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Unstable methoxycyclosiloxanes $[(\text{CH}_3\text{O})\text{SiO}]_n$ ($n = 2, 3$): Thermal generation and direct mass spectral studies

J. Tamás *, A. Gömöry, I. Besenyei

Central Research Institute for Chemistry, Hungarian Academy of Sciences, P.O. Box 17, Budapest H-1525 (Hungary)

V.N. Khabashesku *, Z.A. Kerzina, N.D. Kagramanov, I.O. Bragilevsky

N.D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of the USSR, Leninsky Prospekt 47, Moscow, 117913, (U.S.S.R.)

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Abstract

Direct evidence for formation of unstable methoxy cyclosiloxanes $[(\text{CH}_3\text{O})_2\text{SiO}]_2$ (**1**) and $[(\text{CH}_3\text{O})_2\text{SiO}]_3$ (**2**) in the gas phase has been obtained by a mass-spectral study of the vacuum pyrolysis of 3,3-dimethoxy-6-oxa-3-silabicyclo[3.1.0]hexane (**4**). Intermediates **1** and **2** have been detected in the mass spectra of the pyrolysis products of **4** as the corresponding molecular ions, and identified from their exact masses and compositions. The metastable transitions recorded by B/E scan show the fragmentation trends of **1**, **2** and **4** under electron impact (70 eV).

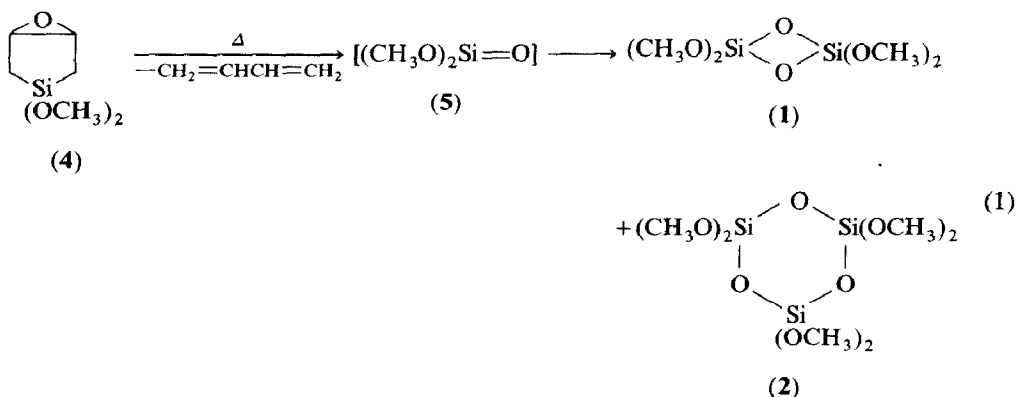
The ionization energies (*IE*), determined for **1** (8.81 ± 0.1 eV) and **2** (8.50 ± 0.1 eV) are considerably lower than the *IE* of linear methoxysubstituted silanes and alkanes.

Introduction

The simplest 1,3-cyclodisiloxanes $(\text{R}_2\text{SiO})_2$ (**1**, $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$ etc.) have been postulated as intermediates in various reactions of silanones [1], such as in their transformations into tri- and tetracyclosiloxanes, which are usually stable under normal conditions. However, some of the tricyclosiloxanes $(\text{R}_2\text{SiO})_3$ (**2**), bearing electron-withdrawing substituents R (F, Cl, Br, OCH_3) at the silicon atom, have not been previously isolated owing to their ready oligomerization to more stable linear siloxanes. In this connection, a successful approach to studies of unstable cyclosiloxanes **1** and **2** consists in their generation in vacuo accompanied

* To whom correspondence should be addressed.

