

Mass Spectra of Octaspherosiloxanes

B. Aebi,¹ G. Calzaferri,² D. Herren,² R. Imhof² and U. P. Schlunegger^{1*}

¹ Institute of Organic Chemistry, University of Berne, CH-3000 Berne 9, Switzerland

² Institute of Inorganic and Physical Chemistry, University of Berne, CH-3000 Berne 9, Switzerland

The mass spectra of 14 different octasilasesquioxanes $R_8Si_8O_{12}$ are presented. The well-known uniformly substituted compounds ($R_8 = H_8, Me_8$ or Et_8) were re-examined and consequently used for comparison. The initial characterization of all the compounds examined was achieved with 1H -NMR spectroscopy. The influence of the different substituents (hydrogen, methyl, ethyl, ethyl phenyl and styrene) under electron impact ionization and collision-induced dissociation conditions was examined. The compounds with hydrogen substituents demonstrated minor cage destruction, whereas the compounds with organic substituents showed multiple losses of the substituents but no destruction of the cage system at all. The stability of the cubic Si_8O_{12} system seems to increase further with an increasing number and size of organic substituents. The additional information gained by collision experiments was modest. All mass spectra also contained doubly charged ions.

In recent years, the interest in spherosilasesquioxanes of the type $(RSiO_{1.5})_{2n}$ [$n=3, 4, 5 \dots$], has been growing as evidenced by the rapidly increasing number of publications. The discovery of new reaction paths and the improvement of the yields of the older, well-known compounds opened a broad field of potential applications for this class of substances. Recent studies by Banaszak Holl *et al.* showed, that octahydrosilasesquioxane $H_8Si_8O_{12}$ **1** can be vaporized onto silicon to form films of single connected molecules on the surface so as to afford an atomic scale design and synthesis of a Si/SiO₂ solid–solid interface.⁹ Thermal decomposition of such films leads to high quality SiO₂ films and there is also some evidence for preservation of the Si_8O_{12} subunits during silica formation.² Feher *et al.* presented an attractive model silica molecule for supported transition metal catalysts by use of the incompletely condensed heptamer trisilanol $R_7Si_7O_9(OH)_3$, $R = \text{cyclo-}C_6H_{11}$.³ Very recently Herrmann *et al.* have extended similar studies on rare earth metals.⁴

Spherosilasesquioxanes have also been used in the synthesis of new inorganic–organic and inorganic–organometallic polymers.^{5,6} Roesky *et al.* synthesized a new titanasilasesquioxane as a potential model substance for titanium-doped zeolites.⁷ Recent studies by some of us showed that $H_8Si_8O_{12}$ is a remarkable model for understanding the vibrational structure of zeolite A and of the higher hydrosilasesquioxanes.^{8–10}

In a series of publications about heterogeneously substituted octasilasesquioxanes, mass spectrometric data of several derivatives are now presented. These data supplement our studies of substituted hydrosilasesquioxanes of the type $RH_7Si_8O_{12}$, $REt_7Si_8O_{12}$ and $R_2Et_6Si_8O_{12}$ which, up to now, have concerned synthesis, vibrational spectroscopy and X-ray crystal structure determination.

A method for the monosubstitution of one hydrogen of $H_8Si_8O_{12}$ by hydrosilylation with retention of the cubic siloxane cage structure was introduced four years ago^{11,12} and recently, a second reaction type leading to $RH_7Si_8O_{12}$ molecules with one silicon metal bond, was published.¹³ We assume that the mechanism of this reaction proceeds via five-coordinated Si analogously to the reaction path for the palladium-catalyzed deuterium exchange of $H_8Si_8O_{12}$ to $D_8Si_8O_{12}$.¹⁴ X-ray crystal structures of two monosubstituted $RH_7Si_8O_{12}$ molecules, $R = -Co(CO)_4$ ¹³ and $R = -C_6H_{13}$ ¹⁵ are now available and support the model in which the

number of intramolecular Si ··· O contacts determines the distortion of the local symmetry of the Si_8O_{12} cage from ideal O_h . First infra-red examinations show that the interpretation of the spectra by correlation with the well-understood model substance $H_8Si_8O_{12}$ is straightforward.¹⁵

Different compounds of the octasilasesquioxane type $R_8Si_8O_{12}$ have been examined by mass spectrometric methods in the present investigation. Uniformly substituted compounds have already been studied with mass spectrometry by Voronkov *et al.*¹⁶ In this case, one-dimensional mass spectra as well as tandem mass spectrometry (MS/MS) experiments with collision-induced dissociation were obtained from several new compounds. The different behavior of the structural isomers and the stability of the cubic Si_8O_{12} structure under mass spectrometric conditions (EI-MS, CID-MS/MS) were of primary interest to us. Figure 1 summarizes the compounds studied and their substituents.

The starting compound is the uniformly substituted octahydro silasesquioxane $H_8Si_8O_{12}$ **1**. Also uniformly substituted are octamethyl silasesquioxane $Me_8Si_8O_{12}$ **2** and octaethyl silasesquioxane $Et_8Si_8O_{12}$ **3**. Compounds **4** and **5** include one 1-ethylphenyl or one 2-ethylphenyl and seven hydrogen substituents, while compound **6** contains one *geminal* styrene substituent and seven hydrogen substituents (*gem*-StyH₇Si₈O₁₂) and compound **7** contains one *trans* styrene substituent and seven hydrogen substituents (*t*-StyH₇Si₈O₁₂). Compounds **8** and **9** are substituted with one styrene substituent and 7 ethyl groups. Only the *geminal* (*gem*-StyEt₇Si₈O₁₂, **8**) and the *trans* isomer (*t*-StyEt₇Si₈O₁₂, **9**) were obtained from the chromatographic separation, but no *cis*-isomer. Mixed *geminal*- and *trans* styrene substituents (Sty₂Et₆Si₈O₁₂) are contained in compounds **10** and **11**, each with one *geminal*- and one *trans* styrene substituent. Compounds **12** to **14** have two *trans* styrene substituents (Sty₂Et₆Si₈O₁₂) in the three possible positions.

