Lower Members of Diethoxycyclopolysiloxanes from Diethoxydichlorosilane

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Many series of synthesized compounds of linear and cyclopolysiloxanes have been described in the literature[1]. Diorganocyclopolysiloxanes, $(RR'SiO)_n$ and organohydrocyclopolysiloxanes, $(RHSiO)_n$ have been prepared by the hydrolysis of the corresponding dichlorosilanes or dialkoxysilanes. In these cyclopolysiloxanes, cyclotrimer $(n=3)$ was found to be the first member of the series. In the mineral silicates of natural source, skeletal structure of cyclotrisiloxane was also found[2]. Among the alkoxycyclopolysiloxanes which may be considered to be similar to the mineral silicates in their structure, only a seris of dibutoxycyclopolysiloxanes[3], $((C_4H_9O)_2SiO)_n$ $(n=3, 4, \ldots\ldots)$ was studied. In a series of diethoxycyclopolysiloxanes, only cyclotetramer[4], $((C_2H_5O)_2SiO)_4$ was prepared and the other members of this series have not been reported. This paper will describe the preparation and properties of the lower members of diethoxycyclopolysiloxanes $(n=3$, 4 and 5).

Diethoxydichlorosilane reacts vigorously with water or water vapor instantaneously and the liberated hydrogen chloride causes the fission of ethoxy group from silicon and there remain silica and ethanol as the hydrolysis products. In the previous paper[5] the hydrolysis of triethoxychlorosilane, $(C_2H_5O)_3SiCl$ against the bound water of inorganic salts such as $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ was carried out to assure whether the selective hydrolysis of Si-Cl without the fission of ethoxy group could occur or not. The result obtained showed that the selective hydrolysis occurred in part but the accompanying fission of ethoxy group could not be prevented.

In this experiment, the reaction of diethoxydichlorosilane with sodium bicarbonate, which has the ability to convert Si-Cl to Si-O-Si and the acid accepting function in a molecule, was carried out in the hope of acquiring silanediol or siloxanes by the following reaction.

$$(C_2H_5O)_2SiCl_2+2NaHCO_3$$
$$=(C_2H_5O)_2Si(OH)_2+2NaCl+2CO_2.$$

But the result of this experiment showed that the product was mainly composed of tetraethoxysilane and a high boiling viscous liquid. This reveals that the fission of ethoxy group occurred in the course of the reaction. Then the hydrolysis was car ried out by us-

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[1] E. Rochow, "An Introduction to the Chemistry of the Silicones" John Wiley & Sons, New York, 1951.

[2] W. L. Bragg, "Atomic Structure of Minerals" London, 1937.

[3] R.K. Iler, *Ind. Eng. Chem.*, **39**, 1384 (1947).

[4] T. Takatani, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **72**, 765 (1951); **74**, 890 (1953) (in Japanese).

[5] R. Ōkawara, *J. Chem. Soc. Japan. Ind. Chem, Sec.*, **55**, 678 (1952) (in Japanese).

ing pyridine as an acid acceptor and the lower members of diethoxycyclopolysiloxanes could be isolated. The conditions of hydrolysis are given in Table I.

At first, the hydrolysis was carried out at the constant temperatures of 0°C, 30°C, 50°C and 70°C, respectively. On fractionation, a small amount of the cyclotrimer was found to be formed accompanying the linear trimer in limited ranges of the hydrolysis temperature, e. g., at 30°C and 50°C, while the cyclotetramer was found to appear at each hydrolysis temperature except 70°C. At 70°C, only the linear polymers could be obtained owing to the increasing fission of the ethoxy group. As it seemed very difficult to separate the cyclotrimer from the linear trimer by fractionation, the hydrolysis conditions have been pursued which liberate each one of these compounds independently. It was found that when the hydrolysis was rapidly carried out by adding chlorosilane to the ice-cooled hydrolyzing medium with vigorous stirring, good yield of the cyclotrimer could be obtained without the formation of the linear trimer. From the residue of these hydrolyzates, the cyclopentamer was also obtained. Data of these cyclocompounds are given in Table III.

The cyclotrimer reserved in a sealed glass ampulla became viscous on prolonged standing. The changes of refractive index, density and molecular weight were determined after 200 and 300 days. Trimethylcyclotrisiloxane, $(CH_3HSiO)_3$[6] has been the only example of an unstable cyclotrimer. Now, hexaethoxycyclotrisiloxane seems to be another example of the unstable cyclotrimer.