by direct investigation by physical methods, viz., vacuum pyrolysis-mass spectrometry. Recently [2], we obtained the first direct mass-spectrometric evidence for the formation of the unstable cyclodisiloxane **1** ($R = CH_3$), which was detected in the mass spectra of the vacuum pyrolysis products of 3,3-dimethyl-6-oxa-3-silabicyclo[3.1.0]hexane (**3**) and its 1,5-dimethyl derivative together with cyclotrisiloxane **2** ($R = CH_3$). This technique was used to generate and directly detect the cyclodisiloxanes **1** and **2** ($R = OCH_3$) in this study. The intermediates **1** and **2** have been obtained by the vacuum pyrolysis of 3,3-dimethoxy-6-oxa-3-silabicyclo[3.1.0]hexane (**4**).



Experimental

Parent compound **4** was prepared by a published procedure [3], the epoxidation (with $p\text{-CH}_3\text{OC(O)C}_6\text{H}_4\text{COOH}$) of 1,1-dimethoxy-1-silacyclopent-3-ene, obtained by the reaction of 1,1-dichloro-1-silacyclopent-3-ene with methanol. Epoxide **4** was isolated from the reaction mixture by vacuum distillation at $133^\circ\text{C}/90$ Torr with a purity of 90%. The structure of **4** was established from ^1H NMR and MS data.

Pyrolysis of **4** was carried out in quartz pyrolyzer (2.5 mm internal diameter) with a 35 mm heated zone ending near the electron beam (~ 10 mm). The pressure in the vacuum chamber of a mass spectrometer was varied between 0.6×10^{-7} and 4×10^{-7} Torr.

Preliminary information on the products of the vacuum pyrolysis of **4** as well as of the products of the chemical trapping of silanone **5** was obtained by a monopole MKh-7303 mass spectrometer. The determination of the exact ion mass numbers, detection of metastable ions and determination of ionization energies of cyclodisiloxanes **1** and **2** were carried out by use of an AEI MS 902 type double focussing mass spectrometer equipped with linked scanning facilities.

Results and discussion

The mass numbers and relative peak intensities of characteristic ions in mass spectra of **4** and its pyrolysis products at pyrolyzer temperatures of $25\text{--}1100^\circ\text{C}$ and at a pressure of 0.6×10^{-7} Torr in the vacuum chamber of a mass spectrometer are listed in Table 1. It was found that 3,3-dimethoxysubstituted epoxide **4**, in contrast

Table 1. Mass spectrum of compound 4 at various pyrolyzer temperatures (°C) (70 eV)

<i>m/z</i>	<i>I</i> (%)							
	25	260	400	550	700	820	950	1100
499				1.1	3.9	7.2	7.0	6.1
498				2.3	7.0	12	11.0	9.2
453				1.8	4.8	9.2	9.0	5.2
437				1.8	5.2	8.4	9.0	4.8
407				1.5	5.2	10.0	10.0	8.2
393				3.2	13	19	22	13
392				4.8	20	32	33	21
347				3.2	12	20	24	12
333				2.3	8.7	13	14	9.3
332				4.5	18	28	28	16
318				3.6	19	36	33	21
287				3.4	16	28	34	24
273				1.6	8.7	16	18	16
257				3.9	19	36	42	31
243				1.4	6.5	16	14	14
227				10	42	80	88	48
226				5.9	30	56	64	38
212				2.3	20	68	60	38
211				1.8	6.1	14	20	10
197				4.8	23	48	54	28
196				4.1	21	36	44	31
182				2.7	20	84	80	55
181				2.7	13	40	42	28
167				2.7	14	32	28	31
160	7.0	6.7	6.3	6.4	10	13	20	21
159	26	25	24	27	29	28	32	34
152	0.6	0.5	0.5	20	120	320	280	170
151	—	—	—	5.0	20	110	100	90
145	100	100	100	100	100	100	100	100
137	—	—	—	3.2	38	48	44	24
133	36	38	35	36	39	40	44	48
132	36	33	32	32	33	28	40	41
131	21	23	21	27	26	28	35	34
130	29	33	29	36	39	44	48	48
129	13	13	12	15	17	18	19	21
128	43	46	47	50	52	64	68	75
121	2.8	3.2	3.4	32	180	520	570	415
117	190	210	210	225	235	240	250	240
107	54	54	53	68	87	140	160	135
91	130	140	135	160	235	400	440	345
90	25	28	27	38	87	85	80	83
87	79	83	82	86	87	84	190	95
77	64	71	71	82	96	130	140	120
74	29	33	29	36	35	40	44	34
61	36	40	41	50	61	110	120	105
59	140	145	150	165	175	200	240	240
54	24	25	29	110	360	1080	1700	1880
53	6.3	7.5	7.4	68	235	720	1200	1480
45	34	38	35	41	65	200	240	205
39	12	15	17	91	305	880	1500	1750
31	23	17	15	19	43	240	460	550
29	16	16	14	27	52	240	520	690
27	20	23	25	68	190	560	940	1030
15	24	23	22	36	61	160	340	450

