

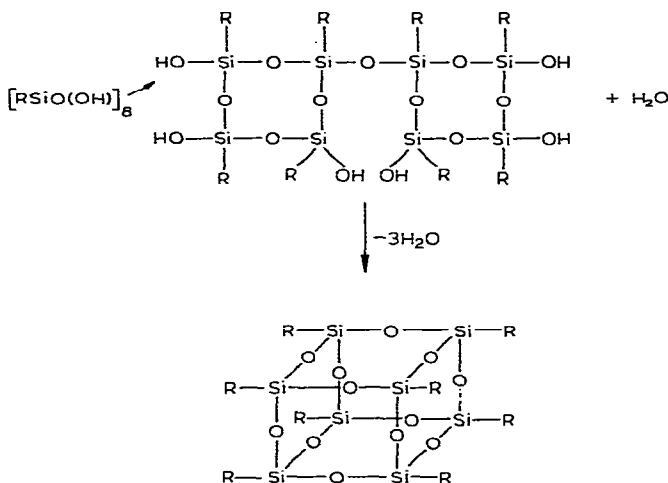


TABLE I  
PHYSICAL PROPERTIES OF PRODUCTS OF HYDROLYSIS

No. of compound	Formula of products	$n_D^{20}$	$d_4^{20}$	OH (%)		Mol. wt.		MR <sub>D</sub>	
				Found	Calcd.	Found (cryoscopically)	Found (ebullioscopically)	Found	Calcd.
I	[(C <sub>6</sub> H <sub>13</sub> )SiO(OH)] <sub>8</sub>	1.4530	1.0398	11.62	11.62	1181	1200	304.10	303.34
				11.50		1153			
II	[(C <sub>7</sub> H <sub>15</sub> )SiO(OH)] <sub>6</sub>	1.4563	1.0232	10.43	10.61	959	1100	255.70	255.39
				10.51		963			
III	[(C <sub>8</sub> H <sub>17</sub> )SiO(OH)] <sub>6</sub>	1.4560	1.0020	9.24	9.75	1070	1150	283.65	283.28
				9.52		1040			
IV	[(iso-C <sub>9</sub> H <sub>19</sub> )SiO(OH)] <sub>8</sub>	1.4568	0.9902	8.55	9.03	1503	1600	414.19	414.89
				8.46		1513			

$C_9H_{19}$ ). All the products obtained are liquids that cannot be crystallized by standard crystallization methods.

The chemical process of intramolecular condensation during distillation may be expressed by the following reaction :



An analogous pattern is followed in the process of condensation of products having a degree of polymerization,  $n = 6$ .

According to this reaction the end products isolated are alkylsilsesquioxanes: octa (hexylsilsesquioxane), hexa (heptylsilsesquioxane), hexa (octylsilsesquioxane), hexa (iso-nonylsilsesquioxane).

In the investigation of the chemical composition of the end products of the reaction, the absence of functional groups demonstrates that they have the complex cyclic structure figured in (I). The process of hydrolysis and of intramolecular condensation is also confirmed by infrared spectra.

The intensive absorption bands at  $905\text{--}895\text{ cm}^{-1}$  and wide highly intensive bands at  $3410\text{--}3240\text{ cm}^{-1}$  in the infrared spectra of the initial products of hydrolysis (I-IV) indicate the presence of OH-groups. The width of the band at  $3410\text{--}3240\text{ cm}^{-1}$  is explained by the probable formation, by the hydroxyl groups, of molecules of comparatively solid hydrogen bonds. The absorption bands at  $1110\text{--}1030\text{ cm}^{-1}$  are characteristic of the valency oscillations of  $\equiv\text{Si-O-Si}\equiv$  bonds.

