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Abstract

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CHEMISTRY

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CONDENSATION OF HEXAMETHYLDISILOXANE IN A HIGH-VOLTAGE SILENT DISCHARGE OF AUDIO FREQUENCY

(Presented by Academician A. V. Topchiev on May 4, 1960)

Organosilicon compounds containing in the main chain alternating silicon-hydrocarbon (—Si—$(CH_2)_n$—Si—) and siloxane (—Si—O—Si—) units can be obtained by several routes. However, some of these are only laboratory methods ($^{1-3}$), while the proposed hydrolytic ($^{4-7}$) and catalytic (^{8,9}) methods start either from difficultly accessible compounds or from compounds that must first be obtained by organometallic synthesis. The use, for the purpose of obtaining compounds with alternating units, of the electric-discharge method, if the task posed were successfully solved, would make it possible to propose a new, simple, one-stage process also suitable for technical application.

Earlier, one of us (^{10,11}) showed that, under the action of silent discharges of ordinary current frequency (50 cycles/sec), polymeric compounds containing alternating Si and C atoms in the main chain can be obtained from methylchlorosilanes.

Recently (^{12}), the possibility was also shown of condensation of hexamethyldisiloxane in electric discharges with the formation of polymeric compounds of low molecular weight. It was of interest to attempt to carry out a similar condensation, but under conditions analogous to the usual methods of conducting catalytic and pyrogenetic processes, i.e., by a single passage of organosilicon compounds through the discharge zone. Owing to the short residence time of the starting compounds in the discharge zone, in this case various secondary processes should be reduced to a minimum. Thus it would be possible to obtain compounds formed as a result of primary reactions, which would make it possible to approach the elucidation of the mechanism of the chemical processes taking place.

As the first object of study, a compound simple in composition and accessible was taken—hexamethyldisiloxane. On the basis of previously established facts ($^{10-12}$), it was to be expected that, under the action of the discharge in hexamethyldisiloxane, the Si—CH_3 bonds (64 kcal/mole), energetically less stable than the remaining Si—O bonds (117 kcal/mole) and C—H bonds (85.5 kcal/mole) (^{14}), would be cleaved first. To obtain a discharge of sufficient power, the discharge tube in our experiments was supplied with current of frequency 4000 cycles/sec.

For accumulating the condensate, a regime was chosen that made it possible to obtain low-molecular condensation products in good yields, namely: voltage 50 kV, passage rate 8-9 ml/hr. As a result of passing 570 g of hexamethyldisiloxane, after distillation of the unreacted starting compound, 287 g of liquid condensation products were obtained, corresponding to a yield of 51%. The condensate consisted mainly (60-70%) of compounds containing 4-6 Si atoms in the molecule. Approximately 10% consisted of more volatile compounds (with 2-3 Si atoms in the molecule) and 20-25% of high-boiling polymers.

As a result of fractionation of the condensate obtained, a number of individual compounds were isolated: I. octamethyltrisiloxane; II. 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasila-3,7-dioxanonane; III. 2,2,4,4,7,7,9,9-octamethyl-2,4,7,9-tetrasila-3,8-dioxadecane; IV. 2,2,4,4,6,6,8,8,10,10,12,12-dodecamethyl-2,4,6,8,10,12-hexasila-3,7,11-trioxatridecane, and a mixture of high-molecular polymers V corresponding to the average composition $C_{86}H_{242}O_{17}Si_{34}$. The condensate also contained a large number of intermediate fractions consisting of difficultly separable mixtures of various polymers.

The presence in the gases of acetylene, which could have been formed only through cleavage of Si—CH_3 bonds, and the structures of the isolated compounds make it possible to represent the chemistry of the processes taking place as follows. Under the action of electric discharges, cleavage of the Si—CH_3 bond occurs first of all, with formation of two free radicals:

$$(CH_3)_3Si—O—Si(CH_3)_3 \rightarrow \dot{C}H_3 + \dot{S}i(CH_3)_2—O—Si(CH_3)_3.$$

The methyl radical formed is partially or completely converted into acetylene:

$$2\dot{C}H_3 \rightarrow CH \equiv CH + 4\dot{H}.$$

The subsequent reactions probably proceed mainly with the participation of the liberated atomic hydrogen

$$(CH_3)_3Si—O—Si(CH_3)_3 + \dot{H} \rightarrow H_2 + (CH_3)_3Si—O—(CH_3)_2Si\dot{C}H_2$$

or of methyl radicals

$$(CH_3)_3Si—O—Si(CH_3)_3 + \dot{C}H_3 \rightarrow CH_4 + (CH_3)_3Si—O—(CH_3)_2Si\dot{C}H_2.$$