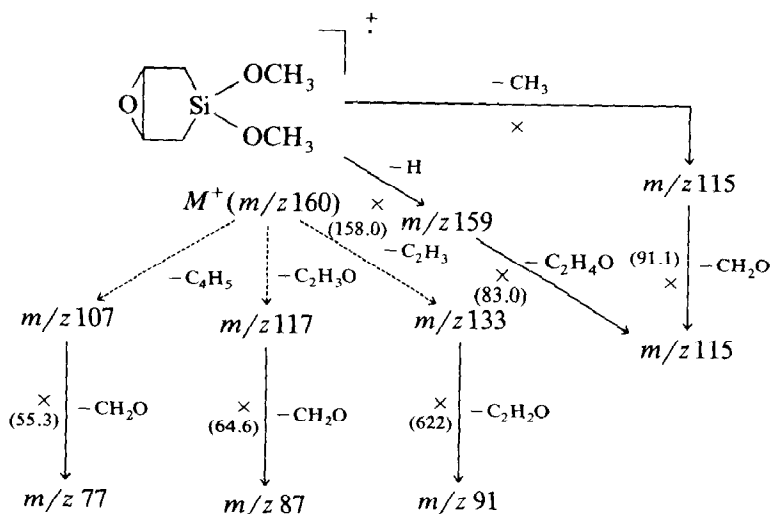
to its 3,3-dimethylsubstituted analog **3**, does form a rather stable molecular ion at m/z 160 under electron impact. It was difficult to obtain strong mass spectrometric evidence for thermal isomerization of **4** to 1,1-dimethoxy-1-silacyclopent-2-en-4-ol (**6**), in analogy to that of **3** [2]. These difficulties were caused by coincidence both of molecular and of fragment ions of **4** and **6**, but judging by the increased peak intensity of the ion at m/z 160 during pyrolysis of **4** (Table 1), the above-mentioned isomerization does probably take place. The data on changes of the relative intensities of ion peaks, listed in Table 1, indicate that the vacuum pyrolysis of the parent epoxide **4** takes place at 550–1100°C. During pyrolysis a large increase of the peak intensity of the m/z 54 ion of butadiene relative to that of the m/z 145 ion ($[M - \text{CH}_3]^+$ ion of parent compound **4**), taken as the base peak in mass spectra of pyrolysis products, was observed together with the appearance and growth of m/z 212 and m/z 318 ion peaks. The stoichiometry of the reaction (eq. 1), which is similar to the pyrolysis of dimethylsubstituted epoxide **3** [2], indicates that the m/z 212 and the m/z 318 ions are probably attributable to methoxycyclosiloxanes **1** and **2**, respectively.

