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THE FORMATION OF POLYHEDRAL ETHYLSILSESQUIOXANES IN THE PROCESS OF OLIGOETHYLHYDROCYCLOSILOXANE POLYCONDENSATION

M.G. VORONKOV,

Institute of Organic Chemistry, Siberian Branch of the USSR Academy of Sciences, 664033 Irkutsk (U.S.S.R.)

V.I. LAVRENTYEV *, and V.M. KOVRIGIN,

Institute of Inorganic Chemistry, Siberian Branch of the USSR Academy of Sciences, 630090, Novosibirsk (U.S.S.R.)

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Summary

A mechanism by which polyhedral oligoethylsilsesquioxanes are formed in the course of alkali-catalyzed polycondensation of oligoethylhydrocyclosiloxanes is suggested on the basis of the identification of 24 intermediates by GC-MS. The main trend in the formation of the silicon-oxygen framework of the oligoethylsilsesquioxanes is the consecutive addition of monomers, $RSiHX_2$ and dimers, $(RSiHX)_2O$, to the initial cyclosiloxanes and to the condensed ethylpolycyclosiloxanes thus formed. The mechanism suggested is confirmed by the data from a chromatographic investigation of the variations in the concentration of the reaction products.

Results and discussion

Oligoorganylsilsesquioxanes, $(RSiO_{1.5})_n$ (n = 8—10) are usually synthesized by hydrolytic polycondensation of the corresponding trifunctional monomers, $RSiX_3$ [1—4]. Use of oligoalkylhydrocyclosiloxanes as the starting monomers in the presence of moderately strong anionic catalysts [5,6] enables polyhedral organosilsesquioxanes to be prepared in sufficiently high yield. Until now, however, no conclusive interpretation of the mechanism of the formation of the silicon-oxygen framework of the above polyhedral compounds has been given.

Using combined gas chromatography and mass spectrometry we have studied the composition of the intermediates and the volatile products formed in the polycondensation of oligoethylhydrocyclosiloxanes in diethyl ether with alcoholic alkali hydroxide as the catalyst. The structure of the compounds identified

(Continued on p. 288)

TABLE 1

MONO- NAD POLYCYCLOSILOXANES, $(C_2H_5SiO_{1.5})_k(C_2H_5SiO)_mX_{m-1}$, IDENTIFIED BY GC-MS OF THE POLYCONDENSATION OF OLIGOETHYLHYDROCYCLOSILOXANES

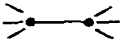
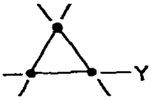
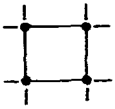
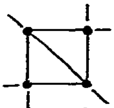
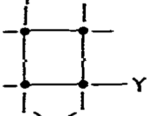
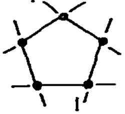
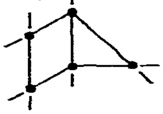
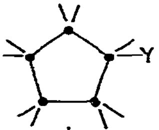
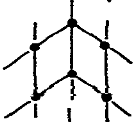
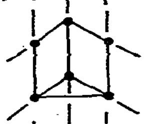
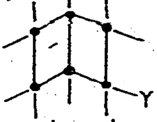
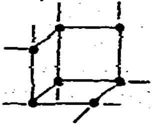
No.	Compound	Structure	Relative retention time	Ref.
1	$[Et(OCH_3)HSi]_2O$		0.7	a
2	$k = 0$, $m = 3$, X = H, Y = OCH_3		0.9	7
3	$k = 0$, $m = 4$, X = Y = H		1.0	7
4	$k = 2$, $m = 2$, X = Y = H		1.67	7
5	$k = 0$, $m = 4$, X = H Y = OCH_3		1.71	7
6	$k = 0$, $m = 5$, X = Y = H		1.83	7
7	$k = 2$, $m = 3$ X = Y = H		2.1	7
8	$k = 0$, $m = 5$, X = H Y = OCH_3		3.1	7
9	$k = 2$, $m = 4$, X = Y = H		6.8	8
10	$k = 4$, $m = 2$, X = Y = H		9.1	a
11	$k = 2$, $m = 4$, X = H Y = OCH_3		8.8	8
12	$k = 4$, $m = 3$, X = Y = H		9.4	9

TABLE 1 (cont.)

