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DEHYDROCONDENSATION OF HYDROGEN-CONTAINING CYCLOSILOXANES

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Summary

The dehydrocondensation of hydrogen-containing cyclosiloxanes under alkali conditions has been studied. The reaction was found to have two alternative courses depending on the conditions. A quantative yield of cyclolinear ladder polymers, their catalytic regrouping resulting in a $(RSiO_{1.5})_n$ oligomer mixture, where $n = 8-12$, $R = CH_3$, C_2H_5, can be obtained. The other reaction course is the formation of octamer ($n = 8$).

The general factors affecting the volatile oligomer yield, such as the temperature, the concentrations of starting reagents, catalyst and water, have been determined.

Based on the structures of some intermediate products and the composition of gaseous products, a mechanism for the oligomer formation is discussed.

Introduction

As we have previously shown [1,2] octa(organylsilsesquioxanes) may be used as radiation-sensitive materials for dry vacuum submicron lithography. They can also serve as starting products for the synthesis of high molecular weight poly(organosilsesquioxanes) [3].

Hydrolytic organotrialkoxy- or organotrichloro-silane polycondensation is the simplest method of preparing these compounds. Linear and cyclic compounds, ladder organopolysiloxanes and low molecular polymers with space-ordered cage-like molecular structures (oligosilsesquioxanes) having general formula $(RSiO_{1.5})_n$, where $n = 6-14$, and R is an organic radical, may be prepared depending on the synthesis conditions. The yield of volatile oligomer is affected by the organic radical and the solvent [4–6]; the octamer T_8 has as a rule the highest yield. Thus the yields of T_8 with branched radicals are 40–50% [7,8] while methyl- and ethyl-T_8 yields are low [4,9].

A wide range of substances (T_8–T_{12}) was found when the alkyl silicon gel obtained by alkyltriethoxysilane hydrolysis was decomposed. The total yield of

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volatile products was 16%, T_8 accounts for 66% of this [10,11].

A directed synthesis method carried out by tetrole condensation [12], which can proceed both intra- and intermolecularly after dimer formation, is known. In the former case T_8 is formed, in the latter one poly(silsesquioxane) is. The nature of the organic radical determines the reaction course. Thus, when the phenyl substituents in the side rings are substituted by methyl ones the reaction takes place mainly as an intramolecular condensation [12]. It is, however, difficult to prepare T_8 by this method because alkyl-containing tetrols are not readily accessible.

Results and discussion

We have previously reported that 2,4,6,8-tetramethylcyclotetrasiloxane ($D_4^{(CH_3,H)}$) and tetraethylcyclotetrasiloxane ($D_4^{(C_2H_5,H)}$) may be used as starting materials for the synthesis of T_8 [13,14]. The aim of the present work was to study the alkyl-T_8 preparation according to the following equation:

$$2\,(R(H)SiO)_4 + 4H_2O \xrightarrow{NaOH} (RSiO_{1.5})_8 + 8H_2 \qquad (1)$$

$R = CH_3, C_2H_5$

The synthesis was performed in organic media in the presence of alcoholic alkali. We divided the reaction conditions into "mild" and "forcing" ones. High starting product concentrations, polar organic solvents and the refluxing reaction medium are implied to be forcing conditions. When performing synthesis under mild conditions, non-polar solvents, starting product concentrations of 4% and cooling were applied.

Cleavage of the Si–H bond may in the presence of alcohol proceed with both hydrogen and hydrocarbon evolution, according to the following equations [15]:

$$\geqslant SiH + OR^- \xrightarrow{HOR} \geqslant SiOR + H_2 + OR^- \qquad (2)$$

$$\geqslant SiH + OR^- \rightarrow \geqslant SiO^- + HR \qquad (3)$$

The reaction with volumetric determination of evolving gases was carried out to determine the quantity and nature of gaseous products. Identification of the gaseous products was carried out by mass spectrometry. The reaction was found to proceed with the evolution of hydrogen with hydrocarbon impurities. The gas volumes corresponded to the theoretical ones calculated from eq. 2 within experimental error; gaseous alkylsilanes formed during $D_4^{(CH_3,H)}$ anion polymerization [16] were not found. This may prove that under such conditions cleavage of the Si–H bond competes with the classic cleavage of the Si–O ring. Hydrogen in a volume half as large as that in the preceding case was found in the diethyl ester medium (the optimum conditions for T_8 synthesis).