EXPERIMENTAL

Mass spectrometry

Most of the mass spectrometry experiments were performed on a double-focusing Fisons VG ZAB 2F (Fisons-VG, Altrincham, Manchester, UK) mass spectrometer with BE-configuration (reversed Nier–Johnson geometry). The accelerating voltage was 8 kV using a combined EI/CI

* Author for correspondence.

Comp	Substituents					MW [Da]
	R1	R2	R3	R4	R5	
1	H	H	H	H	H	423.82
2	Me	Me	Me	Me	Me	535.94
3	Et	Et	Et	Et	Et	648.07
4	1-EtPh	H	H	H	H	527.88
5	2-EtPh	H	H	H	H	527.88
6	g-Sty	H	H	H	H	525.86
7	t-Sty	H	H	H	H	525.86
8	g-Sty	Et	Et	Et	Et	722.08
9	t-Sty	Et	Et	Et	Et	722.08
10	t-Sty	Et	Et	g-Sty	Et	796.10
11	t-Sty	Et	g-Sty	Et	Et	796.10
12	t-Sty	Et	Et	t-Sty	Et	796.10
13	t-Sty	Et	t-Sty	Et	Et	796.10
14	t-Sty	t-Sty	Et	Et	Et	796.10

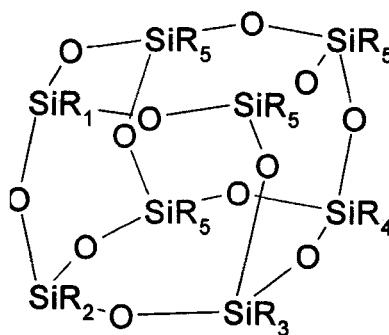


Figure 1. Summary of the spherosiloxanes examined in this work.

source in EI mode with 70 eV electrons. The source temperature was kept at 190 °C and the compounds were introduced using a direct insertion probe with a temperature controller. The mass resolution was adjusted to at least 1000.

The two-dimensional mass spectrometry used the CID mass-analyzed kinetic energy spectrometry (MIKES) technique.¹⁷ The first magnetic sector was set to transmit the analyte ion, thus filtering out all ions with a different mass. The selected ions were then dissociated by collision in a collision cell located in the second field-free region (2FFR) between the sectors. The product ions were finally analyzed by scanning the electrical sector, providing a separation by ion energy.

All MS and MS/MS experiments were performed using a MSP 8103 linked scanning/mass calibrating unit from MSP AG, Felix Friedli, Koeniz, Switzerland. The CID spectra were also carried out with the collision cell in 2FFR and using helium as collision gas, at a pressure that reduced the intensity of the selected analyte ion to 1/3. The energy resolution in these experiments was optimized before each collision experiment and was typically around 2000. Single-sector spectra were also obtained on a Finnigan MAT CH7A (Finnigan MAT, Bremen, Germany) magnetic sector instrument. The doubly charged ions were examined on a Fisons Autospec Q multisection instrument with mass resolution adjusted to at least 2000.

Nuclear magnetic resonance spectroscopy

The characterization of all compounds was obtained with ¹H-NMR and ¹³C-NMR spectroscopy on a Bruker AC-300 (Bruker-Spectrospin, Zug, Switzerland) instrument. The Fourier-transformed datasets were transferred to an IBM-compatible personal computer (AT-286 class) and analyzed with the software package PC-NMR⁺ (Chemistry Dept., University of Wisconsin-Madison, Madison, WI, USA).

Chromatography

A Shandon 200 × 35 mm (alternatively 250 × 20 mm) silica-gel column, modified with TCPP²⁰ (tetrachlorophthalimidopropyl) from Life Science Intl. Ltd., Runcorn, UK was used. A 600 × 25 mm Polymer Lab (pore size 50 Å, particle size 10 μm) size-exclusion column (Polymer Laboratories Ltd., Church Stretton, UK) was also used where cited. Hexanes (Romil HPLC-grade, from Ammann AG, Kolliken, Switzerland) were used as mobile phase at a flow rate of 6 mL/min (L-6200 pump, Merck-Hitachi, Geneva,

Switzerland, and ERC-3511 solvent degasser, Erma Inc, Tokyo, Japan). Detection used a Uvikon CCD 725 UV/VIS detector (Kontron, Switzerland) at 253 nm. The output was directed in parallel to an HP 3396A integrator (Hewlett-Packard, Zürich, Switzerland) at a 'rec 51' recorder (Servograph, Switzerland). All experiments were performed at room temperature.

Synthesis and characterization

The synthesis of H₈Si₈O₁₂ **1** was performed according to the method of Agaskar *et al.* and the product recrystallized from hot cyclohexane.¹⁸ (CH₃)₈Si₈O₁₂ **2** was prepared according to the method of Olsson.¹⁹

For the synthesis of (C₂H₅)₈Si₈O₁₂ **3**, H₈Si₈O₁₂ **1** (100 mg, 0.24 mmol) was dissolved in cyclohexane (10 mL) at 50 °C, then a solution of H₂PtCl₆ (10 μL, 0.01 mol/L in isopropanol) was added and ethylene was bubbled through this mixture (2 h). The reaction was monitored by observing the Si-H bending vibration at 881 cm⁻¹. After evaporation of the solvent, a white solid precipitated. The raw product was dissolved in hexanes and injected on a 600 × 25 mm Polymer Lab size-exclusion liquid chromatography column for purification. The spectral characteristics of **3** were: ¹H-NMR (300 MHz, CDCl₃, Tetramethylsilane TMS, Si(CH₃)₄): δ_H 0.53 (q, 16H), 0.98 (t, 24H). ¹³C-NMR (75 MHz, CDCl₃, TMS): δ_C 4.1 (Si-CH₂), 6.5 (CH₃).

