# Mass spectra of linear and branched methyl(vinyl)siloxanes

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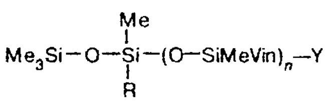
The mass spectra of some linear and branched methyl(vinyl)siloxanes $\mathrm{Me_3SiOSi(Me)(R)(OSiMeVin)_{\it n}Y}$ (R = Vin, $\mathrm{OSiMe_3}$; Y = $\mathrm{OSiMe_3}$, Cl; $n$ = 0—2) were studied. The regularities of their fragmentation and an anomalously high probability of elimination of the ethylene molecule to form the stable 1,3-dioxa-2,4,6-trisilacyclohexane skeleton were revealed.

**Key words:** mass spectra, electron impact, fragmentation, randomization, organylchlorosilanes, organylsiloxanes.

Previously,[1,2] the general regularities of mass spectral fragmentation of linear permethyl- and methyl(phenyl)oligosiloxanes have been studied systematically. The main fragmentation ions in the mass spectra of the corresponding di- and trisiloxanes are formed due to loss of hydrocarbon substituents with retention of the siloxane skeleton.

Mass spectra of higher linear methyl(vinyl)siloxanes are not described in the literature, except for the spectra of methyl(vinyl)disiloxanes, which show that the presence of the vinyl group at the Si atom facilitates the cleavage of the siloxane bond.[3] The spectra of methyl(vinyl)cyclosiloxanes are also studied.[4] Of two primary fragmentation ions A $[\mathrm{M-Me}]^+$ and A′ $[\mathrm{M-Vin}]^+$, the peak of the first one is much more intense. The rest of the vinyl-containing fragmentation ions then usually lose an acetylene molecule and, to a less extent, an ethylene molecule. When the fragmentation ion contains two or more vinyl substituents, the loss of a butadiene molecule is possible.

We studied the electron impact-induced fragmentation of linear and branched methyl(vinyl)siloxanes with the general formula



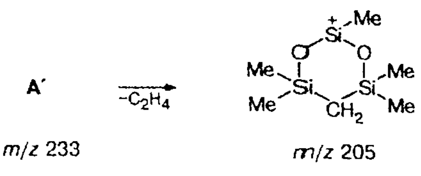
$$\mathrm{Me_3Si{-}O{-}\underset{R}{\overset{Me}{Si}}{-}(O{-}SiMeVin)_{\it n}{-}Y}$$

**1—8**

| | R | Y | $n$ | | R | Y | $n$ |
|---|---|---|---|---|---|---|---|
| **1** | Vin | $\mathrm{OSiMe_3}$ | 0 | **5** | $\mathrm{OSiMe_3}$ | $\mathrm{OSiMe_3}$ | 2 |
| **2** | Vin | $\mathrm{OSiMe_3}$ | 1 | **6** | Vin | Cl | 0 |
| **3** | Vin | $\mathrm{OSiMe_3}$ | 2 | **7** | Vin | Cl | 1 |
| **4** | $\mathrm{OSiMe_3}$ | $\mathrm{OSiMe_3}$ | 1 | **8** | Vin | Cl | 2 |

The majority of regularities established previously can be extended to the fragmentation of 3-vinylheptamethyltrisiloxane (**1**). The peak of the A ion with $m/z$ 233 is the highest, and the intensity of the peak of the A′ ion with $m/z$ 221 is 15%. The cleavage of one siloxane bond results in the $[\mathrm{M-OSiMe_3}]^+$ ion with $m/z$ 159 and trimethylsilicenium cation with $m/z$ 73 (the corresponding intensities are presented in Table 1). The ion $[\mathrm{M-OSiMe_2Vin}]^+$ with $m/z$ 147 and dimethylvinylsilicenium cation with $m/z$ 85 are formed according to the same scheme, but with the preliminary intramolecular disproportionation[1] (randomization) of organic substituents under electron impact. The latter, as the vinyl-containing ion with $m/z$ 159, then loses an acetylene molecule to form the dimethylsilicenium cation with $m/z$ 59 and an ion with $m/z$ 133 (see Table 1).

The peak of the $[\mathrm{A-C_2H_4}]$ ion with $m/z$ 205 was unexpectedly the second in intensity (72%) in the mass spectrum of siloxane **1**. At the same time, the intensity of the peak of the $[\mathrm{A-C_2H_2}]$ ion with $m/z$ 207 was only 3%. The possibility of loss of acetylene from vinyl-containing cations is usually several times higher than that of ethylene elimination. The anomaly observed can probably be explained by the formation of the stable 1,3-dioxa-2,4,6-trisilacyclohexane skeleton



The predominant elimination of the methyl radical (not the vinyl radical) is also characteristic of fragmentation of linear 3,5-divinyloctamethyltetrasiloxane (**2**) and 3,5,7-trivinylnonamethylpentasiloxane (**3**). In the spectra of **2** and **3**, the intensity of the peak of the A ion is 54 and 51% and that of the peak of the A′ ion is 3 and