The Si–H bond is likely to interact with the hydroxyl group according to the reaction:

$$\geqslant SiH + OH^- \rightarrow \geqslant SiOH + H^+ \qquad (4)$$

The effect of alkali concentration on the yield of T_8 was investigated. According to eq. 4, T_8 formation proceedes via intermediate silanols; the cyclosiloxane:alkali ratio was chosen such that the hydroxyl group content was enough for partial or complete $\geqslant$SiH $\rightarrow$ $\geqslant$Si–OH transformation. Synthesis was performed in ethanol with a starting concentration of 2–4% and $\geqslant$SiH:NaOH ratios of 1:1, 2:1 or 4:1.

A gelatinous product not subliming under vacuum up to 400°C was formed under these conditions. Analysis of the IR spectrum showed that the absorption bands at 400–600 cm^{-1} characteristic of the deformation vibrations of the T_8 inorganic framework [17] did not have a pronounced nature. A doublet at 1050 and 1140 cm^{-1} appeared in the absorption region of Si–O–Si stretching vibrations. This is known to be characteristic of oligomers containing both terminal cyclic silsesquioxane groups and ladder polysiloxane fragments [18]. From the data obtained and the element analysis we conclude that under the conditions described the reaction is completly directed to formation of polymers with the ladder molecular structure.

When refluxed for a long period without extraction from the reaction mixture the gelatinous product dissolves and a white powder partially sublimable in vacuum is precipitated. The IR spectrum of this compound coincides in general with that of methyl-T_8 [19]. The elemental analysis data correspond to a $CH_3SiO_{1.5}$ molecular formula. The mass spectrometric study of the sublimate proved that the substance was a methyl-T_n oligomers mixture, where $n = 8–12$, the mixture composition being dependent on the starting cyclosiloxane nature.

In the case of mild conditions for the dehydrocondensation of D_4 (a starting material concentration of 1%, and alkali concentration of 0.5%), the yield (~ 45%) of volatile oligomers, consisting (from mass spectrometric analysis) of T_8 with a small T_{10} impurity (~ 3%), is higher. Thus, the data obtained show that simultaneous Si–H and Si–O bond cleavage takes place under these conditions, leading to mixtures of oligomers in the products. Decreasing the reaction rate would seemingly allow synthesis to be directed to preparation of T_8 and increase its yield. This can be realized by using nonpolar solvents and decreasing the synthesis temperature. The experimental data in Table 2 show that the yield of volatile products depends on the

TABLE 1

THE OLIGOMER MIXTURE OBTAINED BY CYCLOSILOXANE DEHYDROCONDENSATION

Starting material	Sublimate composition	Most intense peaks in the mass spectrum (m/e)	
$D_3^{(CH_3,H)}$ [a]	Methyl-T_{10}, T_8	$(M_{10}-CH_3)^+$	655
		$(M_{10}-2CH_3,H)^+$	639
$D_4^{(CH_3,H)}$	T_8:T_{10}	$(M_8-CH_3)^+$	521
	2:1	$(M_{10}-CH_3)^+$	655
$D_5^{(CH_3,H)}$	T_8:T_{10}	$(M_8-CH_3)^+$	521
	1:1,7	$(M_{10}-CH_3)^+$	655
$D_6^{(CH_3,H)}$	T_8:T_{10}:T_{12}	$(M_8-CH_3)^+$	521
	0.5:1:0.2	$(M_{10}-CH_3)^+$	655
		$(M_{12}-CH_3)^+$	789
$D_4^{(C_2H_5,H)}$ [b]	Ethyl-T_8:T_{10}	$(M_8-C_2H_5)^+$	619
	1:1	$(M_{10}-C_2H_5)^+$	781
$D_3^{C_2H_5,H)}$	T_8	$(M_8-C_2H_5)^+$	619
$D_6^{C_2H_5,H)}$	T_8:T_{10}	$(M_8-C_2H_5)^+$	619
	3:1	$(M_{10}-C_2H_5)^+$	781