The exact masses and elemental compositions of the enumerated ions, which indicate that they arise from the molecular ions of **1** (found 212.019, calc. 212.017, $\text{Si}_2\text{O}_6\text{C}_4\text{H}_{12}$) and **2** (found 318.024; calc. 318.025, $\text{Si}_3\text{O}_9\text{C}_6\text{H}_{18}$). New ion peaks at m/z 393.012, $\text{Si}_4\text{O}_{11}\text{C}_7\text{H}_{21}$ and 499.025, $\text{Si}_5\text{O}_{14}\text{C}_9\text{H}_{27}$, were also found in the high resolution mass spectra of the pyrolysis products of **4**. These mass numbers may be assigned to the $[M - \text{CH}_3\text{O}]^+$ ions of the corresponding tetramer and pentamer of silanone **5**. Their peak intensities are changed aproportionately to those of the m/z 212 and m/z 318 ions during pyrolysis. This probably precludes the possible formation of the latter ions as fragment ions of the above-mentioned oligomers of silanone **5** and hence the assignment of m/z 212 and m/z 318 ions to the molecular ions of cyclosiloxanes **1** and **2**.

The detection of metastable ions by a B/E scan showed the main pathways of fragmentation of both the parent epoxide **4** and the methoxycyclosiloxanes **1** and **2** (Schemes 1, 2, 3) under electron impact.

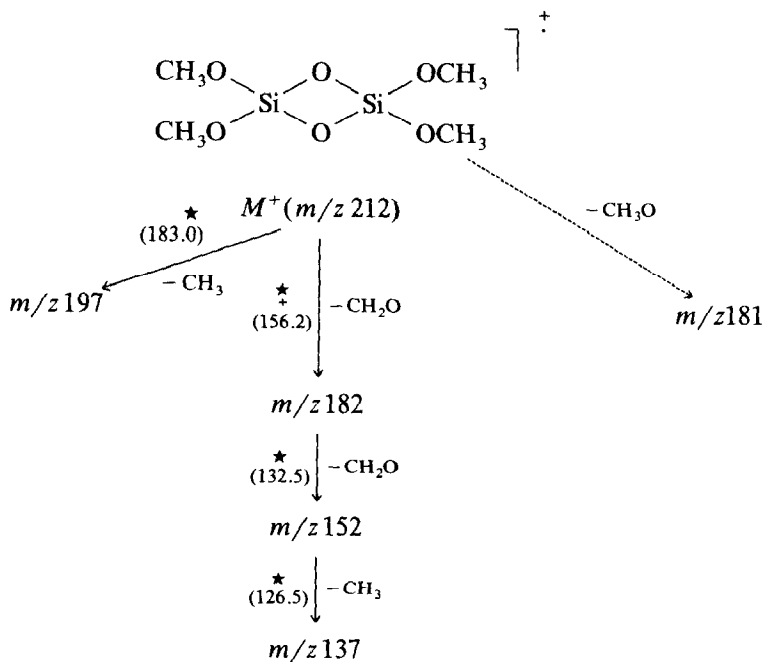
The fragmentations of compounds **1**, **2** and **4** all show the loss of methyl fragment from the corresponding molecular ions. At the same time, the dissociative ionization with loss of methoxyl fragment (Schemes 2 and 3) from molecular ions is also characteristic of cyclosiloxanes **1** and **2**. The loss of neutral molecules of butadiene and silanone **5** from the molecular ion of epoxide **4** was not found, which shows the dissimilarity in the mechanisms of vacuum pyrolysis of **4** and its fragmentation under electron impact.