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**Table 1.** Some $m/z$ values (for chlorine-containing compounds calculated per $^{35}Cl$ isotope) and relative intensities ($I_{rel}$) in mass spectra of methyl(vinyl)siloxanes **1—8**

| Ion | $m/z$ ($I_{rel}$ (%)) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** |
| $[A]^+$ | 233<br>(100) | 319<br>(54) | 405<br>(51) | 381<br>(10) | 467<br>(11) | 179<br>(100) | 265<br>(100) | 351<br>(24) |
| $[A']^+$ | 221<br>(15) | 307<br>(2) | 393<br>(3) | 369 | 455 | 167<br>(4) | 253<br>(8) | 339<br>(5) |
| $[A - C_2H_2]^+$ | 207<br>(3) | 193<br>(2) | 379<br>(2) | 355<br>(2) | — | 153<br>(26) | 239<br>(5) | 325<br>(6) |
| $[A - C_2H_4]^+$ | 205<br>(75) | 191<br>(2) | 377<br>(2) | — | — | 151<br>(7) | 237<br>(11) | 323<br>(3) |
| $[A - SiMe_4]^+$ | 145<br>(2) | 231<br>(24) | 317<br>(11) | 293<br>(16) | 379<br>(6) | — | 177<br>(3) | — |
| $[A - SiMe_3Vin]^+$ | 133<br>(12) | 219<br>(100) | 305<br>(87) | 281<br>(23) | 367<br>(14) | 79<br>(14) | 165<br>(1) | 251<br>(6) |
| $[A - SiMe_2Vin_2]^+$ | — | 207<br>(73) | 293<br>(93) | — | 355<br>(5) | — | 153<br>(7) | 239<br>(6) |
| $[A - SiMeVin_3]^+$ | 109<br>(18) | 195<br>(1) | 281<br>(26) | — | — | — | 141<br>(1) | — |
| $[M - OSiMe_3]^+$ | 159<br>(3) | — | — | — | — | 105<br>(3) | — | — |
| $[M - OSiMe_2Vin]^+$ | 147<br>(7) | — | — | 295<br>(4) | — | 93<br>(14) | 179<br>(7) | 265<br>(5) |
| $[M - OSiMeVin_2]^+$ | — | — | — | 283<br>(6) | — | — | 167<br>(5) | 253<br>(4) |
| $[A - Si_3O_3Me_6]^+$ | — | 97<br>(26) | 183<br>(5) | 159<br>(23) | 245<br>(9) | — | — | 129<br>(1) |
| $[A - Si_3O_3Me_5Vin]^+$ | — | 85<br>(83) | 171<br>(37) | 147<br>(33) | 233<br>(26) | — | — | 117<br>(3) |
| $[A - Si_3O_3Me_4Vin_2]^+$ | — | 73<br>(80) | 159<br>(72) | 135<br>(3) | 221<br>(15) | — | — | 105<br>(2) |
| $[A - Si_3O_3Me_3Vin_3]^+$ | — | — | 147<br>(28) | 123<br>(2) | — | — | — | 93<br>(3) |
| $[Me_3SiOSiMe_2]^{+\,a}$ | (7) | (2) | (28) | (33) | (34) | — | (4) | (13) |
| $[Vin_3Si]^{+\,b}$ | — | — | — | (2) | (1) | — | — | — |
| $[MeVin_2Si]^{+\,c}$ | — | (26) | (32) | — | (13) | — | (33) | (38) |
| $[Me_2VinSi]^{+\,d}$ | (30) | (83) | (77) | (27) | (55) | (8) | (25) | (48) |
| $[Me_3Si]^{+\,e}$ | (64) | (80) | (100) | (100) | (100) | (15) | (30) | (100) |
| $[Me_2HSi]^{+\,f}$ | (18) | (27) | (42) | (23) | (19) | (9) | (17) | (23) |

[a] $m/z$ 147. [b] $m/z$ 109. [c] $m/z$ 97. [d] $m/z$ 85. [e] $m/z$ 73. [f] $m/z$ 59.

2%, respectively. As known,[1,5] in the case of linear permethyltetra- and -pentasiloxanes, cyclization due to the rejection of the tetramethylsilane molecule is the main direction of the fragmentation of the **A** ion. The peak of the $[Me_3Si]^+$ cation is the most intense in the spectra of these compounds. The **A** ions in the spectra of compounds **2** and **3** decompose according to a similar scheme taking into account randomization (see Table 1).

The mass spectrum of siloxane **2** is characterized by the elimination of the hexamethylcyclotrisiloxane $(Me_2SiO)_3$ molecule from the **A** ion. An analogous process, taking into account randomization, is observed for the spectrum of siloxane **3** (see Table 1). Elimination of neutral molecules of acetylene, ethylene, and butadiene from the **A** ions of siloxanes **2** and **3** occurs in an insignificant extent only and results in the formation of ions, whose intensity does not exceed 3%.

It has been shown previously[2] that the electron impact action on siloxanes leads to the randomization of substituents and complete rearrangement of the siloxane skeleton resulting in the identity of mass spectra of isomers of branched and linear structures. Therefore, all regularities of fragmentation of linear siloxane **3** should concern branched 5-(trimethylsiloxy)-3-vinyloctamethyltetrasiloxane **4**, which is observed in practice (see Table 1). Branched 7-(trimethylsiloxy)-3,5-divinylnonamethylpentasiloxane (**5**) decomposes similarly.