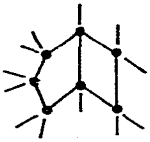
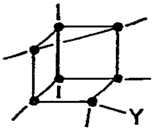
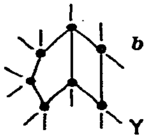
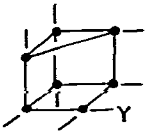
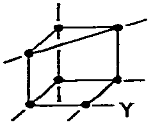
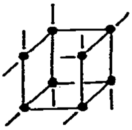
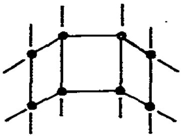
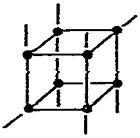
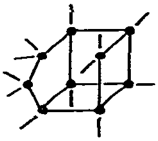
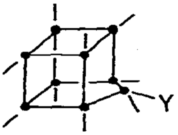
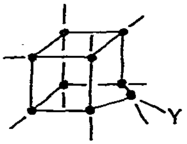
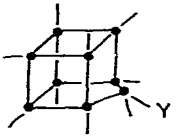
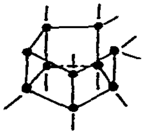
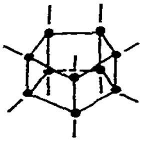
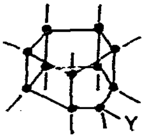
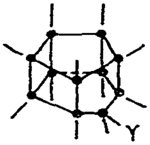
No.	Compound	Structure	Relative retention time	Ref.
13	$k = 2$, $m = 5$, $X = Y = H$		9.8	8
14	$k = 6$, $m = 1$, $Y = H$		10.6	6
15	$k = 2$, $m = 5$, $X = H$ $Y = OCH_3$		10.9	8
16	$k = 6$, $m = 1$, $Y = OCH_3$		12.1	6
17	$k = 6$, $m = 1$, $Y = OH$		12.4	6
18	$k = 6$, $m = 2$, $X = Y = H$		13.5	10
19	$k = 4$, $m = 4$, $X = Y = H$		13.9	8
20	$k = 8$, $m = 0$		15.0	11
21	$k = 6$, $m = 3$, $X = Y = H$		15.6	10

TABLE 1 (cont.)

No.	Compound	Structure	Relative retention time	Ref.
22	$k = 8, m = 1, Y = H$		18.0	6, 10
23	$k = 8, m = 1$ $Y = OCH_3$		19.8	6, 10
24	$k = 8, m = 1, Y = OH$		22.0	6, 10
25	$k = 8, m = 2,$ $X = Y = H$		23.3	10
26	$k = 10, m = 0$		28.3	11
27	$k = 10, m = 1, Y = H$		33.5	6
28	$k = 10, m = 1$ $Y = OCH_3$		34.1	6

[a] The mass spectra will be published later. [b] The position of Y was not established exactly.

(Table 1) and the variations in their concentrations, which were followed chromatographically during the process (Figs. 1 and 2), suggested a mechanism for the formation of polyhedral oligoethylsilsesquioxanes.

The addition of a catalytic amount of methanolic KOH solution to oligoethylhydrocyclosiloxanes, $(RSiHO)_m$ * with $m = 4$ and 5, in diethyl ether leads to

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* Here and further $R = C_2H_5$