No absorption bands at  $3410\text{--}3240\text{ cm}^{-1}$  were detected in the infrared spectra of alkylsilsesquioxanes. An intensive absorption band was found at  $1080\text{ cm}^{-1}$ , characteristic of the valency oscillations of  $\equiv\text{Si-O-Si}\equiv$  bonds: in cyclosiloxanes. The translocation of this band towards somewhat higher frequencies seems to be determined by the special steric structure of these compounds. The infrared spectrograms of all these compounds (obtained with prisms of KBr, NaCl, and LiF) are shown in Fig. 1.

The intramolecular character of the process of hydrolytic poly-condensation seems to be a result of the considerable steric hindrances caused by radical volumes that impede any intermolecular condensation reaction. This leads to the formation of low-molecular closed cyclic systems, and not of polymers. The difficulty of the

TABLE 2  
PHYSICAL PROPERTIES OF INTERMEDIATE PRODUCTS OF CONDENSATION

Initial substance	Formula of products	B.p. (°C/mm)	$n_D^{20}$	$d_4^{20}$	OH (%)		Mol. wt.		MR <sub>D</sub>	
					Found	Calcd.	Found	Calcd.	Found	Calcd.
I a	(C <sub>6</sub> H <sub>13</sub> ) <sub>3</sub> Si <sub>8</sub> O <sub>10</sub> (OH) <sub>4</sub>	171/1.5·10 <sup>-2</sup> -188/2·10 <sup>-2</sup>	1.4548	1.0388	6.00	6.00	1140	1133.8	296.0	296.4
II b	(C <sub>7</sub> H <sub>13</sub> ) <sub>2</sub> Si <sub>6</sub> O <sub>7</sub> (OH) <sub>4</sub>	75-83/2·10 <sup>-2</sup> (distillation)	1.4578	1.0178	7.13	7.21	940	943.5	251.90	251.93
III c	(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> Si <sub>6</sub> O <sub>7</sub> (OH) <sub>4</sub>	136-144/1.2·10 <sup>-2</sup>	1.4576	1.0018	5.93	6.62	1022	1027.6	279.74	279.82
d	(iso-C <sub>9</sub> H <sub>19</sub> ) <sub>2</sub> Si <sub>8</sub> O <sub>9</sub> (OH) <sub>6</sub>	116-123/1.1·10 <sup>-2</sup>	1.4603	0.9899	6.43	6.85	1481	1488.5	412.22	411.43
IV e	(iso-C <sub>9</sub> H <sub>19</sub> ) <sub>2</sub> Si <sub>8</sub> O <sub>10</sub> (OH) <sub>4</sub>	130-140/1·10 <sup>-2</sup>	1.4610	0.9882	4.82	4.72	1470	1470.44	408.40	407.97

TABLE 3  
PHYSICAL PROPERTIES OF ALKYLISILSEQUIOXANES

Initial substance	Formula of products	B.p. (°C/mm)	$n_D^{20}$	$d_4^{20}$	Mol. wt.		MR <sub>D</sub>		
					Found (cryoscopically)	Found (ebullioscopically)	Found	Calcd.	
I	[(C <sub>6</sub> H <sub>13</sub> )SiO <sub>1.5</sub> ] <sub>6</sub>	281-282/2.5	1.4590	1.0346	1099	1150	1098	290.15	289.50
II	[(C <sub>7</sub> H <sub>15</sub> )SiO <sub>1.5</sub> ] <sub>6</sub>	292-296/3	1.4600	1.0121	907	1070	907.5	245.59	245.01
III	[(C <sub>8</sub> H <sub>17</sub> )SiO <sub>1.5</sub> ] <sub>6</sub>	319-323/1	1.4610	1.00148	1000	1100	994.66	272.52	272.904
IV	[(iso-C <sub>9</sub> H <sub>19</sub> )SiO <sub>1.5</sub> ] <sub>6</sub>	298-302/2	1.4615	0.9851	1074	1160	1076.0	300.0	300.78