Among siloxanes studied, 1-chloro-1-vinyltetramethyldisiloxane (**6**) is the only representative of methyl(vinyl)disiloxanes, and its fragmentation occurs in accordance with the regularities characteristic of compounds of this type. The peak of the **A** ion with $m/z$ 179 is the most intense, the intensity of the peak of the $[M - Cl]^+$ ion with $m/z$ 159 is 3%, and the peak with *m/z* 153 second in intensity (26%) corresponds to the $[A - C_2H_2]^+$ ion. The probability of ethylene elimination from the A ion is fourfold lower, and the intensity of the peak of the ion with *m/z* 151 is 7%. The cleavage of the siloxane bond, taking into account randomization, results in the formation of the ions $[Me_2ClSi]^+$ with *m/z* 93 (14%), $[MeVinClSi]^+$ with *m/z* 105 (3%), $[Me_3Si]^+$, and $[Me_2VinSi]^+$. Then both vinyl-containing ions lose an acetylene molecule to be transformed into the ions $[MeHClSi]^+$ with *m/z* 79 (13%) and $[Me_2HSi]^+$ with *m/z* 59 (9%) (see Table 1).

The fragmentation of 1-chloro-1,3-divinylpentamethyltrisiloxane (**7**) proceeds according to the regularities described above for fragmentation of siloxane **1**. The peak of the **A** ion with *m/z* 265 is the most intense, and the intensity of the peak of the $[A - C_2H_4]^+$ ion with *m/z* 237 (11%) is substantially higher than that of the $[A - C_2H_2]^+$ ion with *m/z* 239 (5%). Peaks of the ions containing one or two Si atoms have a noticeable intensity: $[M - OSiClVin_2]^+$ with *m/z* 147 (4%), $[M - OSiClMeVin]^+$ with *m/z* 159 (1%), $[M - OSiMeVin_2]^+$, and $[M - OSiMe_2Vin]^+$ (see Table 1). The latter then loses the acetylene molecule, to be transformed into an ion with *m/z* 153 (see Table 1). The ion with *m/z* 133 (6%) is formed due to a similar fragmentation of the ion with *m/z* 159.

In the mass spectrum of linear 1-chloro-1,3,5-trivinylhexamethyltetrasiloxane (**8**), the intensities of peaks of the ions **A** with *m/z* 351, $[A - C_2H_2]^+$ with *m/z* 325, and $[A - C_2H_4]^+$ with *m/z* 323 are 24, 6, and 3%, respectively. In molecule **8**, unlike siloxane **2**, the terminal $SiMe_3$ group is replaced by SiMeVinCl. Seemingly, this replacement should increase the contribution of fragmentation of ions with the cyclic structure, since their formation is possible due to elimination of the dimethyl(vinyl)chlorosilane molecule. In fact, the mass spectrum of siloxane **8** contains only two peaks of ions with the cyclic structure: $[A - SiMe_3Vin]$ and $[A - SiMe_2Vin_2]$ (see Table 1). The majority of fragmentation ions in the mass spectrum of compound **7** appears due to the cleavage of different siloxane bonds, first of all ions with the general formula $[Me_nVin_{3-n}Si]^+$ ($n = 1-3$). The *m/z* and $I_{rel}$ values for these ions and the ions $[M - OSiMeVin_2]^+$, $[M - OSiMe_2Vin]^+$, and $[Me_3SiOSiMe_2]^+$ similar to those formed during the decomposition of siloxane **2** are presented in Table 1.

Thus, fragmentation of linear methyl(vinyl)siloxanes and methyl(vinyl)chlorotrisiloxanes, as well as methyl(vinyl)tetrasiloxanes and methyl(vinyl)pentasiloxanes with the linear and branched structure, obeys mainly the regularities established previously for the corresponding permethyl- and methyl(phenyl)siloxanes.

The anomalously high probability of elimination of the ethylene molecule from the $[M - Me]^+$ ions in the spectra of linear methyl(vinyl)siloxanes **1**—**3** and methyl(vinyl)chlorosiloxanes **6**—**8** is due to the formation of the stable 1,3-dioxa-2,4,6-trisilacyclohexane skeleton.

The replacement in the molecule of linear siloxane **2** of the terminal trimethylsilyl group by the methyl(vinyl)chlorosilyl group decreases sharply the intensity of peaks of fragmentation ions with the cyclic structure.

## Experimental

Mass spectra were recorded at ionizing voltages of 60 and 12 V on an LKB-2091 GLC-MS mass spectrometer using a system of chromatographic injection of a sample into an ion source ($T_{source}$ = 240 °C, a glass capillary column 38 m long, SE-54 as the stationary phase, the temperature of the evaporator was 270 °C, the initial and final temperatures of the column were 60 and 270 °C, respectively, and the rate of temperature increase was 16 deg min$^{-1}$).

The synthesis of siloxanes **1**—**8** under study was described previously.[6]

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