Mass spectrometric study of organocyclosiloxanes*

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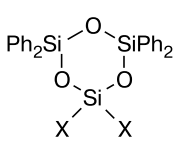
Organocyclosiloxanes of various chemical structures were studied by mass spectrometry using different ionization methods. The electron ionization mass spectra contain no peaks of molecular ions, and the main fragment ions are formed due to complicated rearrangements in a molecular ion, which provides no comprehensive view about the molecular structure. The desorption spectra exhibit peaks of quasimolecular and fragment ions, which characterize both molecular weights and chemical structures of the compounds under study.

Key words: mass spectrometry, electron ionization, desorption ionization methods, organocyclosiloxanes.

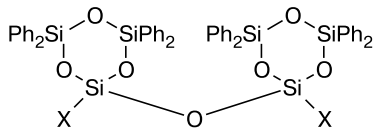
The most efficient physicochemical method for studying structures of major products, intermediates, and by-products should be selected for the optimization of conditions of synthesis of the organoinorganic polycyclosiloxane dendrimer *via* the multistep convergent scheme.[1] In this case, the NMR spectra are poorly informative because of structural similarity of the derivatives, their instability, small amounts of substances, and the frequent formation of complicated multicomponent mixtures of compounds. Presently, mass spectrometry is one of the most universal, informative, sensitive, fast, and reliable methods for studying both individual substances and their mixtures.[2]

The purpose of this work is to develop informative mass spectral procedures for the identification of organocyclosiloxanes of different structure.

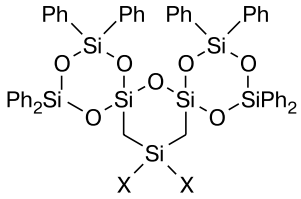
Electron ionization is the most universal ionization method and is most frequently used in modern mass spectrometers. Along with this, for investigation of non-volatile thermally unstable compounds with high molecular masses desorption ionization methods are employed widely. At the same time, these methods are widely used mainly for studying biomolecules,[3] while desorption mass spectrometry of heteroorganic compounds remains poorly studied. Therefore, we first carried out a comparative study of a series of mono- (**1a—c**) and bicyclic (**2a—d**) siloxanes, dendrones **3a,b**, and several model cyclosiloxanes with different structures (**4a—c**) by mass spectrometry using various ionization methods, including electron ionization (EI), desorption chemical ionization (DCI), electrospray ionization (ESI), and matrix laser desorption/ionization (MALDI—TOF).



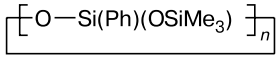
1a—c



2a—d



3a,b



4a—c

1: X = OH (**a**), Cl (**b**), Me_3SiO (**c**)

2: X = H (**a**), OH (**b**), Cl (**c**), Me_3SiO (**d**)

3: X = OH (**a**), Cl (**b**)

4: *n* = 4 (**a**), 8 (**b**), 12 (**c**)

Organocyclosiloxanes **1a—c**, **2a—d**, and **3a,b** are building blocks for the synthesis of the organoinorganic polycyclosiloxane dendrimer,[1] and cyclosiloxanes **4a—c** are of interest as precursors of new polymeric materials with unique properties.[4,5]

Results and Discussion

The EI mass spectra of silaspiroalkanes[6] and methylphenylspirosiloxanes,[7] *viz.*, compounds closest in struc-

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Table 1. The *m/z* values of the major ions in the desorption ionization mass spectra of organocyclosiloxanes

Method	Ion	Molecular weight (compound)									
		474 (**1a**)	510 (**1b**)	618 (**1c**)	898 (**2a**)	930 (**2b**)	966 (**2c**)	1074 (**2d**)	840 (**4a**)	1680 (**4b**)	2520 (**4c**)
DCI	$[M + H]^+$	475	511	619	899	931	967	1075	—	—	—
	$M^{+\bullet}$	474	510	618	898	930	966	1074	—	—	—
	$[M - H]^+$	473	509	617	897	929	965	1073	—	—	—
ESI	$[M + H_2O]^{+\bullet}$	—	—	—	916	948	984	1092	—	—	—
	$[M + Na]^+$	—	—	—	921	953	989	1097	—	—	—
	$[M + K]^+$	—	—	—	937	969	1005	1113	—	—	—
	$[M + H_2O + Na]^+$	—	—	—	939	971	—	1115	—	—	—
	$[M + H_2O + K]^+$	—	—	—	955	987	—	1131	—	—	—
MALDI—TOF	$[M + Na]^+$	—	—	—	921	953	989	1094	863	1703	2543
	$[M + K]^+$	—	—	—	937	969	1005	1113	879	1719	2559

