index and viscosity on storage. Since with unstable $((CH_3)Si(OC_2H_5)O)_3$ a similar decrease in intensity and an increase in viscosity were also found, it is natural to suppose that this band is a characteristic one associated with the cyclotrisiloxane ring, as the band at 1010—1020 cm^{-1} has been found in the spectra of dialkylcyclotrisiloxanes[7]. If the assumption described above were an appropriate one, the decrease in intensity of 1023 cm^{-1} band should be related to the opening of cyclotrisiloxane ring probably to form a higher polymer.

Experimental

Starting Materials. — Methyltrichlorosilane used in these experiments was prepared by fractionation through a Stedman column of about 20 theoretical plates from "98% methyltrichlorosilane" supplied by the Shin-etsu Chem. Ind. Co. The hydrolyzable chlorine of the sample was 70.8—71.2% (Calcd. for CH_3SiCl_3 : Cl, 71.2%). Methylethoxydichlorosilane was prepared by adding 0.8 mole of absolute ethanol to 1 mole of methyltrichlorosilane with vigorous stirring. After the addition, the mixture was heated gradually to 50°C with stirring. Then the mixture, which contained unreacted methyltrichlorosilane (ca. 30%), methylethoxydichlorosilane (ca. 30%) and further ethanolyzed substances, was fractionated through the same column. The methylethoxydichlorosilane fraction which had a constant boiling point of 100°C, having a chlorine content of 43—44% was collected and redistilled through the same column and the middle portion of the distillate was taken as the starting materials.

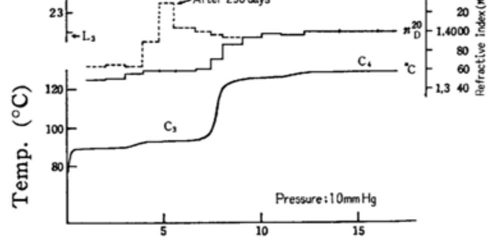
Anal. Found: Cl, 44.6%. Calcd. for $C_3H_8OCl_2Si$: Cl, 44.6%.

Ethylethoxydichlorosilane (b. p. 127°C) was prepared by the similar partial ethanolysis of ethyltrichlorosilane which was obtained from the product of silicon-ethylchloride reaction.

Anal. Found: Cl, 41.0%. Calcd. for $C_4H_{10}OCl_2Si$: Cl, 41.0%.

Hydrolysis and Fractionation of the Hydrolyzate.—Hydrolysis was carried out as described in the preceding paper[4]. The product (*P* g.) was simply distilled at 10 mm. by using a Claisen flask. The weight percentage to *P* of the distillate (*D*) which came out up to the indicated temperature is also given in Table I.

In Table I, the results obtained with methylethoxydichlorosilane (I) as starting material are given in Expt. 1 to 4. In these experiments, the distillate (*D*) was rigorously fractionated through a Stedman column of about 20 theoretical plates and the refractive indices of the distillates were measured throughout the distillation. Two plateaus, which were due to cyclotrimer (94°C/10 mm.) and cyclotetramer (129°C/10 mm.) appeared in Expt. 1 to 3, in which the hydrolysis was carried out rapidly. In these three experiments, the refractive index and the silicon content of the plateau of cyclotrimer were n_D^{20} 1.3955—9, and



Distillate (cc.)

Fig. 1. Distillation curve of methylethoxypolysiloxanes (Expt. 2 of Table I).
L_n: Linear *n*-mer, C_n: Cyclo-*n*-mer

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[5] S. D. Brewer, *J. Am. Chem. Soc.*, **70**, 3962 (1948).

[6] R. Okawara, U. Takahashi and M. Sakiyama, This Bulletin, **30**, 608 (1957).

[7] C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, *J. Am. Chem. Soc.*, **70**, 3758 (1948).

TABLE I

HYDROLYSIS OF DICHLOROSILANE

Expt. No.	Dichlorosilane g. (mole)	Hydrolysis							Simple Distillation of *P*. at 10mmHg	
		Mixture			Highest Temp. attained with mixing °C	Dropping Rate of Chlorosilane g./min.	Product (*P*.)		Temp.** °C	Distillate (*D*.) % to *P*.
		Benzene g.	Pyridine g. (mole)	H_2O g. (mole)			g.	% Theory		
1 I*	159 (1.0)	250	175 (2.2)	19 (1.05)	39	14	66	63	180	33
2 I	159 (1.0)	250	175 (2.2)	18 (1.0)	52	32	75	72	175	33
3 I	159 (1.0)	250	175 (2.2)	18 (1.0)	43	24	82	79	171	39
4 I	80 (0.5)	125	87 (1.1)	9 (0.5)	3	1.6	41	79	148	30
5 II*	173 (1.0)	250	160 (1.0)	18 (1.0)	48	25	92	78	198	49
6 II	173 (1.0)	400	160 (1.0)	18 (1.0)	39	35	95	80	200	53