[a] The oligomers ratio were calculated from the mass spectra in terms of the ratio of $(M-R)^+$ ion intensities. [b] The ratio was determined by GLC analysis.

TABLE 2

DATA ON THE SYNTHESIS OF OCTA(ALKYLSILSESQUIOXANES)

	Starting materials	Solvent	Synthesis conditions				Final products
			Cyclosiloxane concentration (%)	SiH:NaOH ratio	Temperature (°C)	Volatile product yield (%)	
1	$((CH_3,H)SiO)_4$	Diethyl ether	5	4:2	0–5	35.5	Methyl-T_8
2	$((CH_3,H)SiO)_4$	Diethyl ether	5	4:0.8	0–5	68	Methyl-T_8
3	$((CH_3,H)SiO)_4$	Tetrahydrofuran	0.5	4:1	0–5	50	Methyl-T_8
4	$((CH_3,H)SiO)_4$	Methanol	10	4:5	20	Does not sublime	Ladder polymer
5	$((CH_3,H)SiO)_4$	Ethanol	4	1:1	Reflux (10 h)	10	Methyl-T_{10}:T_8 (1:1)
6	$((CH_3,H)SiO)_4$	Ethanol	1	4:1	Reflux (10 h)	45	Methyl-T_8:T_{10} (2:1)
7	$((C_2H_5,H)SiO)_4$	Methanol	10	4:5	20	Does not sublime	Ladder polymer
8	$((C_2H_5,H)SiO)_4$	Ethanol	2.5	4:1	Reflux (20 h)	10	Ethyl-T_8:ethyl-T_{10} (2:1)
9	$((C_2H_5,H)SiO)_4$	Diethyl ether	2.5	4:0.8	0–5	65	Ethyl-T_8
10	$((C_2H_5,H)SiO)_4$	Tetrahydrofuran	2.5	4:0.8	0–5	70	Ethyl-T_8

synthesis conditions; in all cases discrete octamer is obtained; its structure being confirmed by IR and mass spectrometric analysis and the X-ray data corresponding to the published ones [20].

The yield of final product (T_8) was found to be considerably affected by the dehydration rate. Figure 1 shows the dependence of the methyl-T_8 yield on the $D_4^{(CH_3,H)}$ dehydration time. As a result, with the dehydration process prolonged up to 3–4 hours, a large yield of octamer can be obtained with low polymer content. The dehydration rate is regulated by the reaction temperature and it is less dependent on the alkali concentration (Fig. 2). From these data one may suppose that reducing the rate of this reaction step promotes the intramolecular condensation of intermediate dimer to form T_8 and that the yield of high polymer formed by intermolecular condensation is small.

It is interesting to investigate the effect of water in the yield of T_8, according to eq. 4. For this aim, the $SiH:H_2O$ ratio was varied from 1:1 to 1:0.1 (Fig. 3). Considerable excess of water was found to shorten the time required for the synthesis; however, the reaction is then mainly directed to high polymer formation. Low water content in the reaction mixture (~ 0.01%) shortens the synthesis time and allows one to obtain the end product in high yield.

As our studies show, the preparation of T_8 is impossible without traces of water and a catalytic quantity of alkali. Adding some water to the reaction mixture permits one to obtain a discrete octamer. The best results have been obtained in D_4 dehydration with catalytic quantities of alkali and in the presence of water, the ratio of SiH and H_2O being 1:1.5.