In the synthesis of **4** and **5**, the monosubstituted hydrosilasesquioxane **4** was prepared according to the literature.¹¹ Compound **5**, one of several by-products, was isolated by liquid chromatography. Spectral characteristics were as follows: **4**: ¹H-NMR (300 MHz, CDCl₃, TMS): δ_H 1.09 (m, 2H), 2.77 (m, 2H), 4.19 (s, 3H), 4.24 (s, 4H), 7.25 (m, 5H). **5**: ¹H-NMR (300 MHz, CDCl₃, TMS): δ_H 1.47 (d, 3H), 2.43 (q, 1H), 4.19 (s, 3H), 4.21 (s, 3H), 4.22 (s, 1H), 7.23 (m, 5H).

For compounds **6** and **7**, hydrosilylation of H₈Si₈O₁₂ **1** with phenylacetylene was performed similarly to an earlier procedure.¹¹ H₈Si₈O₁₂ **1** (400 mg, 0.94 mmol) was dissolved in cyclohexane (50 mL) at 50 °C, then phenylacetylene (100 μL, 0.91 mmol) and H₂PtCl₆ solution (20 μL, 0.01 mol/L in isopropanol) were added in cyclohexane (5 mL) and the mixture heated at reflux for 2 h under N₂. After evaporation of the solvent, a white solid precipitated and was suspended in hexanes and filtered. This colorless solution of raw product was injected on a 600 × 25 mm Polymer Lab size-exclusion column for separation and purification. Spectral characteristics were as follows: **6**: ¹H-NMR (300 MHz, CDCl₃, TMS): δ_H 4.27 (s, 7H), 6.05

(d, 1H), 6.19 (d, 1H), 7.3–7.5 (m, 5H). 7: $^1\text{H-NMR}$ (300 MHz, CDCl_3 , TMS): δ_{H} 4.27 (s, 7H), 6.14 (d, 1H), 7.27 (d, 1H), 7.35–7.8 (m, 5H).

For the synthesis of **8** and **9**, half of the yield of products **6** and **7**, obtained in the step described above, was hydrosilylated with ethylene according to the procedure described in the synthesis of $(\text{C}_2\text{H}_5)_8\text{Si}_8\text{O}_{12}$ **3**.

For the synthesis of compounds **10** to **14**, $\text{H}_8\text{Si}_8\text{O}_{12}$ **1** (400 mg, 96 mmol), a solution of H_2PtCl_6 (100 μL , 0.01 mol/L in isopropanol) and phenylacetylene (200 μL , 1.8 mmol) were dissolved in hexane (5 mL). The solution was held at reflux under nitrogen for 2 h, following which ethylene gas was bubbled through (5 h). After the evaporation of the solvent, a white solid precipitated. In the first purification step, 700 mg of the raw product were separated on a flash chromatography column (3.5 \times 20 cm, silicagel 40–63 mesh, cyclohexane:toluene 93%:7%) into several fractions. The first fraction (500 mL) yielded 236 mg of a white powder, the second (300 mL) and third (200 mL) 122 mg and 24 mg of colorless oil. The white product of fraction one was dissolved in hexanes and then injected on a 250 \times 20 mm Shandon TCPP-modified column. The five products **10** to **14** were obtained after several separation runs. The yields were **8** (17.5 mg), **9** (59.6 mg), **10** (3.2 mg), **11** (1.7 mg), **12** (2.7 mg), **13** (2.2 mg) and **14** (3.8 mg).

Identification of structural isomers by $^1\text{H-NMR}$

The identification of structures (see Fig. 1) of the doubly substituted compounds **10** to **14** is based on the resonances of the olefinic–aromatic substituents and the signal pattern of the ethyl protons. The monosubstituted compounds **8** and **9** will be used for comparison (see Fig. 2).

$^1\text{H-NMR}$ spectrum of **8** (2-styrene $\text{Et}_7\text{Si}_8\text{O}_{12}$, single geminal-styrene substituent). The signals of the 5 aromatic protons appear in the region 7.43–7.14 ppm. The signals of the olefinic protons are visible in the region of 6 to 6.1 ppm with a characteristically small coupling constant of 2.9 Hz.

According to symmetry arguments, three A_2X_3 systems with intensities 3:3:1 are expected and agree with the experimental data. The signals of two ethyl groups of the intensities 3:1 are accidentally overlapping. There are no ABX_3 types of signals present.

$^1\text{H-NMR}$ spectrum of **9** (1-styrene $\text{Et}_7\text{Si}_8\text{O}_{12}$, single trans-styrene substituent). The signals of the aromatic protons appear at 7.28 to 7.51 ppm. The first olefinic proton (geminal to the aromatic ring) is found at 7.22 ppm. Its coupling constant is typically high for trans-coupling (19.1 Hz). The other olefinic proton (cis to the aromatic ring) is present at 6.2 ppm ($J=19.1$ Hz). As in **1**, three A_2X_3 systems with intensities 3:3:1 are expected and agree with the experimental data. The signals of two ethyl groups of the intensities 3:1 accidentally overlap. There are no ABX_3 types of signals present.