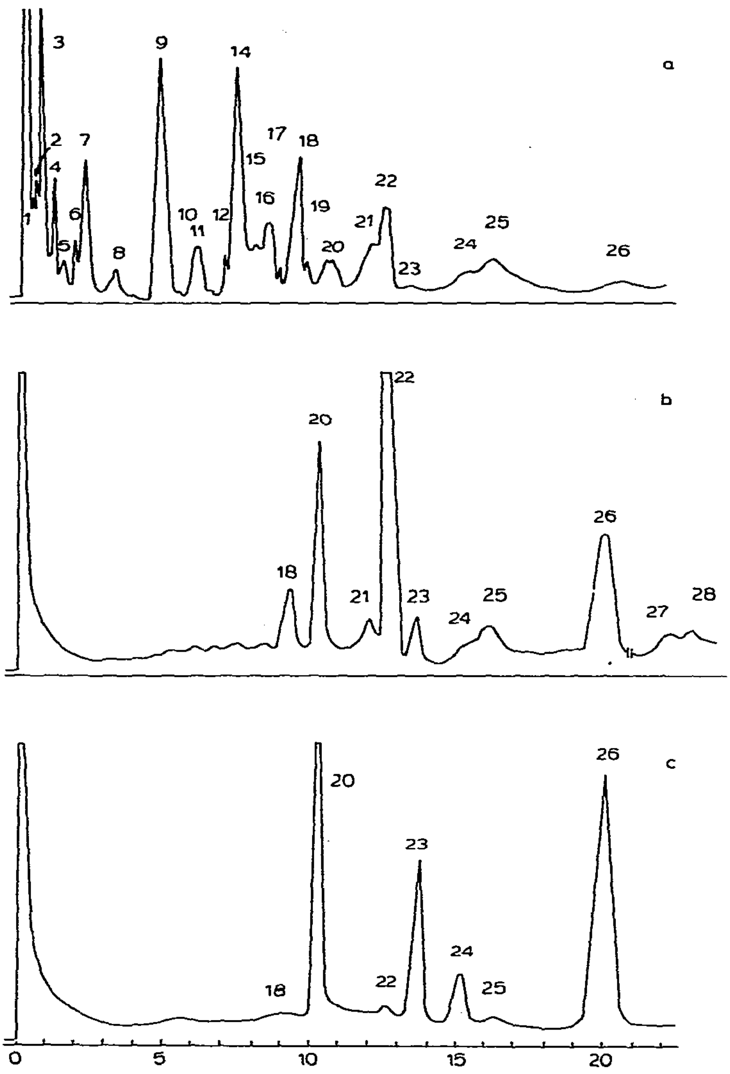


Fig. 1. Chromatograms of oligoethylhydrocyclosiloxane polycondensation products: a, after 5 min; b, after 150 min; c, 120 hours and more after start of the reaction.

rapid decomposition of the cyclic system (Figs. 1 and 2) and formation of rather stable 1,3-diethyl-1,3-dimethoxydisiloxane 1 (Table 1) and evidently the labile linear α-methoxy-ω-hydroxyoligoethylhydrosiloxanes, both having the same or a smaller number of siloxane units than the initial cycles. The process may be accompanied by the formation of monomers of the $RSiHX_2$ and $RSiX_3$ type ($X = OCH_3$, OH), which rapidly become involved in further condensation. This is confirmed by the ethyltrimethoxysilane and ethyldibutoxysilane observed in the initial stage of analogous reactions carried out in excess methanol or butanol, respectively. Highly reactive linear α-methoxy-ω-hydroxyoligoethylhydrosiloxanes undergo rapid cyclization to 1-methoxyoligoethylhydrocyclosiloxanes

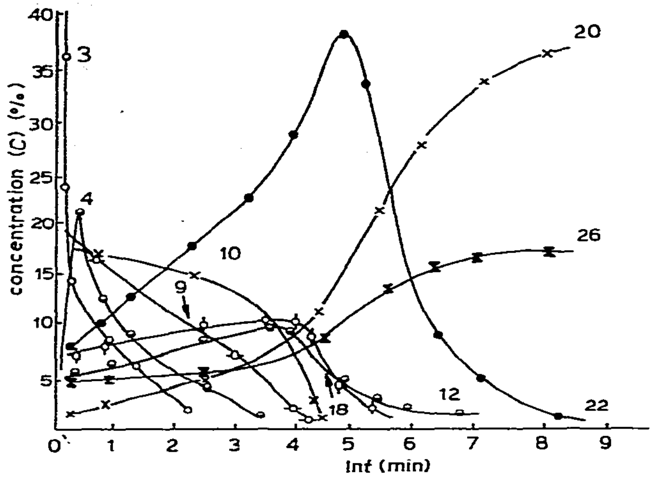
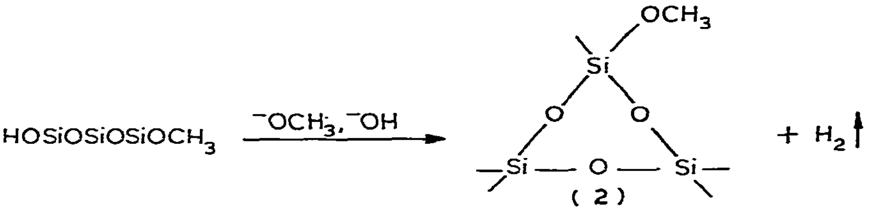
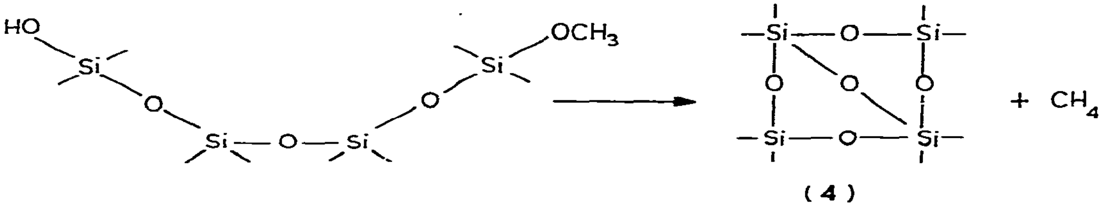


Fig. 2. Variation in the concentration (C) of main products in the polycondensation of oligoethylhydrocyclosiloxanes.