Summarizing the experimental results, we conclude that the reaction course and the preparation of T_8 are affected by the concentrations of both alkali and water present in the reaction mixture. The effect is conditioned by the fact that the presence of a trace of water is required for the formation of enough silanols as a result of the interaction of highly concentrated alkali with alcohols, but there is a need to add more water if the quantities of alkali are catalytic.

A study of the intermediates formed in the reaction was carried out by GLC analysis, IR spectroscopy and mass spectrometry. According to the GLC data, the starting cyclosiloxanes disappear quickly (5–10 min) from the reaction mixture, their

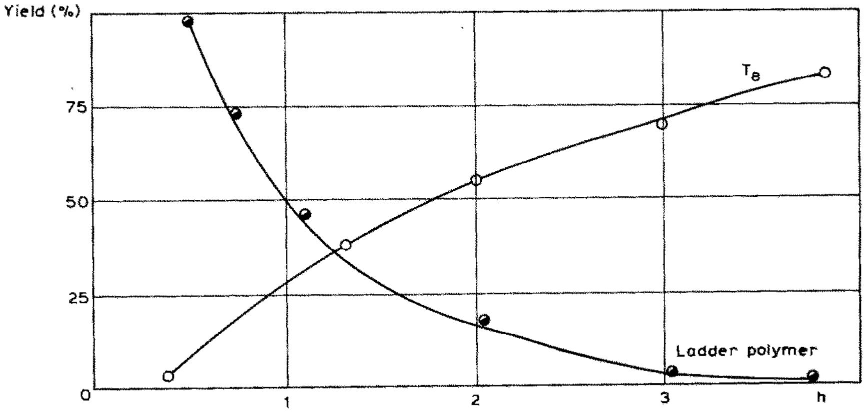


Fig. 1. Dependence of yield of T_8 on time of gas evolution.

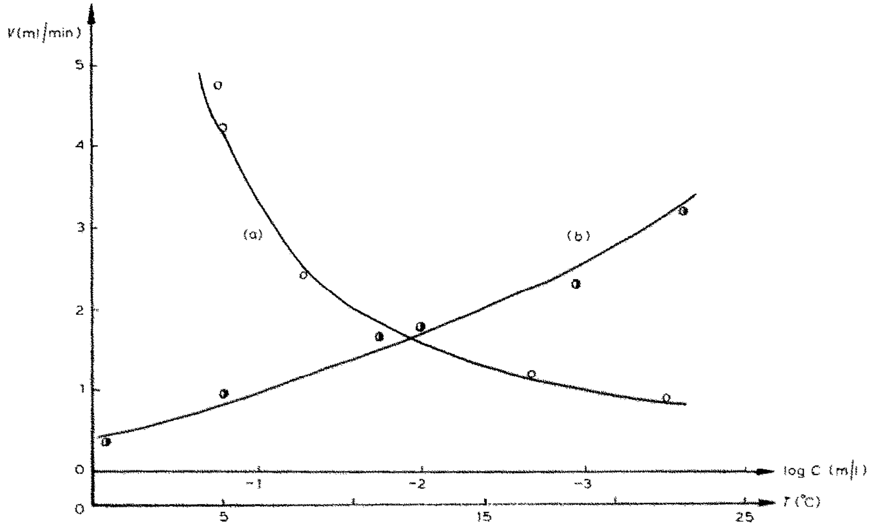


Fig. 2. Dependence of rate of gas evolution in dehydrogenation of $D_4(CH_3,H)$ (a) on alkali concentration; (b) on temperature.

reactivities being dependent on the organic radical and the siloxane ring size. Thus in the ethylcyclosiloxane series the reactivity of D_4 is twice as high as that of D_5, and methylcyclosiloxanes are more active than their ethyl analogs. In the IR spectra the Si–H (2190 cm^{-1}) vibration disappears completely after gaseous product evolution ceases. On the other hand, bands at 400–600 cm^{-1} appear two hours after the reaction started. This phenomenon is usually ascribed to the deformation vibrations of the T_8 molecular silsesquioxane framework [17].