$^1\text{H-NMR}$ spectra of **10** (1-styrene-2-styrene $\text{Et}_6\text{Si}_8\text{O}_{12}$, geminal- and trans-styrene transversally positioned). The signals of the aromatic protons are found in the region of 7.27–7.5 ppm. The signal of one proton of the trans-styrene substituent is found at 7.22 ppm ($J=19.1$ Hz), while the other proton of this substituent shows a signal at 6.2 ppm with the same coupling constant ($J=19.1$ Hz). The signals of the olefinic protons of the geminally substituted styrene are found at 5.99 and 6.11 ppm ($J=2.9$ Hz). Following symmetry arguments, 2 A_2X_3 systems with intensities 3:3 are present. No ABX_3 types of signals are present.

$^1\text{H-NMR}$ spectra of **11** (1-styrene-2-styrene $\text{Et}_6\text{Si}_8\text{O}_{12}$, geminal- and trans-styrene diagonally positioned). The aromatic proton shows signals in the region of 7.27–7.5 ppm. The signal of one proton of the trans-styrene substituent is found at 7.22 ppm ($J=19.1$ Hz), while the other proton of this substituent exhibits a signal at 6.2 ppm ($J=19.1$ Hz). The olefinic protons of the geminally substituted styrene show signals 5.99 and 6.10 ppm ($J=2.9$ Hz).

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , TMS) of compounds **8** to **14**:

<p>8, δ (ppm), Mult, Nr, J</p> <p>3 CH_2, 0.61, q, 6H, J1</p> <p>4 CH_2, 0.63, q, 8H, J1</p> <p>3 CH_3, 0.94, t, 9H, J1</p> <p>4 CH_3, 1.01, t, 12H, J1</p> <p>1 CH, 5.98, d, 1H, J2</p> <p>1 CH, 6.1, d, 1H, J2</p> <p>1 C_6H_5, 7.05–7.45, m, 5H.</p>	<p>9, δ (ppm), Mult, Nr, J</p> <p>4 CH_2, 0.65, q, 8H, J1</p> <p>3 CH_2, 0.68, q, 6H, J1</p> <p>4 CH_3, 1.03, t, 12H, J1</p> <p>3 CH_3, 1.05, t, 9H, J1</p> <p>1 CH, 6.20, d, 1H, J3</p> <p>1 CH, 7.22, d, 1H, J3</p> <p>1 C_6H_5, 7.28–7.51, m, 5H.</p>	<p>12, δ (ppm), Mult, Nr, J</p> <p>6 CH_2, 0.66, q, 12H, J1</p> <p>6 CH_3, 1.02, t, 18H, J1</p> <p>2 CH, 6.17, d, 2H, J3</p> <p>2 CH, 7.20, d, 2H, J3</p> <p>2 C_6H_5, 7.25–7.48, m, 10H.</p>	<p>14, δ (ppm), Mult, Nr, J</p> <p>2 CH_2, 0.64, q, 4H, J1</p> <p>4 CH_2, 0.67, q, 8H, J1</p> <p>2 CH_3, 1.01, t, 6H, J1</p> <p>4 CH_3, 1.03, t, 12H, J1</p> <p>2 CH, 6.20, d, 2H, J3</p> <p>2 $\text{CH}+2 \text{C}_6\text{H}_5$, 7.2–7.48, m, 12 H.</p>
<p>10, δ (ppm), Mult, Nr, J</p> <p>3 CH_2, 0.62, q, 6H, J1</p> <p>3 CH_2, 0.68, q, 6H, J1</p> <p>3 CH_3, 0.95, t, 9H, J1</p> <p>3 CH_3, 1.04, t, 9H, J1</p> <p>1 CH, 5.99, d, 1H, J2</p> <p>1 CH, 6.11, d, 1H, J2</p> <p>1 CH, 6.19, d, 1H, J3</p> <p>1 CH, 7.22, d, 1H, J3</p> <p>2 C_6H_5, 7.27–7.50, m, 10H.</p>	<p>11, δ (ppm), Mult, Nr, J</p> <p>6 CH_2, 0.65, m, 10H,</p> <p>1 CH_3, 0.96, t, 3H, J1</p> <p>2 CH_3, 0.97, t, 6H, J1</p> <p>2 CH_3, 1.02, t, 6H, J1</p> <p>1 CH_3, 1.04, t, 3H, J1</p> <p>1 CH, 5.99, d, 1H, J2</p> <p>1 CH, 6.10, d, 1H, J2</p> <p>1 CH, 6.20, d, 1H, J3</p> <p>1 CH, 7.22, d, 1H, J3</p> <p>2 C_6H_5, 7.27–7.50, m, 10H.</p>	<p>13, δ (ppm), Mult, Nr, J</p> <p>2 CH_2, 0.64, q, 4H, J1</p> <p>2 CH_2, 0.67, q, 4H,</p> <p>2 CH_2, 0.70, q, 4H, J1</p> <p>2 CH_3, 1.03, t, 6H, J1</p> <p>2 CH_3, 1.04, t, 6H, J1</p> <p>2 CH_3, 1.05, t, 6H, J1</p> <p>2 CH, 6.18, d, 2H, J3</p> <p>2 CH, 7.21, d, 2H, J3</p> <p>2 C_6H_5, 7.27–7.48, m, 10H.</p>	<p>Coupling Constants:</p> <p>J1=7.9 Hz,</p> <p>J2=2.9 Hz,</p> <p>J3=19.1 Hz.</p>

Figure 2. $^1\text{H-NMR}$ spectra of compounds **8** to **14**.

Following symmetry arguments, $2A_2X_3$ systems with intensities 4:2 are present. No ABX_3 types of signals are present. All the methyl proton signals are showing the expected pattern, while all methylene-proton signals overlap.

