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

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The action of electric discharges on tetraalkylsilanes has not yet been studied by anyone. It is known that saturated hydrocarbons (⁀1), under the action of silent discharges, are capable of condensing into liquid products consisting of a mixture of polymers of saturated and unsaturated character.

On the basis of the results of previous studies on the action of silent discharges on various organosilicon compounds (^{2}-4), it could be expected that tetraalkylsilanes would also condense with formation of polymeric compounds containing alternating Si and C atoms in the main chain. Trimethylethyl- and dimethyldiethylsilanes were chosen as the objects of study. Both of these silicon hydrocarbons contain four different types of bonds: Si—CH_3 (74-76 kcal/mole) (⁀5); Si—C_2H_5 (59-64 kcal/mole) (⁀5); C—C (80-85 kcal/mole) and C—H (94-97 kcal/mole). For the last two types of bonds the values calculated for hydrocarbons (⁀6) were adopted. Investigation of the composition and structure of the condensation products would make it possible to obtain additional data on the degree of stability of various bonds toward dissociation under the action of silent discharges.

The experimental procedure was analogous to the experiments with hexamethyldisiloxane (⁀4): a single passage of the vapors of the silicon hydrocarbon in a mixture with H_2 through the silent-discharge zone at 6.5-6.8 kV was used. The current frequency was 4000 cycles per second.

Among the gaseous reaction products of trimethylethylsilane, ethylene and acetylene were identified, and among the liquid products—tetramethylsilane (I), hexamethyldisilylethane (II), 3,3,5,5-tetramethyl-3,5-disilahexane (III), and 3,3,4,5,5-pentamethyl-3,5-disilahexane (IV). In addition to these compounds of composition $C_8H_{22}Si_2$ and $C_9H_{24}Si_2$, the presence of silicon hydrocarbons of composition $C_{12}H_{32}Si_3$ (V), representing a difficult-to-separate mixture of isomers, was demonstrated in the higher-boiling products. High-molecular polymers with b.p. $> 220°$ (5 mm) (VI) had an average molecular weight of 1690 and corresponded to the composition $(C_{3.8}H_9Si)_x$. Thus, the C/Si ratio in the condensation products proved to be considerably lower than in the starting $(CH_3)_3SiC_2H_5$ and decreased monotonically from 5 : 1 to 3.8 : 1. It follows from this that the polycondensation process carried out by us was not a simple dehydrocondensation (proceeding by cleavage of C—H bonds), but was a more complex process caused by cleavage of Si—CH_3 or Si—C_2H_5 bonds. The stability of C—C bonds toward dissociation was demonstrated by us in an experiment with *n*-heptane carried out under analogous conditions. The absence of any changes with this hydrocarbon gives us grounds to suppose that the C—C bond in the ethyl radical of trimethylethylsilane must be sufficiently stable and not undergo noticeable cleavage under the conditions of our experiments. The formation of small amounts of $(CH_3)_4Si$ may be attributed not only to dissociation of the bond $\equiv SiCH_2{-}CH_3$, but, more probably, is explained by recombination of the radicals $\dot{C}H_3$ and $(CH_3)_3\dot{Si}$.

The liberation of large amounts of (III) also confirms the fairly high stability of the C—C bond.

The primary act under the action of the discharge should be considered to be dissociation of the Si—C bonds.

$$(CH_3)_3SiC_2H_5 \begin{array}{ll} \nearrow\ (CH_3)_3\dot{Si} + \dot{C}_2H_5 & (1) \\ \searrow\ C_2H_5(CH_3)_2\dot{Si} + \dot{C}H_3 & (2) \end{array}$$

Further transformations of methyl and ethyl radicals lead to the formation of C_2H_2, C_2H_4, and $H\cdot$. The absence in the condensate of compounds with an Si—Si bond gives grounds for assuming that recombination of organosilicon radicals (obtained by reactions (1) and (2)) with one another does not occur.

The formation of the indicated free radicals and H atoms should lead to the occurrence of chain reactions (^{7}). The possibility of chemical reactions with hydrocarbons in electric discharges by a chain mechanism was previously shown by A. A. Balandin, Ya. G. Eidus, and N. G. Zalogin (^{8}).

The initially formed $H\cdot$ and $\cdot CH_3$ can cause the formation of secondary radicals, for example:

$$C_2H_5Si(CH_3)_3 + \dot{H}(\dot{C}H_3) \rightarrow \begin{cases} C_2H_5(CH_3)_2Si\dot{C}H_2 + H_2(CH_4) & (3) \\ (CH_3)_3Si\dot{C}H_2\dot{C}H_2 + H_2(CH_4) & (4) \\ (CH_3)_3Si\dot{C}HCH_3 + H_2(CH_4) & (5) \end{cases}$$

Recombination of these secondary radicals with one another and with the initially formed radicals (obtained by reactions (1) and (2)) leads to the formation of the simplest condensation products of composition $C_8H_{22}Si_2$ and $C_9H_{24}Si_2$, for example II, III, and IV.