For the determination of ionization energies (IE) of cyclosiloxanes **1** and **2** the semilog plotting technique [4] was used. Benzene ($IE = 9.41$ eV [5]) was taken as internal standard. The ionization curves were obtained at pyrolyzer temperatures of 820°C. The following IE values were determined: 8.81 ± 0.1 eV for **1** and 8.50 ± 0.1 eV for **2**. These values, being the first physical characteristics of unstable methoxycyclosiloxanes, can be also used as analytical characteristics for direct detection of these intermediates in various gas-phase reactions. The IE values determined for **1** and **2** are considerably lower than the ionization energies of methoxysubstituted linear molecules, CH_3OCH_3 (10.0 ± 0.02 eV [6]), $(\text{CH}_3\text{O})_2\text{CH}_2$ (9.98 ± 0.03 eV [6]) and $\text{CH}_3\text{OSi}(\text{CH}_3)_3$ (9.79 eV [6]), which indicates that electron loss from cyclosiloxane ring is more facile than that from the methoxyl substituents in **1** and **2**.

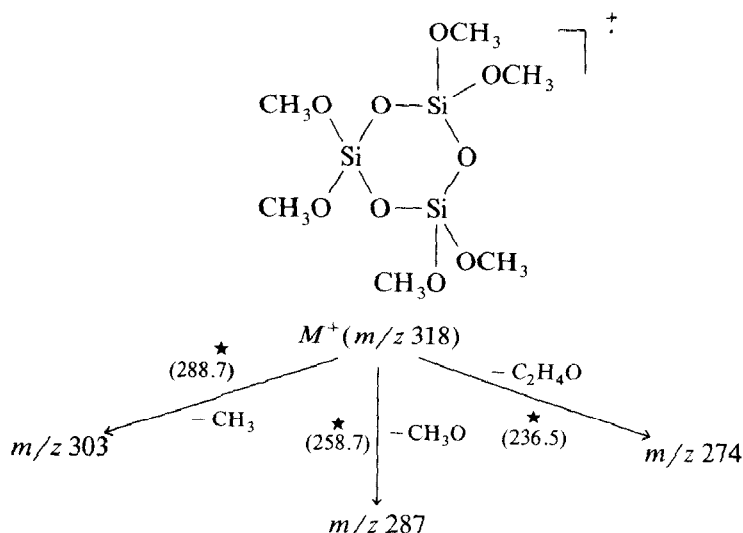


Scheme 1. Fragmentation of epoxide **4** under electron impact conditions (70 eV). $\times$ denotes 2nd field free region (F.F.R.) metastable transition.

Despite the fact that the molecular ion of silanone **5** (m/z 106) was not detected in the mass spectra of the pyrolysis products of **4**, the identification of cyclosiloxanes **1** and **2** under the conditions studies may be regarded as indirect evidence for the formation of the intermediate **5** in reaction 1. More indirect evidence for formation of **5** was obtained by co-pyrolysis of epoxide **4** with methanol (**4**/ CH_3OH = 1 : 1), which was used as the trap for silanone **5**. Hexamethoxydisiloxane (**6**)^{*}, a

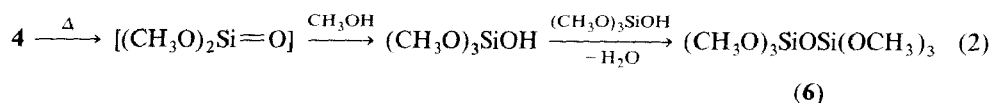


Scheme 2. Fragmentation of cyclosiloxane **1** under electron impact (70 eV). $\star$ denotes 1st (observed by B/E scan), and $\times$ denotes 2nd F.F.R. metastable transition.



Scheme 3. Fragmentation of cyclosiloxane **2** under electron impact (70 eV). ★ denotes 2nd F.F.R. metastable transition.

product of the chemical trapping of **5**, was detected in the mass spectra of the reaction products of eq. 2.



Direct mass spectral detection of silanone **5** is hampered, as in the case of silaacetone, $(CH_3)_2Si=O$, by a constant, low concentration of **5** in the gas phase, owing to the zero activation barrier of dimerization of silanones [7], which occurs mainly on the walls of quartz pyrolyzer. Only by allowing the accumulation of **5** by freezing the pyrolysis products of **4**, have we managed to identify this intermediate by matrix isolation-IR spectroscopy [8].

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