Experimental

Starting Materials.—Diethoxydichlorosilane used in our experiments was prepared by adding 2 moles of absolute ethanol to 1 mole of silicon tetrachloride with vigorous stirring. After the addition, the mixture was heated gradually to 80°C with stirring. Then the mixture, which was mainly composed of ethoxytrichlorosilane, diethoxydichlorosilane and triethoxychlorosilane was fractionated through a helices packed column of about 20 theoretical plates. The crude diethoxydichlorosilane having the boiling point 130°C to 140°C was rigorously fractionated through the same column and the middle portion of the constant boiling fraction (136°C) was taken as the starting material. Analysis for hydrolyzable chlorine by hydrolysis in water and titration of the liberated acid indicated that our sample was pure diethoxdichlorosilane.

Anal. Found: Cl, 37.2%. Calcd. for $(C_2H_5O)_2SiCl_2$: Cl, 37.5%.

Hydrolysis with Sodium Bicarbonate.—Sodium bicarbonate (25 g., 0.3 mole) was added to the mixture of diethoxydichlorosilane (19 g., 0.1 mole) and 100 cc. of benzene. The violent reaction did not occur differently from the case of partially alkolyzed alkylchlorosilanes[7]. The mixture was heated to refluxing with stirring, but the fuming chlorine compound was stil found in the benzene layer after refluxing for two to three hours and it was not easy to make a trace of the fuming compound disappear with a short time.

From the similar three runs 18 g. of the chlorine free product was obtained. On fractionation, 8 g. of tetraethoxysilane and a small amount of hexaethoxydisiloxane were found. The residue was a high viscous liquid. This reaction was not further examined, for the formation of a large amount of tetraethoxysilane in the product reveals the fission of the ethoxy group during the course of reaction.

Hydrolysis in Pyridine Solution.—(a) *Hydrolysis and fractionation of the hydrolyzate.*—As described above, the hydrolysis of diethoxydichlorosilane with sodium bicarbonate failed to obtain the lower members of cyclocompounds; the hydrolysis in a wet pyridine was therefore carried out. After several experiments the most convenient method of hydrolysis was adopted.

In a 2 *l* three-necked flask equipped with an efficient stirrer, a reflux condenser and a dropping funnel, distilled pyridine which was dehydrated on the solid sodium hydroxide, a slight excess of water required to convert $(C_2H_5O)_2SiCl_2$ to $(C_2H_5O)_2SiO$ and benzene as a diluent were placed. To this hydrolyzing mixture, diethoxydichlorosilane was added with vigorous stirring. The amount of the reagents and the conditions of hydrolysis are given in Table I. After the addition of chlorosilane, the mixture was stirred until the odor of hydrogen chloride or chlorosilane had completely disappeared from the mixture. The product was filtered from pyridine hydrochloride and thoroughly washed with ca. 500 cc. of water over five times to separate the product from pyridine hydrochloride and dehydrated on a calcinated sodium sulfate. When the pyridine hydrochloride was present in the product, it caused the product to decompose in the course of fractionation at a high temperature. After benzene and a slight excess of pyridine were distilled off, the product amounted to Pg. as is shown in Table I. The oily product was simply distilled under 10 mmHg by using a Claisen flask. Tetraethoxysilane (L_1) distilled out, then the remaining oily product was further distilled under 1 mmHg and the distillate coming out below 200°C was collected. Since in these distillations, the stil-pot temperature was not over 300°C, it may be supposed that the thermal rearrangement of polysiloxanes[8] did not occur. The total amount of the distillate obtained under 10 and 1 mmHg (T) and the remaining residue (R_1) in weight percent of P. are also given in Table I.

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

[7] R. Ōkawara et al., This Bulletin, 28, 360, 364 and 367 (1955).

[8] W. Patnode and D.F. Wilcock, *J. Am. Chem. Soc.*, 68, 358 (1946).

The distillate under 1 mmHg was rigorously fractionated through a high efficient semi-micro Stedman column of about 60 theoretical plates and the refractive index and the silicon content of the distillate were determined throughout the distillation. The amount of the succeeding plateaus including the intermittent fractions cut on the distillation curve and the silicon content of these plateaus are given in Table II.

TABLE I

HYDROLYSIS OF DIETHOXYDICHLOROSILANE

In each experiment, diethoxydichlorosilane (150 g., 0.8 mole) was added to the mixture of pyridine (140 g., 1.8 moles), water (15 g., 0.83 mole) and the indicated amount of benzene.

Expt. No.	Hydrolysis					Simple Distillation of P.	
	C_6H_6	Temp.	Dropping Rate of Chlorosilane	Product (P.)		~200°C/1 mm. (T)	Residue (R_1)
	g.	°C	g./min.	g.	% Theory	%P.	%P.
1	155	0	1.7	82	77	30	70
2	250	30	2.2	94	89	62	38
3	250	50	2.0	90	85	70	30
4	250	70	2.0	73	70	82	18
5	145	0-(—)	6.0	90	85	55	45
6*	250	-5-(31)**	12.0	90	85	46	54
7*	250	0-(52)	20.0	98	92	54	46
8	250	0-(54)	37.5	89	84	43	57
9*	250	0-(—)	150.0	87	83	58	42

* Diethoxydichlorosilane was cooled to 0°C before hydrolysis.