The large content among them of compound (IV) is quite understandable and is explained by the lower value of the C—H bond energy at secondary carbon atoms compared with primary ones (^{6}). Hence it follows that reaction 5 should have predominated over reactions (3) and (4).

Investigation of the composition of the condensate obtained from dimethyldiethylsilane presented an even more complicated problem, owing to the possibility of formation in this case of an even larger number of isomeric compounds. It was not possible to isolate individual compounds from this condensate. However, investigation of separate fractions of the condensate made it possible to conclude that compounds of composition $C_{10}H_{26}Si_2$, $C_{11}H_{28}Si_2$, $C_{14}H_{34}Si_3$, and $C_{19}H_{48}Si_4$ were present in it. The high-boiling polymers had an average molecular weight of 1050 and corresponded to the composition $(C_{4.5}H_{11}Si)_x$.

For the compounds contained in this condensate, there is also characteristic a continuous decrease in the C/Si ratio from 6 : 1 in the starting $(CH_3)_2Si(C_2H_5)_2$ to 4.5 : 1 in the high-molecular polymers, which indicates that the mechanism of their formation is similar to the process of polycondensation of trimethylethylsilane. Thus, the studied polycondensation reaction under the action of silent discharges makes it possible to obtain, in one stage, with a yield of up to 40% based on the starting tetraalkylsilane, polymeric silicon hydrocarbons containing alternating Si and C atoms in the main chain.

Experimental Part

Experiments with trimethylethyl- and dimethyldiethylsilanes were carried out in the apparatus described earlier (4) and by the same procedure. The starting substances had the following constants: trimethylethylsilane, b.p. 62–63°; n_D^{20} 1.3805; d_4^{20} 0.6846; dimethyldiethylsilane, b.p. 96–97°; n_D^{20} 1.4004; d_4^{20} 0.7166. The flow rate of the silicon hydrocarbons was 8–10 ml/hr, and the hydrogen flow rate was ~2.5 l/hr. The voltage in the secondary circuit in the experiments with trimethylethylsilane was 6.5–6.8 kV, and with dimethyldiethylsilane 4.8–5.2 kV.

Experiments with trimethylethylsilane. 700 g of $(CH_3)_3SiC_2H_5$ were passed through. After distillation of the organosilicon hydrocarbon that had not entered into the reaction, 285 g of condensation products were obtained, which corresponds to a yield of 41% based on the trimethylethylsilane passed through. In the exit gases the presence of small amounts of acetylene and ethylene was detected and, in addition, ∼ 3 g of tetramethylsilane (I), b.p. 23-26°; n_D^{20} 1.3575; d_4^{20} 0.6420. Literature data (9): b.p. 26°; n_D^{20} 1.3578; d_4^{20} 0.6411. The liquid condensation products were a transparent mobile yellowish liquid. According to distillation data, the condensate contained 28-30% of compounds containing 2 Si atoms in the molecule, about 25% of compounds with three Si atoms, ∼ 10% with 4 Si atoms, and 30-35% of high-boiling polymers containing more than 4 Si atoms in their molecules.

As a result of fractional distillations, the following individual compounds were isolated from the condensate:

Hexamethyldisilylethane (II) $(CH_3)_3Si—CH_2—CH_2—Si(CH_3)_3$. B.p. 26°/5 mm, b.p. 151-152°/760.8; n_D^{20} 1.4200; d_4^{20} 0.7514, weight 3.7 g.

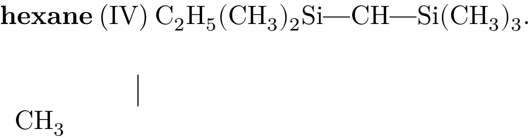
Literature data (¹⁰): b.p. 150-151°; n_D^{20} 1.4204; d_4^{20} 0.7536.

3,3,5,5-Tetramethyl-3,5-disilahexane (III) $C_2H_5(CH_3)_2SiCH_2Si(CH_3)_3$. B.p. 34-36°/5 mm; n_D^{20} 1.4266; d_4^{20} 0.7704; mol. wt. 168; calculated 174.4. MR_D 58.07, calculated 58.43.