2, 5 and 8, and the corresponding bicyclosiloxanes 4 and 7

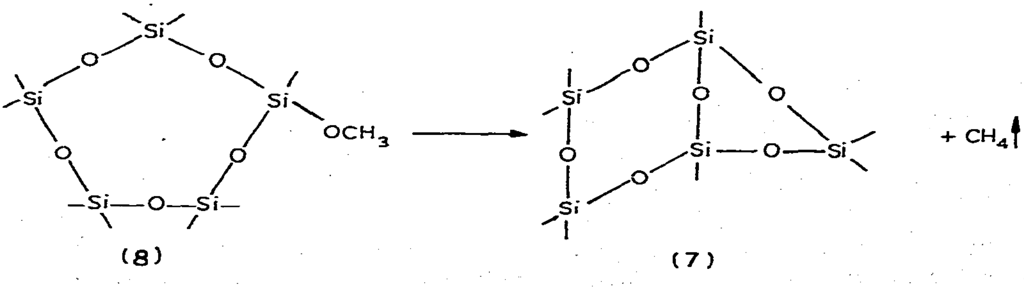


(1)



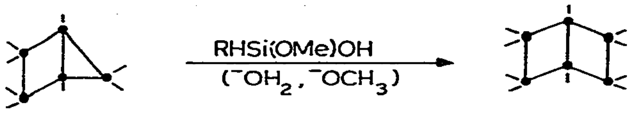
(2)

It is also possible that bicyclosiloxanes 4 and 7 are formed from the corresponding 1-methoxy-oligoethylhydrocyclosiloxanes 5 and 8.



(3)

The higher bicyclosiloxanes 9, 13 and 11, 15 are likely to be formed in two main ways: (i) insertion of monomers into the cyclotrisiloxane edge of their primary homologues (eq. 4) and (ii) addition of disiloxane 1 (or its analogues) to the corresponding cyclosiloxanes (eq. 5).

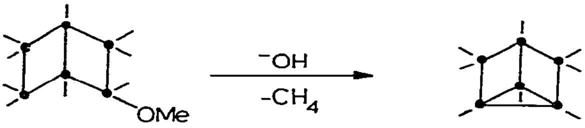


(7) (9)

(4)

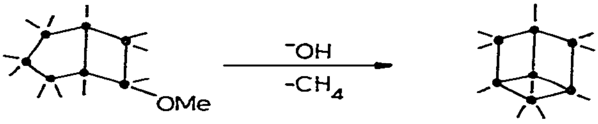
(5)

Intramolecular condensation of 1-methoxybicyclosiloxanes 11 and 15 gives the corresponding tricyclosiloxanes:



(11) (12)

(6)

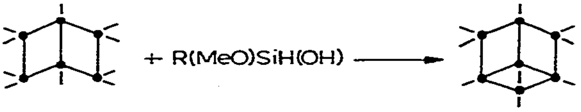


(15) (12)

(7)

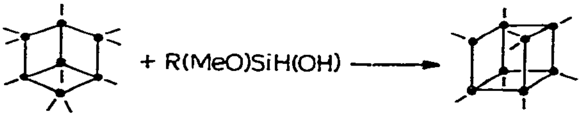
The rapid consumption of the sterically strained bicyclosiloxanes 4 and 7 (Fig. 2) is accompanied by both the formation of higher homologues (eq. 4) and the complete decomposition of the former with elimination of monomers and dimers. The latter, in turn, become involved in further condensations, leading to more complex condensed ethylpolycyclosiloxanes:

complex condensed ethylpolycyclosiloxanes:



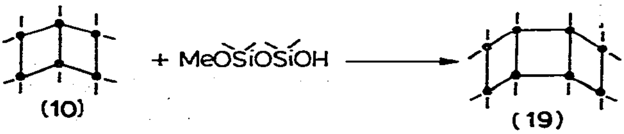
(11) (12)

(8)



(12) (18)

(9)