Polymer formation takes place through recombination of various free radicals, for example:

$$(CH_3)_3Si—O—(CH_3)_2\dot{S}i + \dot{C}H_2Si(CH_3)_2—O—Si(CH_3)_3 \rightarrow$$

$$\rightarrow (CH_3)_3Si—O—(CH_3)_2Si—CH_2—Si(CH_3)_2—O—Si(CH_3)_3 \qquad (II)$$

or

$$2(CH_3)_3Si—O—(CH_3)_2Si\dot{C}H_2 \rightarrow [(CH_3)_3Si—O—Si(CH_3)_2—CH_2—]_2. \quad (III)$$

The formation of higher-molecular polymers occurs either by detachment of hydrogen atoms from low-molecular polymers upon interaction with $\dot{H}$ and $\dot{C}H_3$, or through the breakdown of individual bonds in low-molecular polymers under the direct action of the electric discharge. The new radicals formed recombine and produce higher-molecular compounds.

The presence of octamethyltrisiloxane among the reaction products indicates that, along with cleavage of $Si—CH_3$ bonds in hexamethyldisiloxane, cleavage of Si—O bonds also occurs in part:

$$(CH_3)_3Si—O—Si(CH_3)_3 \rightarrow (CH_3)_3Si—\dot{O} + \dot{S}i(CH_3)_3.$$

Octamethyltrisiloxane is probably formed as a result of recombination of the following two radicals:

$$(CH_3)_3Si—\dot{O}+\dot{S}i(CH_3)_2—O—Si(CH_3)_3 \rightarrow (CH_3)_3Si—O—Si(CH_3)_2—O—Si(CH_3)_3. \qquad (I)$$

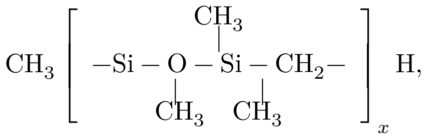
The ratio in the compounds obtained, C/Si = 2.5—2.7, is somewhat lower than in the initial hexamethyldisiloxane (= 3), except for compound III, for which this ratio is also equal to 3. As a rule, this ratio decreases slightly with increasing molecular weight of the polymers.

It follows from this that the polycondensation process carried out by us is accompanied by partial, but not strong, demethylation.

The elemental composition of V corresponds to the ratio C/Si = 2.5, which indicates that the high-molecular polymers contained in V belong to the same type of heterochain linear polymers as II, III, and IV, and also contain alternating silicon-hydrocarbon and siloxane units in the main chain. On this basis, for V one may propose the general formula

Fig. 1

Figure 1: Fig. 1



$$\mathrm{CH_3}\left[-\underset{\mathrm{CH_3}}{\mathrm{Si}}-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_2}-\right]_x \mathrm{H},$$

where $x = 17$.

Thus, as a result of the work performed it has been shown that, by condensing hexamethyldisiloxane in a flow system under the action of a high-voltage silent discharge of audio frequency, polymeric organosilicon compounds can be obtained in 50% yield, mainly of low molecular weight, containing alternating silicon-hydrocarbon and siloxane units in the main chain. This method can undoubtedly be used for the condensation of other organosiloxanes as well.

Experimental part

Condensation experiments were carried out in the apparatus shown in Fig. 1. The reactor was made of No. 29 glass and had the following dimensions of parts: inner diameter of the outer tube (external electrode) 23.0 ± 0.05 mm, outer diameter of the inner tube (internal electrode) 16.9 ± 0.05 mm, thickness of the glass walls 1.0-1.1 mm, distance between the electrodes (width of the discharge gap) 3.05 ± 0.05 mm, length of the discharge zone 300 mm, volume of the discharge space 57.0 cm^3. Both electrodes were cooled with running water. The inner electrode was connected to the high-voltage transformer, the outer one to ground. The step-up transformer was supplied with current of frequency 4000 cycles/sec, obtained from a machine generator.

