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SYNTHESIS AND INVESTIGATION OF OCTAALLYLSILSESQUIOXANE, A NEW RADIATION SENSITIVE SUBSTANCE

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Summary

The hydrolytic polycondensation of allyltrichlorosilane has been investigated, resulting in the obtaining of octaallylsilsesquioxane and nonaallylsilsesquioxane, two new oligoorganosilsesquioxane homologues. Some physico-chemical properties, mass spectra and structures of the substances have been studied. Vacuum thermal evaporation has led to the production of thin octaallylsilsesquioxane films which polymerize upon irradiation. Comparison of the electron sensitivity of octaallylsilsesquioxane with that of widely known radiation-sensitive substances shows the advantages of the former.

Introduction

Lately scientists have taken a great interest in organosilsesquioxanes because of their unusual structures and properties.

We consider such characteristics of this class of compounds as the sensitivity to radiation, the ability to be vacuum sublimed without dissociation and the thermostability, to be of great moment. In this connection, these substances have potential for use as microelectronic objects in the radiation sensitive layers used in vacuum dry lithography processes.

Oligoorganosilsesquioxanes containing unsaturated radicals at the Si atoms in the inorganic framework were the first found [1–3] to show high electron exposure sensitivity. Investigations on vinyltrichlorosilane hydrolysis [4–5] have shown that it is possible to obtain octa- and decavinylsilsesquioxanes under certain conditions and proportions of initial reagents.

This work presents the results of the study of allyltrichlorosilane polycondensation in organic media. The aim of the study was to obtain an individual octaallylsilsesquioxane in sufficient yield.

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Results and discussion

From the previous investigation one may suggest that octaallylsilsesquioxane may be formed according to the following scheme:

$$\underset{}{RSiCl_3 + H_2O \rightarrow} \underset{(I)}{[RSiO_{1.5}]_8} + \underset{(II)}{[RSiO_{1.5}]_9H} + HCl$$

$(R = CH_2{=}CH{-}CH_2)$

In the alkylchlorosilane series, the hydrolysis rate is known to slow down with increase in the hydrocarbon radical length [6].

We compared the rate of hydrolysis of vinyl- and allyl-trichlorosilanes by measuring the change in the initial reagent concentration by means of chromotographic analysis. As a result, it was found that there was an analogous dependence for compounds having unsaturated radicals at Si atoms and compounds with saturated radicals.

At the same time, experiments showed that synthesis of product I required milder conditions than the vinyl analogue, its yield depending inversely on the hydrolysis velocity. In this connection it is expedient to lower the reaction temperature, to add the allyltrichlorosilane at such a rate as to keep the reaction temperature constant, and to reduce the reaction medium acidity by carrying out the hydrolysis in dilute solution (0.1–0.15 *M*).

Product yield is much affected by the nature of the organic solvent. Thus, under similar conditions the maximum yield is obtained in ethyl alcohol, the proportion of allyltrichlorosilane to water being 2/1 by volume. In methyl alcohol the reaction is turned to high polymer production. Small yields of octamer I are obtained in higher alcohols.

The difficulty of isolating substance I, which may be related to the high solubility in organic solvents, is to be noted. Attempts to distil off the solvent or salt-out the product failed because of the formation of an indivisible mixture of oligomers with similar solubility and volatility.

The substance I was isolated in small yield (7%) by deposition with methyl alcohol. Bubbling an inert gas through the reaction mixture gave a higher yield (13%).

The isolated substance was purifed by the removal of solvent traces and impurities in high vacuum at 150–160°C. The purity of the substance was checked by chromatographic analysis, its composition and structure were determined by IR and mass spectrometry or by X-ray structure analysis.

The IR spectrum of substance I is similar to that of octavinylsilsesquioxane [4]; it has however a more complicated structure related to splitting of the double bond absorption band into doublets, which is typical of conjugated systems [7–8]. Thus the band at 980 cm^{-1} splits into two bands at 910 and 940 cm^{-1}; the band at 1010 cm^{-1} splits into those at 1000 and 1060 cm^{-1}; the band at 1410 cm^{-1} splits into those at 1405; 1435 cm^{-1}. Instead of four peaks, six appear in the valence oscillation in the C–H region (2900–3100 cm^{-1}).

For the X-ray structure analysis, single crystals of I were grown from acetone solution. The crystals of I have a triclinic unit cell with a 8.95, b 10.36, c 10.50 Å; α 93.7(2), β 91.3(2), γ 94.7(2)°. The cell contains one $[C_3H_5SiO_{1.5}]_8$ formula composition unit. These data are in agreement with those in ref. 9.

A molecule of I (Fig. 1) consists of six tetrasiloxane rings, but has no symmetry axis in contrast to octavinylsilsesquioxane [10]. Three of the tetrasiloxane rings form three symmetrically independent cube facets, the angles included between the atoms deviating from 90° by not more than 1.5%. As with known octamers [10,11], the Si and O atoms of each ring are disposed in close almost parallel planes, the former being removed in the direction of the centre of the cube. The intensification of Si–O *p–d* interaction in the molecule increases the Si–O–Si valence angle, to 150.7°, as compared with known tetrasiloxane [12].