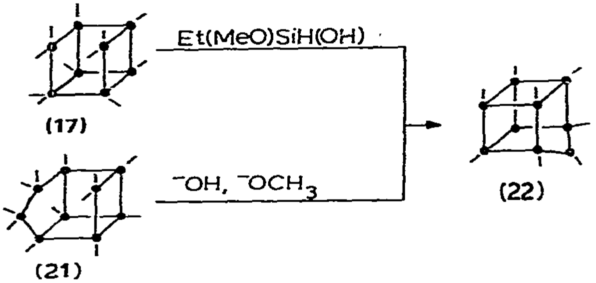


(10) (19)

(10)

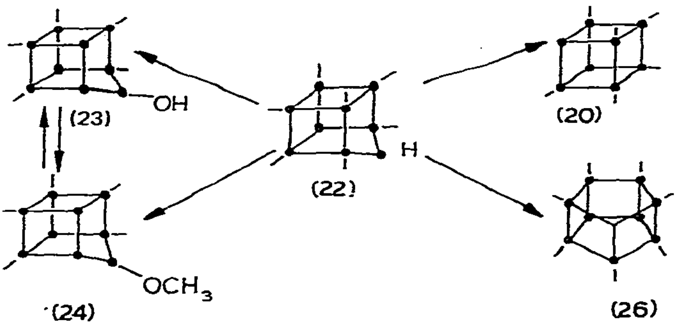
The low yield of ladder tri- and tetracyclosiloxanes points to the small probability of consecutive stepwise polycondensations of oligoethylhydrocyclosiloxanes under the reactions used.

Further polycondensation consists mainly of the reaction of polycyclosiloxanes with monomers. This is confirmed by the great number of 1-substituted perethylhomooligosilsesquioxanes formed: **14**, **16**, **17**, **23**, **24**, **22**, **28** and **27** (Table 1). 1-Hydrononaethylhomooctasilsesquioxane **22** is the main kinetic product of the polycondensation of $(RSiHO)_m$ (Figs. 1 and 2). It can be formed either from two polycycles **17** and **21** (eq. 11) or from addition of the dimer to bicycle **13**.



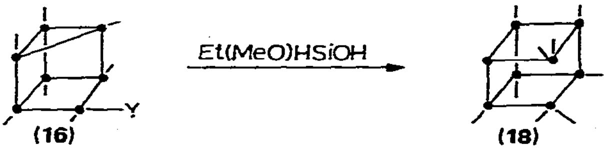
(11)

Furthermore, the hydrogen atom in the reaction product **22** may be substituted by an OH or OCH_3 group. Compound **22** is also converted to octa- and decasilsesquioxanes as evidenced by the data from gas chromatography (Figs. 1 and 2)



(12)

The comparatively low concentrations of 1-substituted heptaethylhomohexasilsesquioxanes (**16**, **13** and **17**) among the kinetic products (Fig. 2) may indicate their ready conversion to polycyclosiloxanes with a less strained structure. These processes are most likely to be due to insertion of the monomers into the siloxane edge, for example



(13)

The above polycondensation schemes are confirmed by the liberation of hydrogen and methane, identified mass-spectrometrically in the course of the reaction.

According to Brown and Vogt [12], the formation of the silicon-oxygen framework of the phenylsilsesquioxanes is caused by consecutive cross-linking of monocyclic macromolecules. In our case, however, this route seems less probable. Thus, the formation of the silicon-oxygen framework of polyhedral oligoethylsilsesquioxanes is a result of the reaction of the initially formed condensed ethylpolycyclosiloxanes with monomers and dimers of the $RSiHX_2$ and $(RSiHX)_2O$ type, where $X = OH, OCH_3$.

Experimental

The composition of the reaction mixture was studied on a MAT 311 A mass spectrometer equipped with a Varian SS-100 MS data system, by the consecutive sample selection method. The spectra were measured at 70 eV, $R = 1000$. The relative contents of the reaction mixture were calculated from peak areas. GC and GC-MS analyses was performed on a Varian 2700 chromatograph with a flame-ionization detector. A 3 × 1500 mm stainless steel column packed with 5% SE-30 Chromosorb W 80/100 mesh was used with He as carrier gas introduced at a rate of 35 ml/min. The column temperature was programmed from 150 to 225°C (±1°). For more volatile products the column temperature was programmed within the 100—225°C range.

Polycondensation of oligoethylhydrocyclosiloxanes

1 ml of 1% methanolic KOH solution was added to 100 ml of a 5% solution of a 9 : 1 mixture of tetraethylcyclotetrasiloxane and pentaethylcyclopentasiloxane in diethyl ether. After 120 h the crystalline octaethylsilsesquioxane was formed in 37% yield.

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