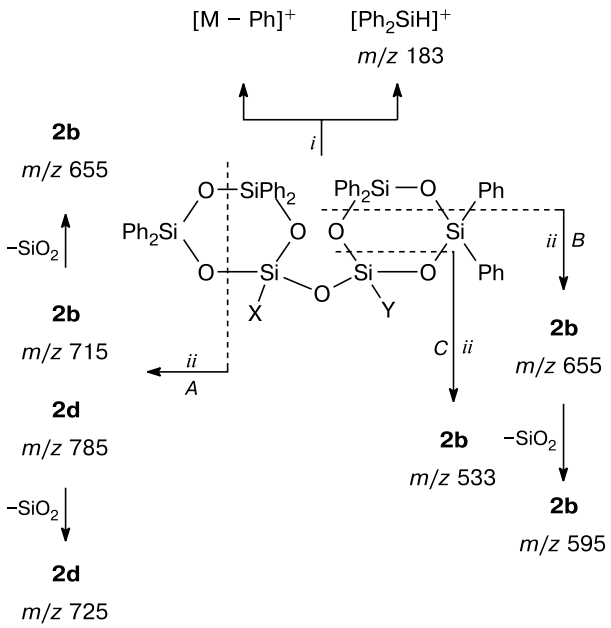
ture to derivatives **1a—c**, **2a—d**, and **3a,b**, are rather informative: the spectra contain together with molecular ion peaks $[M]^{+\bullet}$ of considerable intensity (5—50%)* a set of fragment ion peaks characterizing the chemical structures of the compounds (for example, peaks of ions caused by the direct elimination of a substituent from the silicon atom or cleavage of the siloxane cycle with the elimination of the whole R_2SiO units).

Unlike the earlier studied derivatives,[6,7] in the EI spectra of mono- and disiloxanes and dendrones **1a—c**, **2a—d**, and **3a**,**b** the molecular ion peak with an appreciable intensity (6%) with *m/z* 474 is observed only for **1a**, whereas for **1b—c**, **2a—d**, and **3a,b** the $[M]^{+\bullet}$ peaks are negligible or absent. The region of the molecular ion of compound **1a** is characterized by the $[M - H]^+$ peak with *m/z* 509 (5%), and that of derivative **1c** has the $[M - Me]^+$ peak with *m/z* 603 (9%). The peaks of ions corresponding to the direct elimination of substituents from the silicon atoms and to the elimination of the whole units of the siloxane cycle are absent.

The peaks of fragment ions formed due to intricate rearrangements in the molecular ion predominate in the EI mass spectra of cyclosiloxanes **1a—c**, **2a—d**, and **3a,b**. These are the ions of tri- and biphenylsilanes, biphenylsilaneoxide, and biphenyl (*m/z* 259, 183, 197, and 154, respectively). The general view of the EI mass spectra of cyclosiloxanes **1a—c**, **2a—d**, and **3a,b** suggests only the presence of the phenyl substituents in the molecules. Thus, the EI spectra give no information on the molecular weight and provide no comprehensive concept about the structures of derivatives **1a—c**, **2a—d**, and **3a,b**.

Unlike the EI spectra, the DCI mass spectra of compounds **1a—c** and **2a—d** exhibit the intense peaks of molecular ions and ions of the protonated and deprotonated molecule, which allows the unambiguous determination of the molecular weights of these substances (Table 1). The spectra contain only a minor set of peaks of the fragment ions characterized as both the phenyl substituents at the silicon atom and the fragment of the siloxane cycle $SiPh_2$ (Scheme 1). For instance, in the case of compounds **2a—d**, the maximum peaks in the DCI spectra correspond to $[M - Ph]^+$, and the second in intensity peak corresponds to the $[Ph_2SiH]^+$ ion with *m/z* 183. Thus, unlike the EI spectra, the DCI spectra make it possible to determine the molecular weights of the compounds but, as in the case of EI, they give very restricted information on their structure.

Scheme 1



i. DCI; *ii*. ESI.

The ESI positive ion spectra of compounds **2a**,**b**,**d** exhibit peaks of the solvated molecular ions $[M + H_2O]^{+\bullet}$, adducts of the alkaline metal cations to the molecules

* Relative intensity in % of the maximum peak intensity in the mass spectrum.

$[M + Na]^+$ and $[M + K]^+$, and more complicated aggregates with water molecules and metal cations (see Table 1). It is substantial to mention that the set of the indicated so-called cluster ions is specific for each compound. This can be used as additional information for their identification. The ESI spectrum of the negative ions of dihydroxy derivative **2b** contains the peaks of the molecular ion with *m/z* 930 and deprotonated molecule with *m/z* 929 and the peak of the adduct with oxygen $[M + O]^-$ with *m/z* 946. Thus, the molecular weights of most compounds under study were reliably confirmed by the ESI and DCI methods.