As products of the initial step, alkoxy-hydroxy derivatives of cyclosiloxanes have

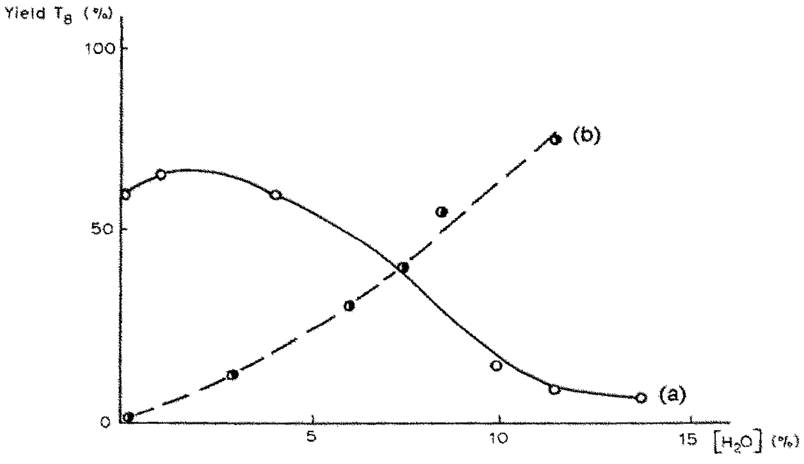


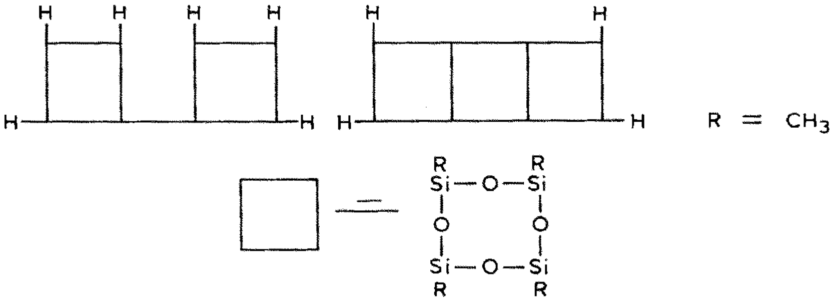
Fig. 3. Dependence of yield of T_8 on water concentration: (a) cyclosiloxane:alkali ratio 1:1, (b) catalytic amount of alkali.

been isolated, which had the following structure:

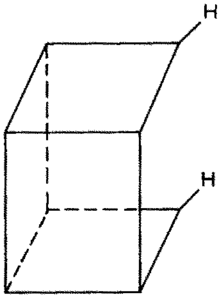
$$(\mathrm{R(OH)}_x(\mathrm{OR})_{4-x}\mathrm{SiO})_4 \quad \mathrm{R} = \mathrm{CH_3, C_2H_5}$$
$$x = 1\text{–}4$$

The reactive functional groups of these compounds were protected by trimethylchlorosilane treatment as reported [9]. The previous paper reports the isolation of the intermediate products during methyl-T_8 synthesis by hydrolytic polycondensation of methyltrichlorosilane.

The intermediate oily products whose concentrations increased during the reaction, were isolated by treating the reaction mixture. GLC analysis demonstrated the two materials whose IR spectra show that they have Si–H bonds (2190 $\mathrm{cm^{-1}}$). The peaks with *m/e* 479 and 493 are the most intensive ones in the mass spectra, the general fragmentation consists of elimination of organic radical without cleavage of the main molecular chain, which is characteristic of cyclic structures [21]. These data suggest that the intermediates have the structures given below and that they are the products of incomplete dehydration and condensation of starting D_4:



The final reaction products were isolated from the solution in the form of transparent crystals, in which an impurity of 10% was founded by GLC analysis. Identifying the mixture by mass spectrometry as reported [22] suggests the presence of T_8 and the incomplete condensation product with a cage-like molecular structure:



Thus, the formation of alkyl-T_8 from alkyl(hydride)cyclosiloxanes is a stepwise dehydration and condensation process; and dimers thus formed undergo intramolecular condensation with T_8 formation. Under the forcing reaction conditions processes forming cyclolinear polymers predominate; catalytic rearrangement of the polymers resulting in volatile oligomers T_n, where $n = 8$–12.