** The value in parentheses indicates the highest temperature attained by the reaction.

TABLE II

COMPOSITION OF THE LOWER BOILING FRACTION

(T in Table I)

Expt. No.	Fraction						
	Monomer (L_1)* 60°C/10 mm.	Dimer (L_2) 73°C/1 mm.	Trimer (C_3, L_3) 105°-10°C/1 mm.		Tetramer (C_4, L_4) 130°-45°C/1 mm.		Residue (R_2) 145°C~/1 mm.
	%P.	%P.	%P.	%Si	%P.	%Si	%P.
1	2	0.5	0	—	21	20.95	6
2	15	11	12	18.3-18.1	9	19.6-19.2	15
3	23	12	11	20.0-18.0	7	19.9-19.6	17
4	27	12	10	17.82	6	18.81	27
5	3	3	8	21.0-20.9	16	21.0-20.8	25
6	2	1	4	—	12	21.1-20.5	27
7	4	1	6	21.00	13	20.8-20.6	30
8	1	1	6	20.95	16	20.61	19
9	8	1	4	17.52	15	21.0-19.9	30

* L_n and C_n indicate the linear n-mer and cyclo-n-mer.

Anal. Calcd. for L_1, L_2, L_3, L_4 and C_n: Si, 13.48, 16.40, 17.67, 18.39 and 20,93% respectively.

(b) *Composition of the hydrolyzate.* (i) *Hydrolyzate obtained from the slow hydrolysis at a constant temperature* (Expt. 1-4).—In Expt. 1-4, hydrolysis was carried out at 0°C, 30°C, 50°C and 70°C by adding chlorosilane slowly (2 g./min.) to the hydrolyzing mixture. In Expt. 1, the trimer fraction was not found and the following plateau was that of cyclotetramer (C_4). In Expt. 2 and 3, the trimer fraction may be seen to be composed of cyclotrimer (C_3) and linear trimer (L_3) and the following fraction may also be seen to be composed of C_4 and a small amount of linear tetramer (L_4). From its silicon content, the trimer fraction found in Expt. 4 was L_3 and the following plateau was that of L_4. The higher the reaction temperature, the larger the amount of the fractions of monomer (L_1) and dimer (L_2) obtained and the more the contamination of the linear compounds in the trimer and tetramer fractions. It was supposed to be caused by the fission of ethoxy group with temperature. From the distillation curve of Expt. 3, the appearance of C_3 in front of the plateau of the trimer fraction was clearly shown by its silicon content and a high refractive index at this portion as shown in Fig. 1.

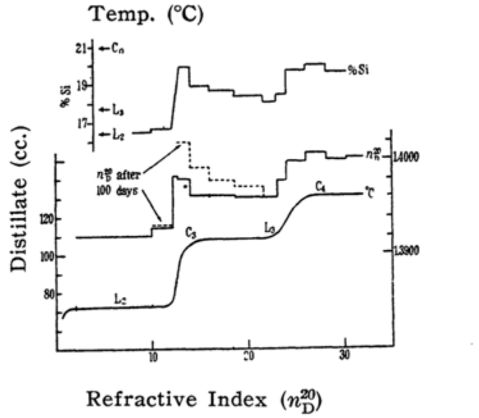

Fig. 1. Distillation curve of Expt. 3 under 1 mmHg.
L_n: Linear n-mer,
C_n: Cyclo-n-mer.

From Fig. 1, C_3 and L_3 may have a close boiling point and it was supposed to be difficult to separate these compounds by the distillation.

(ii) *Hydrolyzate obtained from the rapid hydrolysis* (Expt. 5–9).—From the results obtained in Expt. 1–4, the formation of C_3 was observed, only at the temperature range of 30°C to 50°C and the amount of C_3 was very small by the reaction at the constant temperature. C_3 was successfully obtained without formation of L_3 by the following rapid hydrolysis. The results are given in Table I from Expt. 5 to 9.

By adding the chlorosilane rapidly to the hydrolyzing mixture which was cooled by an ice-salt bath at 0°C, the temperature of the mixture rapidly rose by the reaction. The temperature was observed by the thermometer dipped in the mixture and the highest temperature attained is shown in parentheses in some experiments. After the temperature of the mixture fell down to the temperature of the bath in which ice still remained, stirring was further continued until the chlorosilane odor disappeared completely from the mixture.