* I: $CH_3(C_2H_5O)SiCl_2$ II: $C_2H_5(C_2H_5O)SiCl_2$

** Distillate was collected up to this temperature (the stil-pot temperature was 250—260°C).

26.86—26.97% (Calcd. for $C_3H_8O_2Si$: Si, 26.96%) respectively. The refractive index of the plateau of cyclotetramer gradually approached to a constant value, n_{D}^{20} 1.4001, and the silicon content of this portion was also satisfactory to take it as a cyclocompound. For example, the distillation curve of Expt. 2 is shown in Fig. 1.

In Expt. 4, chlorosilane was dropped very slowly to make sure that the presumption that the formation of the cyclotrimer is related to the dropping rate in this case too. Because a half mole of the chlorosilane was used in this run, the distillate (*D*) which could be put to use for fractionation was 12 g. Only 2 cc. of the fraction which distilled out below 120°C/10 mm. was separated into four portions. Though the silicon content of the third portion (0.5 cc.) boiling at 89°—94°C/10 mm. showed the presence of cyclotrimer, its plateaus did not appear.

The residues of the simple distillation under 10 mm. were collected and further distilled simply under 1 mm. To the distillate coming out below 200°C (stil-pot temperature, 260°C), the fractionation residues of (*D*) were added and redistilled rigorously through a high efficient Stedman column of about 50 theoretical plates. Two gradually rising plateaus were found at 114°—118°C/1 mm. and 140°—143°C/1 mm., but the silicon contents of these plateaus were 25.7—24.8% 25.0—24.3% respectively, which shows that these plateaus are not those of pure cyclocompounds. (Calcd. for cyclocompounds; Si, 26.96%).

The data starting with ethylethoxydichlorosilane (II) are given in Expt. 5 and 6 in Table I. The distillate (*D*) was clear oil and the residue was highly viscous oil. The distillate was fractionated through the high efficient Stedman column. A small amount of dimer (n_{D}^{20} 1.4024, d_4^{20} 0.9500. Reported[8]: n_{D}^{20} 1.4006, d_4^{20} 0.9473. *Anal.* Found: Si, 18.65%. Calcd. for $C_{12}H_{30}O_5Si_2$: Si, 18.06 %) then the succeeding plateaus of cyclotrimer, linear trimer (n_{D}^{20} 1.4074, d_4^{20} 0.9764. Reported[8]: n_{D}^{20} 1.4074, d_4^{20} 0.9750. *Anal.* Found: Si, 19.76%. Calcd. for linear trimer: Si, 19.64 %) and cyclotetramer were obtained as shown in Fig. 2.

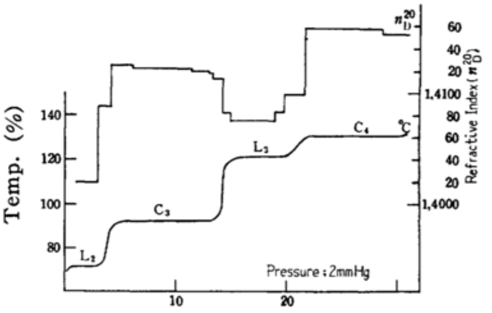

Fig. 2. Distillation curve of ethylethoxypolysiloxanes (Expt. 5. of Table I).
L_n: Linear *n*-mer, C_n: Cyclo-*n*-mer

The residue of each experiment was collected and fractionated through the same column. A small amount of linear tetramer (n_{D}^{20} 1.4127, d_4^{20} 0.9900. Reported[8]: n_{D}^{20} 1.4148, d_4^{20} 0.9960. *Anal.* Found: Si, 20.47%. Calcd. for linear tetramer: Si, 20.63%) and impure cyclopentamer (b. p. 147°C/1 mm., n_{D}^{20} 1.4204. *Anal.* Found: Si, 23.26%. Calcd. for cyclopentamer: Si, 23.76%) were obtained. Properties of the cyclocompounds are given in Table II.