Fig. 1

The substance under study was fed from a graduated burette at a specified rate into a flask heated by an electric hot plate. At the same time, a stream of purified dry hydrogen entered the flask, and the mixture of vapors of the substance and hydrogen passed through a side arm into the upper part of the reactor. A slight excess pressure was maintained in the burette by means of a bulb with mercury. The feed rate of hexamethyldisiloxane was 8-9 ml/hour; the hydrogen feed rate was 5 l/hour. The experiments were carried out under the following secondary-circuit conditions: voltage 5 kV, current 4.5-5 mA. The gases leaving the reactor were passed through two traps cooled with solid carbon dioxide and liquid nitrogen. Apart from the initial hexamethyldisiloxane, no other compounds were detected in them. The initial hexamethyldisiloxane had the following constants: b.p. 100-101°, n_D^{20} 1.3780, d_4^{20} 0.7620. A total of 570 g of hexamethyldisiloxane was passed through. After distillation, not

From the siloxane that had entered into the reaction, 287 g of condensation products were obtained in the form of a mobile yellow liquid. Yield 51%.

By fractionation of the condensation products the following individual compounds were isolated:

Octamethyltrisiloxane I $(CH_3)_3Si—O—Si(CH_3)_2—O—Si(CH_3)_3$. B.p. 150–151° (757 mm); n_D^{20} 1.3847; d_4^{20} 0.8184; molecular weight found 233, calculated 236.5; MR_D found 67.67, calculated 67.56.

Found, %:	C 40.44;	Si 35.48;	H 10.18
$C_8H_{24}O_2Si_3$. Calculated, %:	C 40.62;	Si 35.63;	H 10.23

Literature data (^{13}): b.p. 153; n_D^{20} 1.3843; d_4^{20} 0.8200.

2,2,4,4,6,6,8,8-Octamethyl-2,4,6,8-tetrasila-3,7-dioxanonane (II) $(CH_3)_3Si—O—Si(CH_3)_2—CH_2—(CH_3)_2Si—O—Si(CH_3)_3$. B.p. 72–78° (3 mm); n_D^{20} 1.4119; d_4^{20} 0.8462; molecular weight found 307, calculated 308.7; MR_D found 90.75, calculated 91.08.

Found, %:	C 42.52;	Si 36.13;	H 10.53
$C_{11}H_{32}O_2Si_4$. Calculated, %:	C 42.79;	Si 36.40;	H 10.45

Literature data (^{1}): b.p. 132–133° (54 mm); n_D^{20} 1.4121; d_4^{20} 0.8447.

2,2,4,4,7,7,9,9-Octamethyl-2,4,7,9-tetrasila-3,8-dioxadecane (III) $[(CH_3)_3Si—O—Si(CH_3)_2—CH_2—]_2$. B.p. 104–106° (4 mm): n_D^{20} 1.4190; d_4^{20} 0.8546; molecular weight found 328, calculated 322.7; MR_D found 95.37, calculated 95.71.

Found, %:	C 44.82;	Si 34.63;	H 10.34
$C_{12}H_{34}O_2Si_4$. Calculated, %:	C 44.62;	Si 34.80;	H 10.62

2,2,4,4,6,6,8,8,10,10,12,12-Dodecamethyl-2,4,6,8,10,12-hexasila-3,7,11-trioxatridecane (IV) $[(CH_3)_3Si—O—Si(CH_3)_2—CH_2—Si(CH_3)_2—]_2O$. B.p. 135–140° (4 mm); n_D^{20} 1.4253; d_4^{20} 0.8770; molecular weight found 460, calculated 455; MR_D found 132.76, calculated 133.44.

Found, %:	C 41.73;	Si 36.54;	H 10.30
$C_{16}H_{46}O_3Si_6$. Calculated, %:	C 42.23;	Si 37.06;	H 10.19

Literature data (^{1}): b.p. 184–185° (34 mm); n_D^{20} 1.4243; d_4^{20} 0.8725.

High-boiling polymers with b.p. > 280° (20 mm) V. n_D^{20} 1.4606; d_4^{20} 0.9593; molecular weight found 2476, calculated 2504.

Found, %:	C 40.92;	Si 38.12;	H 9.86
$C_{86}H_{242}O_{17}Si_{34}$. Calculated, %:	C 41.25;	Si 38.14;	H 9.75

The elemental analyses were carried out in the microanalytical group of the institute under the direction of Yu. N. Platonov.

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Note: Figure translations are in progress. See original paper for figures.