In Expt. 5–8, a small amount of L_1 and L_2 was obtained. In the trimer fraction, L_3 was not found, while in the tetramer fraction, C_4 was supposed to be contaminated with a small amount of L_4 at the back part of the plateau. Too rapid addition of chlorosilane to the hydrolyzing mixture as in Expt. 9, may also causes the fission of ethoxy group owing to an instantaneous rise of the reaction temperature, and there was obtained a relatively large amount of L_1 and further only L_3 was found in the trimer fraction and the contamination of L_4 was observed in the tetramer fraction.

(c) *Characterizationof the Cyclopolysiloxanes.*—After redistillation, C_3 was reserved at the room temperature (10°C) and the measurement of its physical properties and analysis were carried out during a week. For the characterization of C_4, the tetramer fractions in Table II having the silicon content 19.6 to 21.1 were gathered and redistilled rigorously through the efficient column described above. To obtain the cyclocompounds higher than C_4, the residues (R_2) of Expt. 5–8 were fractionated as above. The gradually rising plateau (b.p. 148°–150°C/0.3 mmHg) with the distillate (12 cc.), having the silicon content of 20.18 to 20.85%, was obtained. From these data, C_5 may seem to be somewhat contaminated with the neighbouring linear compounds. Properties of these cyclopolysiloxanes are given in Table III.

Stability of the Cyclotrimer.—The cyclotrimer obtained above was sealed in a soft glass ampulla and the refractive index, density and molecular weight were measured after 200 and 300 days. The typical results obtained were as follows.

After days	n_D^{20}	d_4^{20}	Mol. Wt. (in benzene)
—	1.3981	1.0764	398
200	1.4032	1.1083	ca. 1000
300	1.4052 (1.4070)*	—	—

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* Value obtained after the sample had been left open at room temperature for thirty minuites. This change may be caused by the escaping of some volatile matter formed by the decomposition of C_3, for the weight of the sample in a platinum crucible was reduced by about 3.1% of its weight after two hours.

TABLE III

DIETHOXYCYCLOPOLYSILOXANES

C_n: $((C_2H_5O)_2SiO)_n$

Name	Boiling Point °C/mmHg	Refractive Index n_D^{20}	Density d_4^{20}	Molecular Weight Found* (Calcd.)	%Si Found (Calcd.)
Hexaethoxycyclotrisiloxane (C_3)	106/0.7	1.3982	1.0764	400 (402.6)	20.95 (20.93)
Octaethoxycyclotetrasiloxane** (C_4)	125/0.3	1.4015	1.0971	534 (536.8)	20.99 (20.93)
Decaethoxycyclopentasiloxane (C_5)	150/0.3	1.4042	1.1039	660 (671.1)	20.85 (20.93)

* Cryoscopic measurements in benzene.

** T. Takatani, loc. cit., b.p. 138–40/1.5, n_D^{20} 1.4001 and d_4^{20} 1.0946.

As it was of interest to know the compounds which have been formed by the decomposition of C_3, the sample (10 g.) was carefully fractionated through a semi-micro Stedman column of about 30 theoretical plates after 350 days. About 3% of the volatile compound, 2% of L_2 (b.p. 78°C/1 mmHg) and 20% of the trimer fraction (b.p. 106°C/1 mmHg, n_D^{20} 1.3966 and d_4^{20} 1.0364. Anal. Found: Si, 18.19%) were obtained. From the silicon content, this trimer fraction was supposed to be composed of about 84% of L_3 (Reported: b.p. 107°C/0.8 mmHg⁹⁾, n_D^{20} 1.3952⁹⁾ and d_4^{20} 1.0301¹⁰⁾) and 16% of unchanged C_3. The higher fraction could not be obtained until the stil-pot temperature reaches 235°C. The residue was a viscous liquid and the silicon content of it was found to be 22.00%.

With all the samples which were contaminated by C_3, the elevation of the refractive index was also observed. For example, it is shown in Fig. 1 in dotted lines. But the change was not observed by the other compounds within one year.

Analysis of Silicon.—Silicon was determined by decomposing the sample with concentrated sulfuric acid.

Summary

(1) Diethoxydichlorosilane did not easily react with sodium bicarbonate.

(2) Diethoxycyclopolysiloxanes beginning with cyclotrimer could be obtained from the hydrolysis of diethoxydichlorosilane by using pyridine as an acid acceptor.

(3) The lower members of diethoxycyclopolysiloxanes having three to five silicon atoms have been characterized.

(4) The cyclotrimer was found to be formed only in the limited conditions of hydrolysis and it was decomsosed spontaneously in a sealed soft glass ampulla.

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9) R. Ōkawara, T. Tanaka and K. Maruo, This Bulletin, 28, 189 (1955).

10) T. Takatani, *J. Chem. Soc. Japan, Pure Chem. Sec.*, 73, 409 (1952) (in Japanese).