¹H-NMR spectra of **12** (1-styrene₂Et₆Si₈O₁₂, doubly-trans-styrene substituted, transversally positioned). The aromatic proton signals are found at 7.25–7.48 ppm. The signals of the olefinic protons are found at 7.22 and 6.2 ppm ($J=19.1$ ppm). Due to the high symmetry of this molecule, only one type of A_2X_3 system is expected and matches with experimental data.

¹H-NMR spectra of **13** (1-styrene₂Et₆Si₈O₁₂, doubly-trans-styrene substituted, diagonally positioned). The signals aromatic proton signals are found at 7.27–7.48 ppm. The olefinic protons show signals at 7.20 and 6.18 ppm ($J=19.1$ ppm). According to symmetry, 3 types of A_2X_3 system (2:2:2) are expected and match with experimental data. All methylene and methyl protons give well separated signals.

¹H-NMR spectra of **14** (1-styrene₂Et₆Si₈O₁₂, doubly-trans-styrene substituted, diagonally positioned). The aromatic protons give signals at 7.2–7.48 ppm. The olefinic protons show signals at 7.20 and 6.18 ppm ($J=19.1$ ppm). According to symmetry, 2 types of A_2X_3 system (4:2) are expected and match with experimental data. All methylene and methyl protons give well separated signals.

RESULTS

The uniformly substituted compounds 1 to 3

The mass spectrum of octahydro silasesquioxane H₈Si₈O₁₂ **1** (Fig. 3(a)) showed the loss of one mass unit (molecular weight is 423.82 Da, calculated as the sum of the lightest isotopic masses) as base signal. Less intense signals indicate the losses of SiO and SiO₂ units while a minor signal close to m/z 211 represents the doubly charged ($M-1$) ion. While the molecular ion of octamethyl silasesquioxane

Me₈Si₈O₁₂ **2** (molecular weight 536 Da) is weak, the ($M-15$) signal at m/z 521 is very intense (Fig. 3(b)). Doubly charged ions are present at m/z values close to and below 253. The signals at m/z 655 and 789 (very low intensity) indicate the presence of the (CH₃)₁₀Si₁₀O₁₅ and (CH₃)₁₂Si₁₂O₁₈ isomers, each showing the ($M-15$) ion as the most significant signal. They also contribute doubly charged ions around m/z 320 and 387 with low intensity. Octaethyl silasesquioxane (C₂H₅)₈Si₈O₁₂ **3**, (Fig. 3(c), molecular weight 648.07 Da) shows only an ($M-29$) ion as intense signal. Other weaker signals indicate different losses of ethylene molecules.

The ethylphenyl- and styrene-hydrogen substituted compounds 4 to 7

The spectra of the 1- and 2-ethylphenyl compounds **4** and **5** are shown in Fig. 4(a), (b). Both spectra show the molecular ion, the ($M-1$) ion and the loss of the ethylphenyl unit as important signals. The spectrum of **4** shows additional signals. The signal at m/z 91, indicating the tropylium cation C₇H₇⁺, is intense in the spectrum of the 1-ethylphenyl compound **4** but absent in the spectrum of the 2-ethylphenyl compound **5**, as might be expected, since this compound is branched at the benzylic position. The signal at m/z 379 indicates the loss of the ethylphenyl-SiO group. The signal is also present in the spectrum of **5**, although much less intense. By increasing the multiplier gain the doubly charged molecular ions can be observed, although still only of the order of about 1% relative intensity.

The geminal- and the trans-StyH₇Si₈O₁₂ compounds **6** and **7** exhibit similar mass spectra (Fig. 4(c)–(d)). The molecular ion is also the base peak while the loss of the styrene unit gives another intense signal. The signal due to the ($M-1$) ion is also quite intense. A very small signal in the spectrum of **7** indicates doubly charged species at m/z 262. The ion at m/z 379 signifies breaking of the cage structure, although the intensity is not more than a few percent.

The styrene-ethyl substituted compounds 8 to 14

Both compounds **8** and **9** show similar mass spectra (Fig. 5(a), (b)). The molecular ion is intense, but the ($M-29$) ion is the base peak. Several losses of ethylene molecules or of

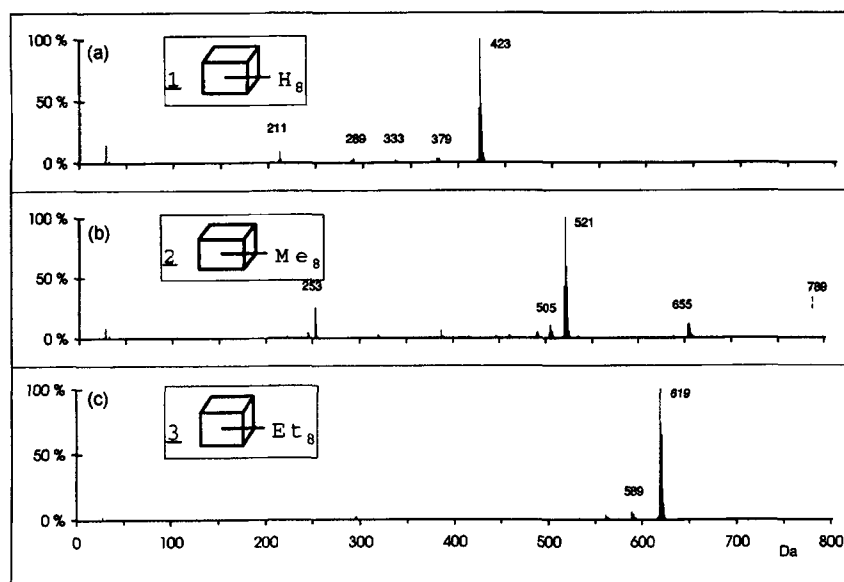


Figure 3. Mass spectra of compounds 1 to 3.