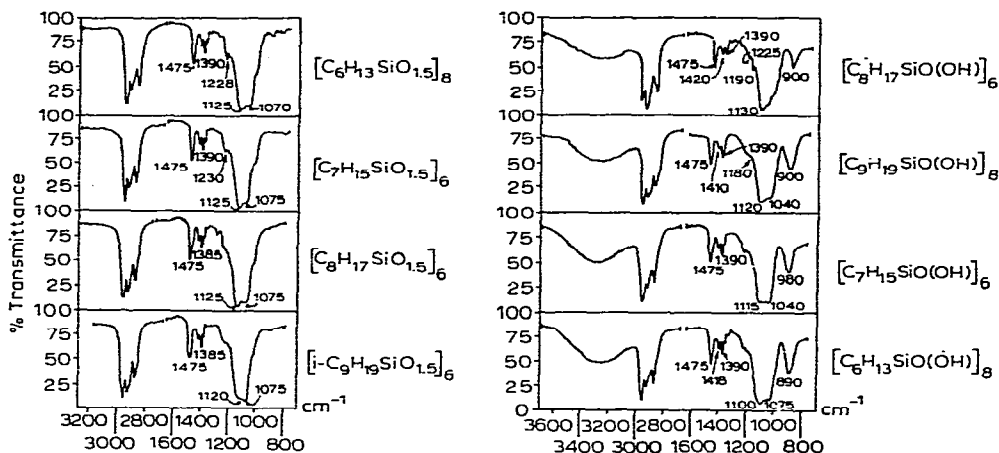


Fig. 1. The infrared spectra of the synthesized compounds.

intermolecular reaction in oligomers (I–IV, Table 2) is proved by the fact that the cyclic products obtained were not polymerized although nucleophilic and also electrophilic reagents were used.

However, there is more to this subject than steric difficulties created by radical volumes. The ready formation of tri- and tetramers in the hydrolysis is very significant. This may be brought about by specific interaction—attraction or repulsion of the organic groups in the chain. This interaction increases or decreases depending on the degree of solvation of the chain and organic radicals as determined by the nature of the solvent.

## EXPERIMENTAL

### Hydrolytic poly-condensation of hexyltrichlorosilane

71.7 g of hexyltrichlorosilane (b.p. 188–193°;  $n_D^{20}$  1.4446; Cl, 48.55%) in 72 ml of ether was introduced with vigorous stirring into 72 ml of ether and double the quantity of distilled water at 24–26° and stirred for 10 min. The organic layer was separated washed with distilled water until neutral, dried by filtering through a paper filter, and the ether distilled under a 5-mm vacuum. 44.8 g of the product (I, Table I) was obtained (found: C, 49.50, 49.30; H, 9.71, 9.61; Si, 18.85, 18.93.  $C_{48}H_{112}O_{16}Si_8$  calcd.: C, 49.28; H, 9.65; Si, 19.18%).

(a) Distillation of product (I) under  $1.5 \cdot 10^{-2}$  mm of Hg gave 1.65 g of product (a, Table 2) (Found: C, 50.77, 50.65; H, 9.37, 9.54; Si, 19.91, 18.85.  $C_{48}H_{108}O_{14}Si_8$  calcd.: C, 50.84; H, 9.60; Si, 19.79%) and 1.59 g of still residue.

(b) Vacuum distillation of 20.0 g of product (I) yielded 14.56 g of a substance boiling at 269–285° at 2.5 mm and 2.13 g of still residue as a solid, fragile, and insoluble product.

Redistillation of the fraction distilled under 2.5 mm of Hg yielded 10.0 g of octa(hexylsilsesquioxane), Table 3 (Found: C, 52.73, 52.87; H, 9.50, 9.47; Si, 20.24, 20.51.  $C_{48}H_{104}O_{12}Si_8$  calcd.: C, 52.65; H, 9.55; Si, 20.41%).

