Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

HYDROLYTIC POLY-CONDENSATION OF HIGHER ALKYLTRICHLOROSILANES

K. A. ANDRIANOV AND B. A. IZMAYLOV
Academy of Sciences, Department of Organo-Elements Compounds, Moscow (U.S.S.R.)

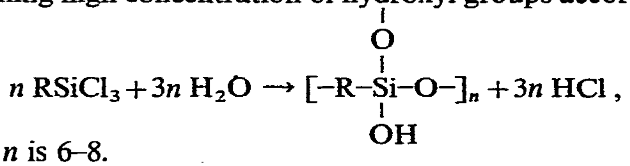
(Received October 4th, 1966)

The hydrolytic poly-condensation reaction of the higher alkyltrichlorosilanes has not hitherto been studied. The lower alkyltrichlorosilanes, methyl-, ethyl-, butyl-trichlorosilanes are known to form unstable compounds when hydrolysed with water; these polymerise either spontaneously or on heating.

In the present paper, the hydrolytic poly-condensation reaction of hexyltrichlorosilane, heptyltrichlorosilane, octyltrichlorosilane, and iso-nonyltrichlorosilane is investigated. It was found that the hydrolysis of these compounds differs considerably from the hydrolysis of the lower alkyltrichlorosilanes. In the hydrolytic process, relatively stable hydrolysis products containing numerous hydroxyl groups are formed initially. The compounds obtained contain a number of hydroxyl groups corresponding to the number of silicon atoms in the molecule and have low molecular weights (*cf.* Table 1).

The hydrolysis products of the higher alkyltrichlorosilanes may be quantitatively vacuum distilled. In the distillation process no high molecular compounds are formed. High vacuum distillation of these products give substances having lower hydroxyl numbers than the initial compounds (*cf.* Table 2). This indicates that in the process of high vacuum distillation the condensation is due to hydroxyl groups. However, condensation is not accompanied by a decrease in the molecular weight; this indicates an intramolecular condensation; furthermore, molecular weight decreases somewhat with removal of water.

To confirm the intramolecular condensation reaction the hydrolysis products of Table I were distilled under more extreme temperature conditions to ensure favourable conditions for the condensation. The hydrolysis products were quantitatively distilled and the compounds obtained did not contain terminal hydroxyl groups. Their molecular weights were somewhat lower than those of the initial compounds (*cf.* table 3). The experimental data demonstrate that the hydrolysis of the higher alkyltrichlorosilanes is accompanied by the formation of oligomers containing high concentration of hydroxyl groups according to the reaction:



$$n\,\mathrm{RSiCl_3} + 3n\,\mathrm{H_2O} \rightarrow [-\mathrm{R}-\underset{\underset{\mathrm{OH}}{|}}{\overset{\overset{|}{\mathrm{O}}}{\overset{|}{\mathrm{Si}}}}-\mathrm{O}-]_n + 3n\,\mathrm{HCl}\,,$$

where n is 6–8.

The composition of the resulting compounds is as given in the equation and does not depend on the size of the radical at the silicon atom (from C_6H_{13} to iso-

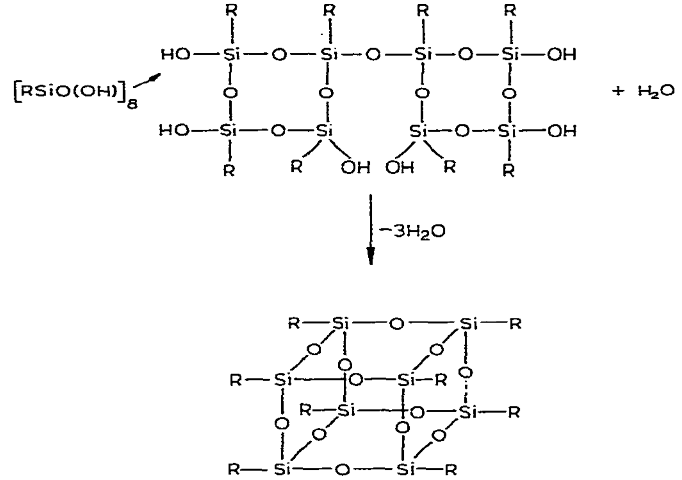
TABLE 1

PHYSICAL PROPERTIES OF PRODUCTS OF HYDROLYSIS

No. of compound	Formula of products	n_D^{20}	d_4^{20}	OH (%)		Mol. wt.			MR_D	
				Found	Calcd.	Found (cryoscopically)	Found (ebullioscopically)	Calcd.	Found	Calcd.
I	$[(C_6H_{13})SiO(OH)]_8$	1.4530	1.0398	11.62 11.50	11.62	1181 1153	1200	1169.8	304.10	303.34
II	$[(C_7H_{15}SiO(OH)]_6$	1.4563	1.0232	10.43 10.51	10.61	959 963	1100	961.55	255.70	255.39
III	$[(C_8H_{17})SiO(OH)]_6$	1.4560	1.0020	9.24 9.52	9.75	1070 1040	1150	1045.7	283.65	283.28
IV	$[(iso\text{-}C_9H_{19})SiO(OH)]_8$	1.4568	0.9902	8.55 8.46	9.03	1503 1513	1600	1506.2	414.19	414.89

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 905–895 cm^{-1} and wide highly intensive bands at 3410–3240 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 3410–3240 cm^{-1} is explained by the probable formation, by the hydroxyl groups, of molecules of comparatively solid hydrogen bonds. The absorption bands at 1110–1030 cm^{-1} are characteristic of the valency oscillations of $\equiv$Si–O–Si$\equiv$ bonds.