$C_8H_{22}Si_2$.	Found %:	C 55.53;	Si 32.21;	H 12.23
	Calculated %:	C 55.08;	Si 32.21;	H 12.71

Literature data (¹¹): b.p. 157-159°; n_D^{20} 1.4272; d_4^{20} 0.7713,

3,3,4,5,5-Pentamethyl-3,5-disilahexane (IV)



$C_2H_5(CH_3)_2Si\text{—}\underset{CH_3}{CH}\text{—}Si(CH_3)_3$.

B.p. 63-65°/4 mm; n_D^{20} 1.4410; d_4^{20} 0.7900; mol. wt. 203; calculated 188.4. MR_D 63.08, calculated 63.06.

$C_9H_{24}Si_2$.	Found %:	C 57.69;	Si 29.14;	H 12.70
	Calculated %:	C 57.36;	Si 28.81;	H 12.84

Literature data (¹²): b.p. 60°/10 mm; n_D^{20} 1.4405; d_4^{20} 0.7905.

In addition, three more organosilicon hydrocarbons were isolated: a) b.p. 53-55°/6 mm, n_D^{20} 1.4350; d_4^{20} 0.7798 and b) b.p. 65-67°/6 mm; n_D^{20} 1.4381; d_4^{20} 0.7860, mol. wt. 187-192; MR_D 62.90 and 63.07, corresponding to the same composition $C_9H_{24}Si_2$ and representing isomers of undetermined structure, and c) b.p. 99-102°/4 mm (V); n_D^{20} 1.4590; d_4^{20} 0.8235; mol. wt. 269; calculated 260.6. MR_D 85.44, corresponding to $C_{12}H_{32}Si_3$, calculated 86.58.

Found %:	C 55.72;	Si 31.63;	H 12.53
Calculated %:	C 55.30;	Si 32.33;	H 12.37

The high-boiling polymers with b.p. $> 220^\circ/5$ mm (VI); n_D^{20} 1.4993; d_4^{20} 0.9272, were a transparent yellowish oil, had an average molecular weight of 1690 and corresponded to the average composition $(C_{3.8}H_9Si)x$.

Experiments with dimethyldiethylsilane $(CH_3)_2Si(C_2H_5)_2$. 374 g of dimethyldiethylsilane were passed through. The condensate was light yellow in color. After distillation of the organosilicon hydrocarbon that had not entered into the reaction, 82 g of condensation products were obtained. The yield was 22% based on the dimethyldiethylsilane passed through. The presence of acetylene was noted in the exit gases.

In fractional distillation it was not possible to isolate individual compounds. Fractions were isolated in which the presence of polymeric organosilicon hydrocarbons of the following compositions was established:

1. B.p. 80-85°/5 mm; n_D^{20} 1.4450; d_4^{20} 0.8019; molecular weight 202, calculated 202.5. MR_D 67.21, calculated 71.46.

Found, %:	C 59.66;	Si 27.65;	H 13.18
$C_{10}H_{26}Si_2$. Calculated, %:	C 59.30;	Si 27.86;	H 12.93

2. B.p. 95-100°/5 mm; n_D^{20} 1.4487; d_4^{20} 0.8122; molecular weight 228, calculated 216. MR_D 71.46, calculated 72.32.

Found, %:	C 60.66;	Si 25.69;	H 12.87
$C_{11}H_{28}Si_2$. Calculated, %:	C 60.95;	Si 25.95;	H 13.04

3. B.p. 125-140°/5 mm; n_D^{20} 1.4620; d_4^{20} 0.8359; molecular weight 273, calculated 286.5. MR_D 94.4, calculated 93.71.

Found, %:	C 58.51;	Si 30.00;	H 12.16
$C_{14}H_{34}Si_3$. Calculated, %:	C 58.63;	Si 29.40;	H 11.96

4. B.p. 165-180°/5 mm; n_D^{20} 1.4710; d_4^{20} 0.8559; molecular weight 348, calculated 388. MR_D 126.8, calculated 128.6.

Found, %:	C 58.53;	Si 28.75;	H 12.40
$C_{19}H_{48}Si_4$. Calculated, %:	C 58.67;	Si 28.89;	H 12.44

High-boiling polymers with b.p. $> 210°$/3 mm; n_D^{20} 1.5056; d_4^{20} 0.9357; viscous oil of composition $(C_{4.5}H_{11}Si)_x$, molecular weight 1050.

Found, %:	C 58.01;	Si 30.27;	H 11.84
$(C_{4.5}H_{11}Si)_x$. Calculated, %:	C 57.97;	Si 30.13;	H 11.89

On cooling to $-78°$, all fractions of both condensates remained fluid and did not form crystals.

The analyses were carried out in the microanalytical group under the direction of Yu. N. Platonova.

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