*Hydrolytic-poly-condensation of heptyltrichlorosilane*

76.1 g of heptyltrichlorosilane (b.p. 201.5–202°;  $n_D^{20}$  1.4495; Cl, 45.98%) gave 48.5 g of product (II, Table 1) (Found: C, 52.86, 52.87; H, 10.15, 10.08; Si, 17.47, 17.64.  $C_{42}H_{96}O_{12}Si_6$  calcd.: C, 52.45; H, 10.06; Si, 17.50%.)

(a) Distillation of product (II) under  $2 \cdot 10^{-2}$  mm of Hg gave 1.08 g of product (b, Table 2) (Found: C, 53.30, 53.52; H, 10.00; 10.11; Si, 17.82, 17.83.  $C_{42}H_{94}O_{11}Si_6$  calcd.: C, 53.46; H, 10.04; Si, 17.84%) and 5.16 g of still residue (OH, 3.21; 3.41%).

(b) Vacuum distillation of 20.55 g of product (II) gave 14.77 g of a substance boiling at 290–305° at 2 mm. Repeated distillation of the distilled fraction under 2 mm of Hg produced 9.18 g of hexa(heptylsilsesquioxane) (Table 3). (Found: C, 55.86, 55.61; H, 9.94, 10.19; Si, 18.47, 18.55.  $C_{42}H_{90}Si_6O_9$  calcd.: C, 55.58; H, 9.99; Si, 18.55%.)

*Hydrolytic poly-condensation of octyltrichlorosilane*

16 g of octyltrichlorosilane (b.p. 94–97° at 10 mm of Hg;  $n_D^{20}$  1.4490; Cl, 42.50%) gave 11.0 g of product (III, Table I) (Found: C, 54.94, 54.82; H, 10.32, 10.27; Si, 16.00, 15.90.  $C_{48}H_{108}O_{12}Si_6$  calcd.: C, 55.12; H, 10.41; Si, 16.10%.)

(a) Distillation of product (III) under  $1.2 \cdot 10^{-2}$  mm of Hg gave 0.66 g of product (c, Table 2). (Found: C, 56.54, 56.76; H, 10.37, 10.42; Si, 16.25, 16.14.  $C_{48}H_{106}O_{11}Si_6$  calcd.: C, 56.09; H, 10.39; Si, 16.38%) and 1.18 g of an intermediate fraction (OH, 3.30, 3.50%). The still residue was 5.4 g of hexa(octylsilsesquioxane) (Table 3). (Found: C, 57.65; 57.65; H, 10.21, 10.25; Si, 17.24, 17.12.  $C_{48}H_{102}O_9Si_6$  calcd.: C, 57.92; H, 10.33; Si, 16.92%.)

(b) 20.9 g of product (III) on vacuum distillation gave 14.5 g of a substance boiling at 315–324° at 1 mm of Hg and 0.65 g of a dry fragile insoluble still residue. Redistillation under 1 mm of Hg of the fraction distilled produced 11.1 g of hexa(octylsilsesquioxane) (Table 3).

*Hydrolytic poly-condensation of iso-nonyltrichlorosilane*

72.45 g of iso-nonyltrichlorosilane (b.p. 66–68° at 2 mm of Hg,  $n_D^{20}$  1.4530; Cl, 40.77%) gave 50.2 g of product (IV, Table I). (Found: C, 56.85; H, 10.52, 10.62; Si, 14.89, 14.81.  $C_{72}H_{160}O_{16}Si_8$  calcd.: C, 57.40; H, 10.71; Si, 14.90%.) Distillation under  $1 \cdot 10^{-2}$  mm of Hg, of product (IV) gave 1.0 g of product (d, Table 2). (Found: C, 57.83; H, 10.68; Si, 15.12.  $C_{72}H_{158}O_{15}Si_8$  calcd.: C, 58.09; H, 10.69; Si, 15.08%.) Also, 2.44 g of product (e, Table 2) was produced. (Found: C, 58.56; H, 10.66; Si, 15.30.  $C_{72}H_{156}O_{14}Si_8$  calcd.: C, 58.80; H, 10.69; Si, 15.26%.) The still residue, 10.03 g, was a mixture of the products of the subsequent stage of the condensation.