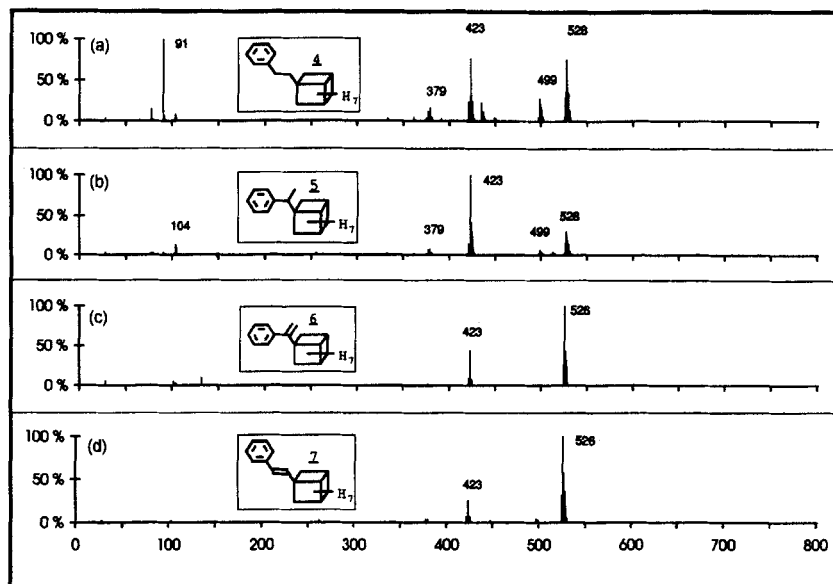


Figure 4. Mass spectra of the heptahydro compounds 4 to 7.

the styrene group are observed. The mass spectra of both compounds show similar fragmentation patterns. Doubly charged ($M - 29$) ions are present in the region of m/z 347. Consecutive losses of ethylene molecules produce other doubly charged species. A special section for the doubly charged ions and a discussion follows later.

The two compounds 10 and 11, with mixed *geminal*- and *trans*-styrene substituents also show similar mass spectra (Fig. 5(c) (d)). Again, the molecular ions and the ($M - 29$) ions are the most intense signals. The doubly charged molecular ion is only of low intensity. Several other doubly charged ions are present as well. Both spectra show some differences in their ion intensities although with mostly the same fragments.

The mass spectra of the three possible isomers 12 to 14 with two *trans* styrene and six ethyl substituents are shown in Fig. 6, (a)–(c). Again, molecular ions and ions due to the loss of an ethyl or styrene substituent are intense. Doubly charged species are present in all these spectra. Nevertheless, their mass spectra show several significant differences. Several intense ions, which are unique to each spectrum, can be observed. Even after measurement by peak

matching, no reasonable molecular formulae and structures could be found. The most intense doubly charged ions are also different for each compound.

CID-spectra of the compounds 1 to 3

All CID-MS/MS spectra show very broad decomposition signals. The signals could not be narrowed by tuning the resolution slits and electrostatic lenses of the mass spectrometer. The results obtained can still be used to estimate the number and type of fragments and the stability of the compounds towards collision-induced dissociation. But it is not possible to make statements about charge and proton transfers.

The CID spectra of the ($M - 1$) ion of compound 1 revealed several losses of hydrogen substituents and the losses of SiO , SiO_2 , Si_2O_2 and Si_2O_3 , indicating the breaking up of the cage structure (Fig. 7(a)). For the CID spectra of the ($M - 15$) ion of 2 (Fig. 7(b)), several parallel losses of methyl units were observed. The CID spectrum of the ($M - 29$) peak of the octaethyl compound 3 (Fig. 7(c)) showed the intense loss of another ethyl substituent.

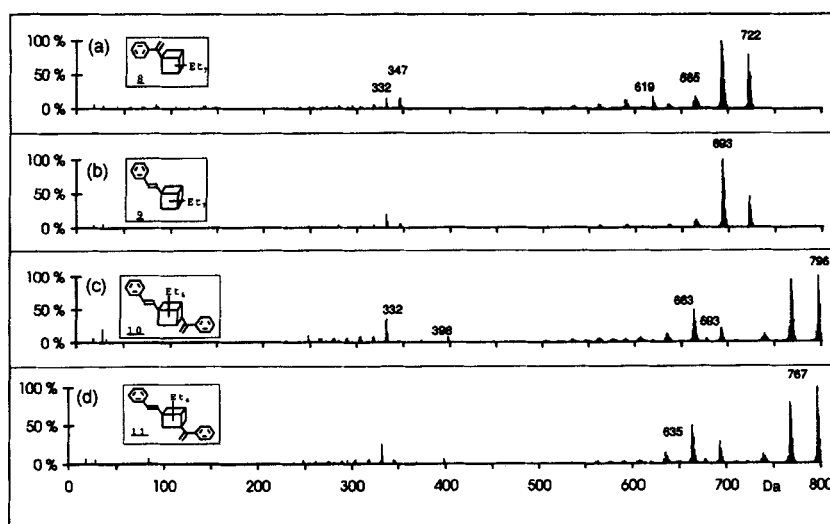


Figure 5. Mass spectra of compounds 8 to 11.