The ESI mass spectra of the positive ions of the dihydroxy and trimethylsiloxy derivatives (**2b** and **2d**, respectively) contain peaks of the fragment ions formed by the cleavage of the siloxane cycle with the elimination of the whole units. These are the processes of cleavage of two oxygen—silicon bonds followed by the rejection of a silicon dioxide molecule (see Scheme 1, fragmentation paths *A* and *B*).* The elimination of two whole Ph_2SiO units from the siloxane cycle is also characteristic of the ESI spectrum of the negative ions of derivative **2b** (see Scheme 1, fragmentation path *C*). Thus, the ESI mass spectra suggest molecular weights of compounds and also their chemical structure.

As in the case of electrospray ionization, the matrix laser desorption/ionization of cyclosiloxanes **2a—d** and **4a—c** is mainly characterized by the adducts of the molecules with the alkaline metal cations (see Table 1). The formation of similar products characterizes, for instance, the behavior of crown ethers under conditions of various procedures of desorption mass spectrometry.[8] Note that siloxanes **4a—c**, similarly to crown ethers,[9] possess mesomorphic properties.[4,5]

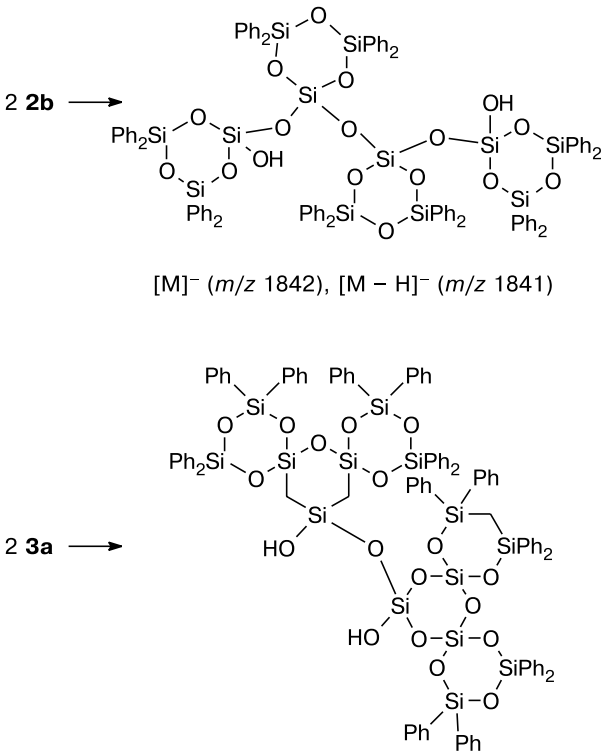
Using the determined regularities of the behavior of oligocyclosiloxanes under the electrospray conditions, we found and identified by the mass spectra of the negative ions of compounds **2b** and **3a** two by-products formed by the condensation of two molecules of dihydroxybicycle **2b** and two molecules of dihydroxydendrone **3a** (Scheme 2). In addition to the simple adducts that characterize the molecular weights, the ESI gives more intricate systems impeding the interpretation of the mass spectrum. For example, the spectrum of dihydroxy derivative **2b** is impeded by the peaks of the dimeric clusters $[2 M + H_2O]^{+\bullet}$, $[2 M + Na]^+$, $[2 M + K]^+$, and $[2 M + Na + H_2O]^+$.

Chemical transformations of the molecules under study can also occur during electrospray ionization. For instance, dichloro-substituted derivatives **2c** and **3b** can be hydrolyzed upon electrospraying. This is confirmed by similarity of the ESI mass spectra of the positive and negative ions of dichlorobicycle **2c** and corresponding dihydroxy-substituted derivative **2b** and the presence of the intense peaks in the negative ion spectrum of dichloride **2c** corresponding to both the starting molecule and adduct with oxygen $[M + O_2]^-$ and the product of partial hydrolysis of **2c**. The ESI negative ion spectrum of dichlorodendrone **3b** also contains the molecular ion peaks corresponding to the products of its partial and complete hydrolysis. The structure of complete hydrolysis product **3a** is confirmed by the fragment ion peaks corresponding to silicon dioxide elimination followed by the rejection of one and two units of the siloxane cycle (Scheme 3).

It should be mentioned that upon electrospray ionization the compounds under study decompose to form large fragments directly related to their structures, unlike the EI and DCI mass spectra.