18.9 g of product (IV) on vacuum distillation gave 12.38 g of a substance boiling at 298–312° at 2 mm, and 1.84 g of a solid, fragile, insoluble still residue. Redistillation under 2 mm of Hg of the product obtained yielded 10.6 g of hexa(iso-nonylsilsesquioxane) (Table 3). (Found: C, 60.22, 60.16; H, 10.55, 10.55; Si, 15.57, 15.71.  $C_{54}H_{114}O_9Si_6$  calcd.: C, 60.23; H, 10.65; Si, 15.65%.)

Condensation under 1 mm of Hg at 250–270° of 1.58 g of substance (IV) produced 1.5 g of octa(iso-nonylsilsesquioxane),  $n_D^{20}$  1.4630;  $d_4^{20}$  0.9869. (Found: C, 59.55, 59.82; H, 10.55, 10.44; Si, 16.0, 16.0; mol.wt. 1420, 1430 (cryoscopically), 1560 (ebullioscopically);  $MR_D$  400.3.  $C_{72}H_{125}O_{12}Si_8$  calcd.: mol.wt. 1434.4;  $MR_D$  401.05.)

*Polymerization of alkylsilsesquioxanes in the presence of nucleophilic and electrophilic reagents*

(a) 2.26 g of octa(hexylsilsesquioxane) and 0.113 g of 20% KOH solution in ethanol were heated with stirring at 250–270° during 10 h.

(b) 1.9 g of octa(hexylsilsesquioxane), 0.61 of Dowtherm A, and 0.304 g of 10% KOH solution in ethanol were heated with stirring at 280° for 10 h.

(c) 3.38 g of octa(hexylsilsesquioxane) and 1.19 g of the monosodium salt (iso-C<sub>9</sub>H<sub>19</sub>)Si(OH)<sub>2</sub>ONa, were heated with stirring at 250° for 10 h.

(d) 1.65 g of octa(hexylsilsesquioxane) and 0.017 g of (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> [O<sup>-</sup>Si(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-O-N<sup>+</sup>(CH<sub>3</sub>)<sub>4</sub> were heated at 90° for 5 h.

(e) 1.49 g of octa(hexylsilsesquioxane) and 0.018 g of concentrated sulphuric acid were heated at 250° for 10 h.

(f) 2.83 g of hexa(iso-nonylsilsesquioxane) and 0.1416 g of 20% KOH solution in ethanol were heated with stirring at 250° for 10 h.

In experiments (a), (b), (c), (d), (e) and (f) the specific viscosities of a 1% toluol solution of the initial and final products were the same.

#### SUMMARY

1. The hydrolytic poly-condensation reaction of the higher alkyl trichlorosilanes is studied. It is concluded that the hydrolysis of these compounds yields oligomers with high concentrations of hydroxyl groups.

2. It is demonstrated that the condensation reaction of the hydrolysis products of the higher alkyl trichlorosilanes proceeds stepwise according to an intramolecular mechanism and produces the corresponding alkylsilsesquioxanes.

3. It is found that the polymerization of octa(hexylsilsesquioxane), hexa(heptylsilsesquioxane), hexa(octylsilsesquioxane), and hexa(iso-nonylsilsesquioxane) in the presence of nucleophilic and electrophilic reagents does not produce high molecular compounds.

#### REFERENCES

- 1 E. WIBERG, AND W. SOMMER, *Z. Anorg. Allgem. Chem.*, 282 (1955) 330.
- 2 K. A. ANDRIANOV AND A. A. ZDANOV, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 6 (1954) 1033.
- 3 A. BARRY, W. DAUDI, T. DOMICONE AND T. GILKEY, *J. Am. Chem. Soc.*, 77 (1955) 4248.

*J. Organometal. Chem.*, 8 (1967) 435–441