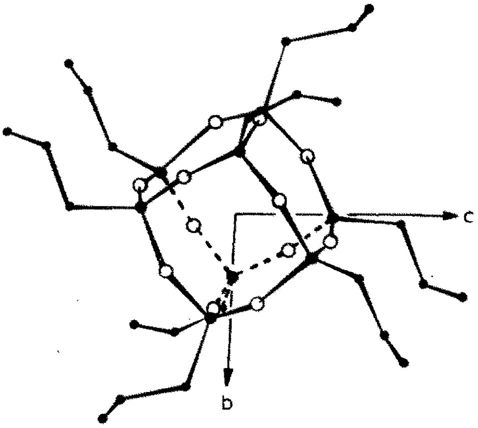


Fig. 1. The molecular structure of I.

The non-equivalent position of the substance I radicals is confirmed by considerable variation of the Si–C distance from 1.71 to 1.97 Å, while the conventional range is 1.81–1.85 Å.

Compared with II, the low density of I (1.28 g/cm^3) is connected with the allyl radical disorder and the increase in thermal vibration of the end carbon atoms (high value of the general heat factor), resulting in weakening of the molecular interaction in the crystal. This is also confirmed by the high solubility of substance I in organic solvents.

However, all of these structure peculiarities do not affect the structure of the inorganic molecular framework, as the mean Si–O bond value coincides with that of known octamers [10,11]. The packing of the molecules also has no influence on the silsesquioxane framework, the Si–Si distance corresponding to the literature data [10–12].

The structural peculiarities of substance I, which consist of a greater allyl radical disorder than that in known octamers having only two radicals in nonequivalent position [4], change the general nature of the mass spectrum of substance I (see Fig. 2). It is interesting that the product I fragmentation mechanism is similar to that of isostructural decamers [13]. In the spectrum one can observe a molecular ion of small intensity (13%) with m/e 744, its isotopic composition corresponding to the substance I molecule with an accuracy of 1%. The ion peaks with m/e 703 $(M-R)^+$ and 702 $(M-\mathrm{H, R})^+$, formed by succesive loss of the C_3H_5 and C_3H_6

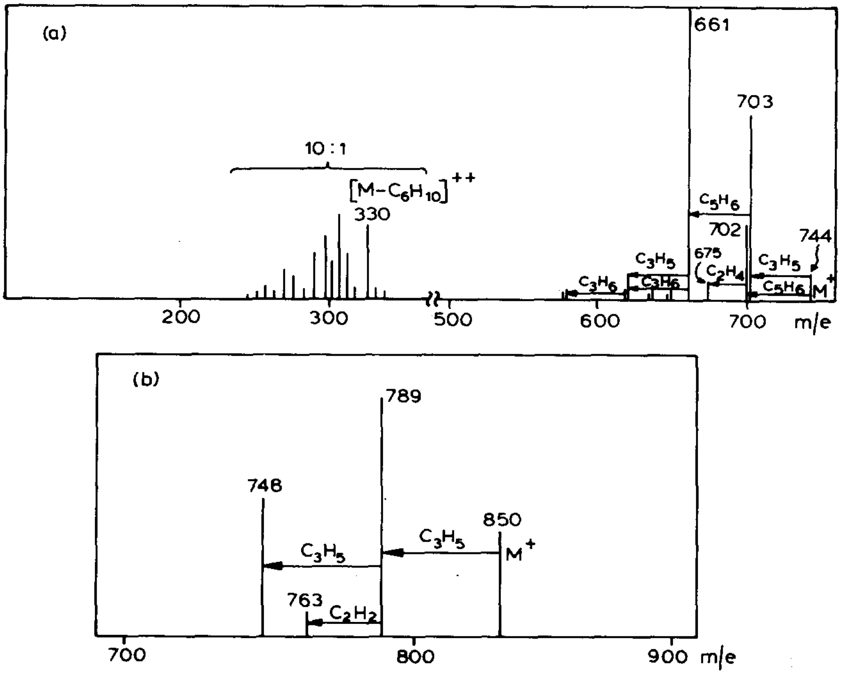


Fig. 2. The mass spectra of allyltrichlorosilane hydrolysis products: (a) Spectrum of substance I; (b) The most intensive lines in the mass spectrum of substance II.

radicals from the parent molecular ion, are the most intensive ones, with intensities of 75 and 25% relative to the maximum intensive peak with m/e 661 $(M - \mathrm{H}, 2\mathrm{R})^+$. There is also a series of considerably smaller intensity ions formed by cleavage of various hydrocarbon fragments from the inorganic molecular I framework. A series of doubly-charged ions $(M - 2\mathrm{R})^{++}$, of small intensity, with m/e 330 or less, is seen in the spectrum, as with octaorganosilsesquioxane fragmentation. For light ions, the most intensive peak is for the allyl radical, with m/e 41, and the smaller intensity peaks corresponding to the heavier C_4H_7, C_6H_{10} fragments, whose existence testifies to hydrocarbon radical migration.