No absorption bands at 3410–3240 cm^{-1} were detected in the infrared spectra of alkylsilsesquioxanes. An intensive absorption band was found at 1080 cm^{-1}, characteristic of the valency oscillations of $\equiv$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_D	
					Found	*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*
I a	$(C_6H_{13})_8Si_8O_{10}(OH)_4$	$171/1.5 \cdot 10^{-2}$ $-188/2 \cdot 10^{-2}$	1.4548	1.0388	6.00 5.90	6.00	1140 1130	1133.8	296.0	296.4
II b	$(C_7H_{15})_6Si_6O_7(OH)_4$	$75–83/2 \cdot 10^{-2}$ (distillation)	1.4578	1.0178	7.13 7.18	7.21	940 935	943.5	251.90	251.93
III c	$(C_8H_{17})_6Si_6O_7(OH)_4$	$136–144/1.2 \cdot 10^{-2}$	1.4576	1.0018	5.93 6.10	6.62	1022 1077	1027.6	279.74	279.82
d	$(iso\text{-}C_9H_{19})_8Si_8O_9(OH)_6$	$116–123/1.1 \cdot 10^{-2}$	1.4603	0.9899	6.43 6.55	6.85	1481 1478	1488.5	412.22	411.43
IV e	$(iso\text{-}C_9H_{19})_8Si_8O_{10}(OH)_4$	$130–140/1 \cdot 10^{-2}$	1.4610	0.9882	4.82 4.55	4.72	1470 1480	1470.44	408.40	407.97

TABLE 3

PHYSICAL PROPERTIES OF ALKYLSILSESQUIOXANES

Initial substance	*Formula of products*	*B.p. (°C/mm)*	n_D^{20}	d_4^{20}	*Mol. wt.*			MR_D	
					Found (cryoscopically)	*Found (ebullioscopically)*	*Calcd.*	*Found*	*Calcd.*
I	$[(C_6H_{13})SiO_{1.5}]_8$	281–282/2.5	1.4590	1.0346	1099 1102	1150	1098	290.15	289.50
II	$[(C_7H_{15})SiO_{1.5}]_6$	292–296/3	1.4600	1.0121	907 903	1070	907.5	245.59	245.01
III	$[(C_8H_{17})SiO_{1.5}]_6$	319–323/1	1.4610	1.00148	1000 998	1100	994.66	272.52	272.904
IV	$[(iso\text{-}C_9H_{19})SiO_{1.5}]_6$	298–302/2	1.4615	0.9851	1074 1079	1160	1076.0	300.0	300.78

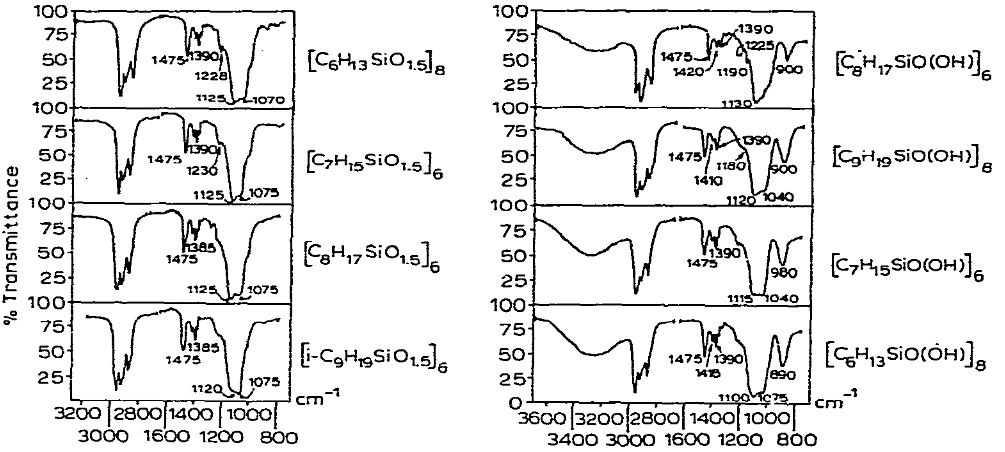


Fig. 1. The infrared spectra of the synthesized compounds.

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 $(iso\text{-}C_9H_{19})Si(OH)_2ONa$, were heated with stirring at 250° for 10 h.

(d) 1.65 g of octa(hexylsilsesquioxane and 0.017 g of $(CH_3)_4N^+[\bar{O}Si(CH_3)_2]_2\text{-}\bar{O}\text{-}N^+(CH_3)_4$ 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. Daudt, T. Domicone and T. Gilkey, *J. Am. Chem. Soc.*, 77 (1955) 4248.