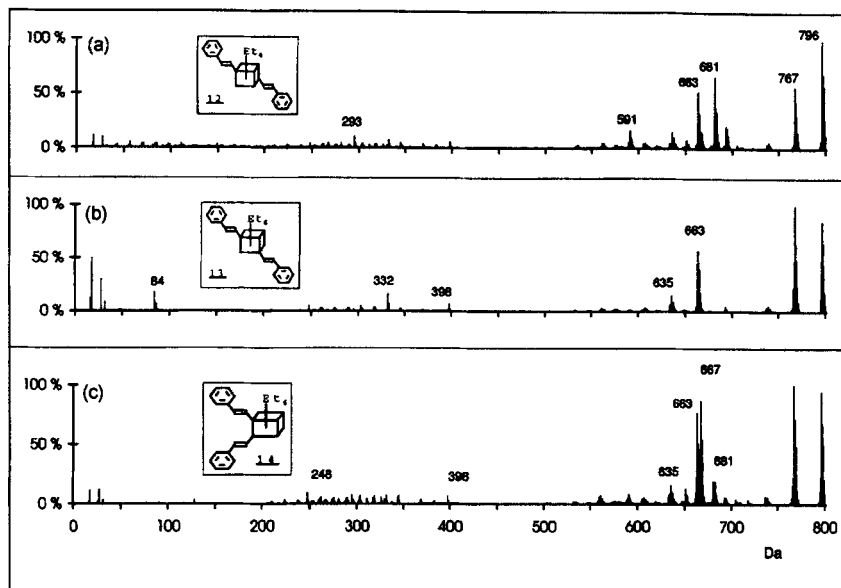


Figure 6. Mass spectra of compounds 12 to 14.

Doubly charged ions of the octasphero siloxanes 1 and 3

The cluster in the region of the molecular ion of the octahydro compound **1** (molecular weight=423.82 Da) is shown as the spectrum in Fig. 8(a). All the peaks are shifted by one mass due to the loss of one hydrogen substituent from the molecular ion. The comparison with the calculated molecular ion cluster shows that the production of molecular ions (without the loss of one or more hydrogen substituents) is negligible. The cluster around half the molecular weight of **1** (Fig. 8(b)) gives the typical Si_8O_{12} pattern. The mass difference between two peaks which is 0.5 mass units, indicates doubly charged ions. Doubly charged ions are observed, only after the loss of another hydrogen substituent, so that the most intense peak in this mass range is at m/z 210.89, which is the doubly charged $((M-1)-H)$ ion.

The mass spectrum of **3** (Fig. 8(c)) around the molecular ion cluster shows the $(M-29)$ peak and its isotopic pattern. The calculated molecular weight is 648.07 Da. The loss of

another ethyl substituent yields the cluster at m/z 295 and above (Fig. 8(d)). The mass difference of the peaks is 0.5 mass units and which confirms the doubly charged status of the ions. As can be seen in Fig. 3(c), the overall signal intensity of this cluster is quite small. The cluster of the molecular ion at m/z 648 is missing as well as the cluster of doubly charged $(M-29)$ ions.

DISCUSSION

The breakdown of the cubic Si_8O_{12} -structure can be seen best in the octahydro compound **1**. Compared to the intense signal of the $(M-1)$ ion, all the ions formed after the cracking of the cubic structure are very small. The degree of destruction is still quite small when the intensities of the resulting ions are added up. Using collision-induced dissociation experiments, only weak signals indicating the rupture of the cage system are obtained. The heptahydro compounds **4** and **5** with one ethylphenyl substituent also show minor decomposition of the cage system. Only the

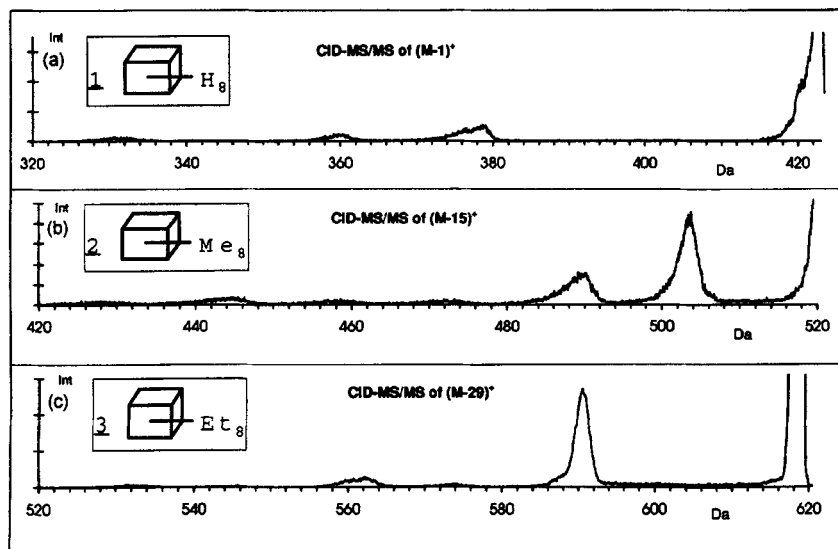


Figure 7. CID spectra of compounds 1 to 3.

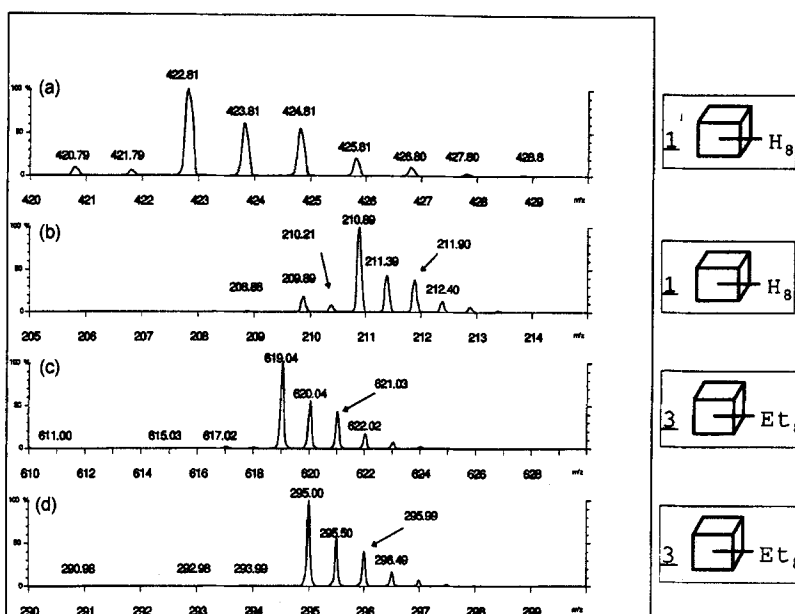


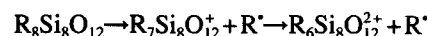
Figure 8. Doubly charged ions of compounds 1 and 3.