The isotopic composition of these ions was coincident with that expected with an accuracy of 1%.

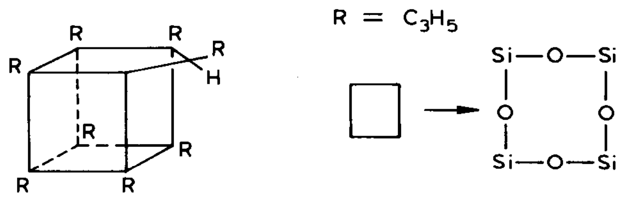
Evaporation of the filtrate remaining after separation of substance I to half of the initial volume, and bubbling of nitrogen allowed isolatation of a wet crystalline substance consisting of two products (from chromatographic analysis data). Substance II, of 80% purity, was obtained from the mixture by cold methanol extraction. Its structure was determined by IR methods and mass spectrometry.

In general the IR spectrum of substance II is analogous to that of substance I; it differs in the appearence of a band with a peak at 2190 cm^{-1} corresponding to the Si–H bond absorption.

It is clear from mass spectrum analysis that the fragmentation mechanism of substance II is like that of substance I and oligoorganosilsesquioxanes [4].

There is the peak of the parent molecular ion $(M)^+$, with m/e 830, the ion isotopic composition corresponding to the substance II molecule. Substance II, as with known analogues, fragments to produce intensive peaks for fragments $(M - R)^+$ with m/e 798, $(M - 2R)^+$ with m/e 748 and doubly-charged ions characteristic of organosilsesquioxanes.

The results of this investigation allowed one to suggest, by analogy [14], that substance II has the following structure:



It should be emphasized that more stringent conditions (higher temperature and reagent concentration) enabled the substance to be isolated in the form of well-faceted transparent crystals, their properties distinguishing them from those of product I. That substance is practically insoluble in most organic solvents and does not sublime in vacuum at temperatures up to 400°C.

Attempts to synthesise allylsilsesquioxane by acidic and alkaline condensation of allyltriethoxysilane as in [15] have failed.

Product I was to determine its characteristics as a radiation sensitive substance. With this aim, conditions for its vacuum film deposition have been studied and its electron sensitivity and resolution have been compared with those of octavinylsilsesquioxane. As a result, the substance studied was shown to have excellent film-forming properties; its sensitivity (at 10^{-7} C/cm^2) is higher than that of octavinylsilsesquioxane; its resolution (0.2–0.3 μ) is however worce, at least under our experimental conditions. This result is not unexpected, but is in good agreement with data on liquid polymer composition based on polymethylacrylate, which are notable for abrupt resolution deterioration when the sensitivity increases. Thus with the composition of sensitivity 10^{-6} C/cm^2, it is 0.3–0.5. The comparison of these results shows that the new radiation-sensitive substance is fit for the dry vacuum lithography process and exceeds its liquid analogues in its technical characteristics.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer using KBr tablets. Chromatographic analyses were performed with a LHM-72 chromatograph equipped with a columm of stainless steel, 2 m × 3 mm, packed with chromosorb W, and using 5% SE-30 as the liquid phase.

The X-ray structure study was made using an automatic "Syntex P2" diffractometer. The crystal density and refractive index of substance I were estimated by the flotation and immersion method [16].

Mass spectra were obtained using MS-902 and MI-1305 apparatus with an ionizing voltage of 50 eV, and at 160°C.

Octaallylsilsesquioxane synthesis

Example I. To a flask containing ethanol (500 ml) and cooled to −40°C allyltrichlorosilane (freshly distilled) (20 ml) is added slowly, drop by drop, with energetic mixing over two hours. Then the mixture is stirred for an extra hour, and water (10 ml) was put in it. The reaction mass was kept in a cool bath for 20 h, and then methyl alcohol (150 ml) was added in 30 ml portions over one h. The precipitate was filtered off, dried in air, and purified by sublimation in vacuum (10^{-6}mm Hg) at 150–160°C, to give I (7%); n_d^{20}, 1.545; d_4^{20}, 1.269 (Found: C, 39.00; H, 5.56; Si, 29.23; Mol. wt. (ebull), 730. $C_{24}H_{40}Si_8O_{12}$ calcd.: C, 38.70; H, 5.37; Si, 30.10%; Mol. Wt., 744.)

Example II. The synthesis was carried out as described above for example I but the final product was obtained by bubbling liquid nitrogen vapor through the reaction mixture for two hours. The sediment was filtered off and purified as described above, to give I (13%); n_d^{20}, 1.542; d_4^{20}, 1.273 (Found: C, 38.88; H, 5.60; Si, 31.00. $C_{24}H_{40}Si_8O_{12}$ calcd.: C, 38.70; H, 5.37; Si, 30.10%.)

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