Thus, it is evident that all necessary information on the molecular weights and chemical structures of the compounds under study can be obtained only using a complex of supplementing mass spectral methods. In this case, the molecular weights of the oligocyclosiloxanes under study can be determined using desorption chemical ionization, electrospray, and matrix laser desorption, whereas the structural characteristics can be determined only by a comparative analysis of the data of electron impact, chemical, electrospray, and laser ionization mass spectrometry.

Scheme 2

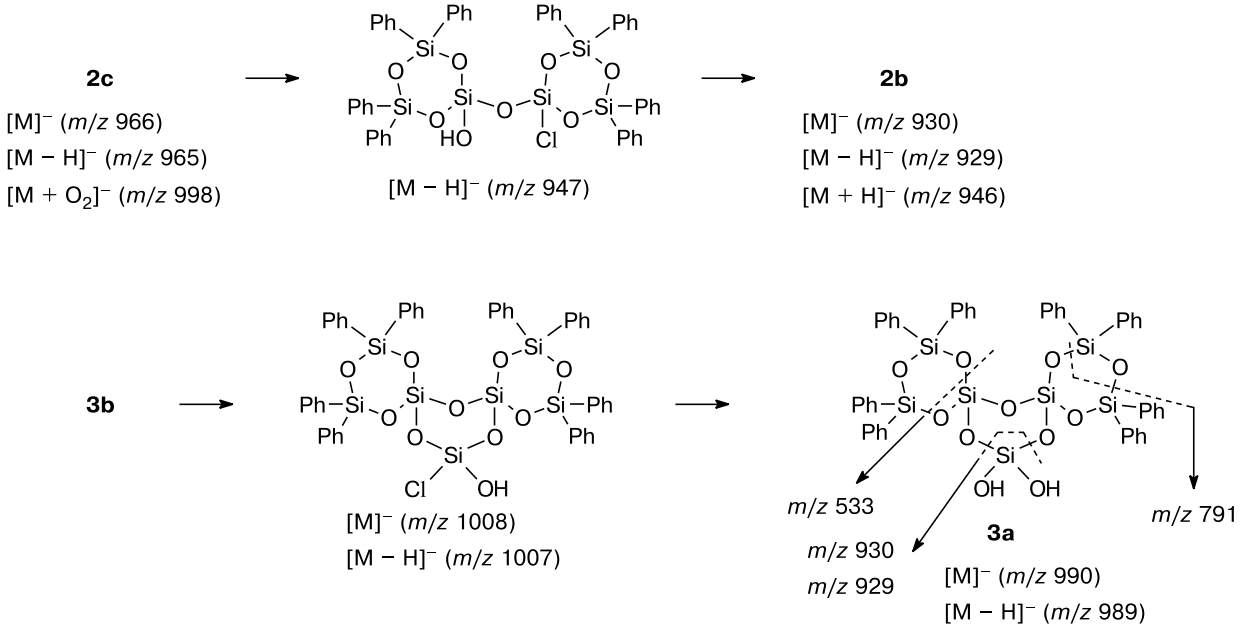


$[M]^-$ (*m/z* 1842), $[M - H]^-$ (*m/z* 1841)

$[M]^-$ (*m/z* 1962), $[M - H]^-$ (*m/z* 1961)

* The secondary mass spectra (MS/MS) obtained by collision activation are given herein.

Scheme 3



Experimental

The EI mass spectra were obtained on a MAT 95X instrument at an ionization energy of 70 eV. The DCI spectra were recorded on a Varian MAT 311A instrument. Isobutane was used as a reagent gas. A sample was heated from 100 to 1000 °C with a temperature rise rate of 100 deg s^{-1}. The ESI mass spectra were measured on a Finnigan MAT LCQ instrument (temperature of the heated capillary 190 °C, electric potential 4.5 kV, and mass range 100—3000 Da) in the MS and MS/MS modes with the XCalibur 1.5 automated program for data collection and processing. Helium served as a gas for collision activation in the MS/MS experiments. The activation energy of ions was optimized by the peak intensity of the parent ions (signal amplitude from 20 to 35% of the relative maximum of the collision energy). Solutions of samples (5 μL) in MeCN were introduced with a flow rate of the mobile phase of 30 μL min^{-1}. The MALDI—TOF mass spectra were recorded on a Bruker Reflex IV instrument in the linear mode. 2,5-Dihydroxybenzoic acid was used as a matrix. Compounds **1a—c**, **2a—d**, and **3a,b** were synthesized according to described procedures.[10,11] Cyclosiloxanes **4a—c** were synthesized according to known procedures.[4,5]

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