ions around m/z 379, which arise from the loss of one SiO unit, are present. Compared with the significant intensities of the other ions resulting from fragmentation, without cage destruction, these intensities are again small. The heptahydro compounds 6 and 7, with the styrene substituent, show the loss of this substituent and no other important fragmentation. Ions at m/z 379 are of the order of one percent. The octahydro and heptahydro compounds proved to be rather stable under electron impact ionization and collision-induced dissociation conditions.

The octamethyl compound 2 and all the styrene-ethyl compounds 8 to 14 as well as the octaethyl compound 3 showed the consecutive losses of their substituents. No important signals indicating the destruction of the cage system were obtained. The three possible isomers of the $\text{Sty}_2\text{Et}_6\text{Si}_8\text{O}_{12}$ formula displayed several unknown peaks. The interpretation of these peaks was attempted by high resolution peak matching mass spectrometry but without success. The compounds have been checked for purity by

both $^1\text{H-NMR}$ spectroscopy and mass spectrometry.

Doubly charged ions, some with intensities lower than 1%, can be found in all the mass spectra. The most abundant doubly charged ions are found in the styrene-ethyl compounds 8 to 14 with less abundant ions in the spectra of compounds 4 to 7 which contained one styrene or ethylphenyl substituent and seven hydrogen substituents. From a comparison of the observed and the calculated ion clusters, the formation of the doubly charged species from the uniformly substituted compounds 1 to 3 can be described as a double-step electron impact ionization inside the ion source:



The doubly charged species of the non-uniformly substituted compounds 4 to 14 showed competitive losses of the substituents with the formation of various doubly charged ions.

The use of mass spectrometry under electron impact ionization gave good results and supported the identification of the proposed structures. Impurities in the form of homologues, such as those in the mass spectrum of $\text{Me}_8\text{Si}_8\text{O}_{12}$ 2, consisting of $\text{Me}_{10}\text{Si}_{10}\text{O}_{15}$ (signal at m/z 655 from $(\text{M}-15)^+$) and $\text{Me}_{12}\text{Si}_{12}\text{O}_{18}$ (signal at m/z 789 from $(\text{M}-15)^+$) could easily be recognized. The doubly charged ions of these impurities were also present, although with small intensities.

The CID-MIKES technique was used to obtain additional structural information. Due to the broad product ion signals, mass assignment was in most cases not possible. The energy resolution had been adjusted on the precursor signal without collision gas and set to 2000. A further increase in the energy resolution did not decrease the signal width. The high flexibility of the Si_8O_{12} structure most likely allows these compounds to store and release energy from the ionization process and from collisions with the collision gas. This results in a wide energy distribution of the product ions and therefore broad signals in the collision spectra. Many of the collisionally-obtained peaks were composite (irregular peak shapes and shoulders) and could not be

Calc. Molecular Cluster of 1		Calc. Molecular Cluster of 3	
m/z	Int (%)	m/z	Int (%)
424	100.00	648	100.00
425	41.35	649	59.73
426	36.77	650	45.96
427	11.51	651	19.02
428	5.38	652	8.32
429	1.38	653	2.63
430	0.47	654	0.83
		655	0.21

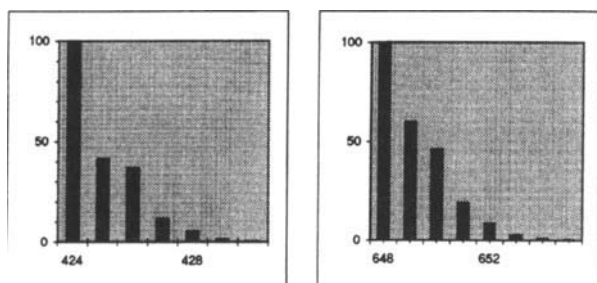


Figure 9. Calculated molecular ion clusters of compounds 1 and 3.

separated. The additional information gained by doing collision experiments was moderate. The CID spectra of the molecular ions (or of the most abundant ions) in most cases showed the same fragments as the normal mass spectrum. This could also be explained by the ability of the spherosiloxanes to absorb collisionally-obtained energy in an elastic manner and to pass through the collision cell without dissociation.

Finally, all compounds exhibited a good stability under electron impact and collision-induced dissociation conditions. The octahydro compound **1** showed weak losses of different silicon containing fragments, while the compounds with seven hydrogen substituents showed weak losses of one SiO unit only. The other compounds were substituted with organic groups only and no sign of decomposition of the cage structure was found. Compounds with similar substituents yielded spectra with small differences. Several unidentified ions were found in the spectra of the (*trans*-sty)₂Et₆Si₈O₁₂ compounds. The combination of mass spectrometry and nuclear magnetic resonance spectroscopy was successful for the characterization of the presented compounds. The stability of the cage structure of these octasphero silasesquioxanes was demonstrated. Experiments using CID-MS/MS were only partially successful due to the broad product-ion signals.

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