We conclude that the specific synthesis conditions guaranteeing high final product yields promote the preparation of the octamer; TU-6-09-11-1378-79 of Minchimprom demonstrates the practical value of this work.

Experimental

The starting cyclosiloxanes were prepared by hydrolysis of the corresponding alkyldichlorosilanes in a water-ether medium. The product mixture isolated was separated in a fractionating column. Final purification was performed with a LXM-72 chromatograph equipped with a preparative isolation attachment and stainless steel 2000 × 5 mm column filled with chromosorb W impregnated with 5% SE-30. He carrier gas rate was 50 ml/min. The evaporation temperature was 215°C, the column temperature was programmed linearly from 100 to 200°C with a rate of 2°/min. As a result chromatographically pure D_n ($n = 3$–6) having properties agreeing with those reported [2,3] were prepared.

D_4 dehydrocondensation under mild conditions

100 ml of a 0.001 *N* solution of the corresponding cyclosiloxane were cooled in ether or tetrahydrofuran to 0°C, then 2 ml of 1% NaOH solution were slowly added to the reaction mixture keeping the reaction medium temperature not above 5°C. A crystalline precipitate was filtrated off and dried in the open air over 4–5 days. The yield was 70–80% of starting D_4. For the methyl derivative: Found: C, 17.88; H, 4.50; Si, 42.02. $C_8H_{24}Si_8O_{12}$ calcd.: C, 17.90; H, 4.47; Si, 41.86%. Molecular weight; 536 (by mass spectrometry), theoretically, 536. $n_d^{20} = 1.510$; $d_4^{20} = 1.514$.

For the ethyl derivative: Found: C, 29.55; H, 6.23; Si, 34.90. $C_{16}H_{40}Si_8O_{12}$ calcd.: C, 29.62; H, 6.16; Si, 34.40%. Molecular weight; 649 (by mass spectrometry), theoretically 648. n_d^{20} 1,490; d_4^{20} 1,306.

IR spectrum (cm^{-1}); deformation of the inorganic framework at 385–565 cm^{-1}, ν_{as}(Si–O–Si) at 1120 cm^{-1}, ν(C–H) at 1270–1470 cm^{-1}. X-ray data correspondent to those reported [20].

D_4 dehydrocondensation under forcing conditions

The synthesis was performed, as previously described, in methyl alcohol medium with 0.1 *N* starting material concentrations and in refluxing solvent. The precipitate was filtered off after 2 hours, treated with methanol and dried in the open air. The product is practically insoluble in most organic solvents and does not sublime in vacuum at temperature up to 400°C. IR spectrum: doublet at 1140–1160 cm^{-1}.

The reaction mixture prepared was boiled for 8 hours, to transform the gel into a solution, and then a powder precipitates which was filtered off, dried in the air and sublimed in vacuum. The yield of volatile products was 10% of the starting D_4. A chromatogram shows three peaks; identifying them by mass spectrometry, they are methyl-$T_8 - (M_8 - CH_3)^+$ with m/e 521; $T_{10} - (M_{10} - CH_3)^+$ with m/e 655; $T_{12} - (M_{12} - CH_3)^+$ with m/e 789.

The IR spectra were recorded on a UR-20 two beam spectrophotometer in KBr pellets. Chromatography was carried out Tsvet-100 and LXM-72 chromatographs as reported above. The mass spectra were determined at an ionization voltage of 70 eV on the MX-1303 and MS-902 apparatus. The X-ray investigation was performed on a Syntex-P2 automatic diffractometer. The density and refractive indexes were determined by the flotation and immersion methods [24].

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