Preparation and Physical Constants of Linear Metylethoxypolysiloxanes.—The fractionation residue of the partially ethanolyzed methyltrichlorosilane (186 g., chlorine content: 20.1%) was treated with 49g. of sodium bicarbonate[8]. Chlorine-free product (107 g.) was rigorously fractionated through a high efficient

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[8] R. Okawara et al., This Bulletin, **28**, 360, 364, 367 (1955).

TABLE II

CYCLIC METHYL-, AND ETHYL-ETHOXYPOLYSILOXANES

Polymer Size n	Boiling Point °C/mmHg	Refractive Index n_D^{20}	Density d_4^{20}	Molar Refraction Found (Calcd.)*	Molecular Weight Found** (Calcd.)	%Si*** Found (Calcd.)
$(CH_3(C_2H_5O)SiO)_n$						
3	94/10	1.3959	—	—	—	26.94
				(72.09)	(313)	(26.96)
4	129/10	1.4001	1.0462	96.48	417	26.97
				(96.12)	(417)	(26.96)
$(C_2H_5(C_2H_5O)SiO)_n$						
3	92/2	1.4125	1.0292	85.86	349	23.77
				(85.98)	(355)	(23.76)
4	131/2	1.4158	1.0317	115.0	477	23.72
				(114.2)	(473)	(23.76)

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

** Cryoscopic measurements in benzene.

*** Silicon was determined by decomposing the sample with sulfuric acid.

column. Succeeding to a small amount of ethanol (5%), monomer (15%), dimer (16%), trimer (10%) and tetramer (5%) of the methylethoxypolysiloxanes were obtained. Properties of the linear polymers until trimer accorded well with the values reported by Fletcher and Hunter[2] which are indicated in parentheses.

Monomer: b. p. °C/760 mm. 141 (143), n_D^{20} 1.3834 (1.3835), d_4^{20} 0.8979 (0.8923).

Dimer: b. p. °C/mm. 86 /10 (100/20), n_D^{20} 1.3910, n_D^{25} 1.3893 (1.3895), d_4^{20} 0.9547, d_4^{25} 0.9516 (0.9441).

Trimer: b. p. °C/mm. 126/10 (73/0.5), n_D^{20} 1.3960, n_D^{25} 1.3935 (1.3934), d_4^{20} 0.9855, d_4^{25} 0.9840 (0.9744).

Stability of Cyclotrimer. — The measurements of the physical properties of cyclotrimer were carried out immediately after the fractionation. Gradual increase in refractive index and viscocity was found by the samples of $(CH_3Si(OC_2H_5)O)_3$, which were sealed in a soft glass ampulla; though they became very viscous the gelation did not take place after 500 days. The typical results obtained with two samples are shown in Table III.

TABLE III

days	0	80	140	250	500
n_D^{20}	1.3956	1.3986	1.4004	1.4040	—
	1.3959	1.3990	1.3992	1.4030	1.4052

With all the samples which were contaminated by this cyclotrimer, the elevation of the refractive index was also observed. For example, it is shown in Fig. 1 in dotted lines. The other three compounds shown in Table II gave no changes of refractive index within one year.

Infrared absorption spectra were obtained with a Hilger H-800 infrared spectrophotometer with a rock salt prism in the range of 700—1300 cm^{-1}. Samples were observed as solution 2% in carbon disulfide. The position of the strong band which appeared in the range 1000—1120 cm^{-1} is shown in Table IV.

TABLE IV

COMPOUND	ABSORPTION SPECTRA (in cm^{-1})		
$(CH_3Si(OC_2H_5)O)_3$	1023	1078	1111
〃 after 500 days	(1027)*	1075	1118
$(CH_3Si(OC_2H_5)O)_4$	—	1068	1117
$(C_2H_5Si(OC_2H_5)O)_3$	1023	1083	1112
$(C_2H_5Si(OC_2H_5)O)_4$	—	1070	1120

* very weak.

It is interesting to follow the change of bands of $(CH_3Si(OC_2H_5)O)_3$ with reference to the change of refractive index. The results showed that the three strong bands observed in the spectra did not change remarkable after 140 days, but it was found clearly that that the strongest band at 1023 cm^{-1} became very weak after 500 days.

Summary

1) Methyl- and ethyl-ethoxydichlorosilane were hydrolyzed with considerable dropping rate using pyridine as an acid acceptor.

2) Methyl- and ethyl-ethoxycyclotrisiloxane have been prepared and characterized. The former was found to be an unstable compound.

3) Methyl- and ethyl-ethoxycyclotetrasiloxane have been prepared and characterized.

4) Some brief data of infrared absorption spectra of those compounds have been presented.

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