

Mass spectrometric evidences for the formation of unstable 1,1,3,3-tetramethyl-1,3-cyclodisiloxane in the gas phase

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Abstract

Mass spectrometry during the vacuum pyrolysis of either 3,3-dimethyl-6-oxa-3-silabicyclo[3.1.0]hexane (**1**) or its 1,5-dimethyl derivative (**2**), both of which are dimethyl silanone (D^1) precursors, indicated that 1,1,3,3-tetramethyl-1,3-cyclodisiloxane (D^2) was present among the pyrolysis products in the gas phase. D^2 is unstable under normal conditions.

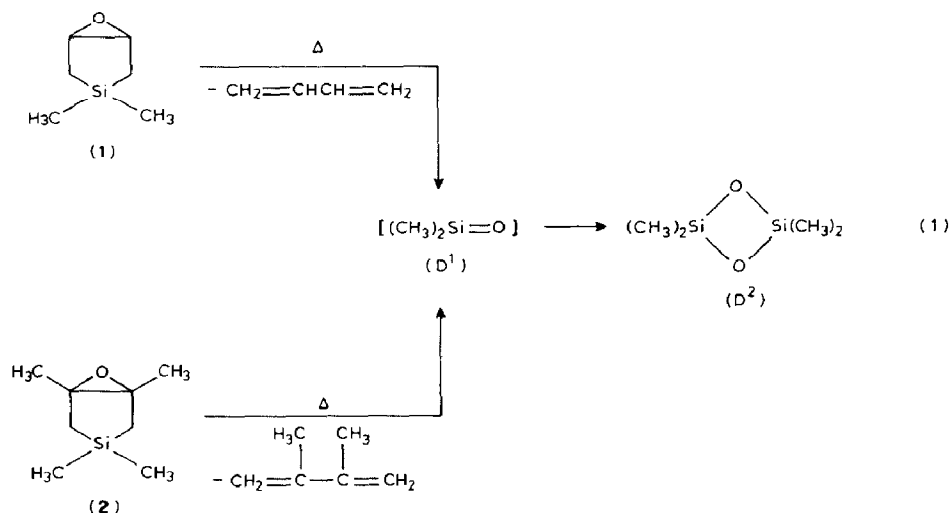
1,3-Cyclodisiloxanes (R_2SiO)₂ are often used as intermediates in various reactions of silanones [1], e.g. in their transformation to tri- and tetra-cyclosiloxanes. Recently cyclodisiloxanes with bulky substituents at the silicon atom ($R = \text{Mes}$, $t\text{-Bu}$) were isolated and their structures determined by X-ray diffraction studies [2]. The simplest disiloxanes ($R = \text{H}$, CH_3 , C_2H_5), however, are not stable at normal conditions and up to now no convincing evidence has appeared that they can occur in the gas phase.

To whom some light on this problem we studied the vacuum pyrolysis of bicycloepoxides **1** and **2**. A study of the low and medium pressure pyrolysis of **1** has been published recently [3,4] and the intermediacy of D^1 and its cyclodimer D^2 was proposed.

The method of vacuum pyrolysis–mass spectrometry used in this study is outlined in the Experimental section. The mass spectra obtained at various tempera-

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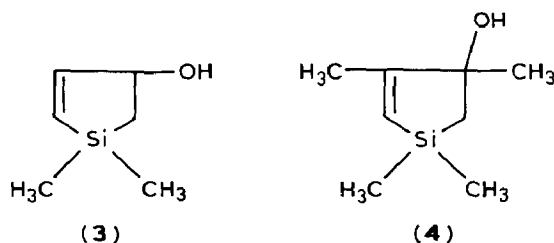


tures for the gas entering the ion chamber from the pyrolyser indicated that between 650 and 950 °C the pyrolysis of **1** and **2** took place to a large extent (see Table 1). In the case of **1**, in accord with the earlier observations [3,4], D^3 , D^4 and butadiene were found to be the main stable products. Furthermore, isomerization of **1** to **3** also

Table 1

The main products of the vacuum pyrolysis of **1** and **2** as represented by their main characteristic ions

Compound	m/z	ions	Abundance (%) (70 eV) Temperature of the pyrolyzer			
			25 °C	550 °C	700 °C	950 °C
1	128	$[\text{M}^3]^{++}$	–	0.5	2.8	7.0
	113	$[\text{M}^1-15]^+ + [\text{M}^3-15]^+$	100	100	100	100
	133	$[\text{D}^2-15]^+$	–	0.4	11	35
	207	$[\text{D}^3-15]^+$	–	0.3	8.3	21
	281	$[\text{D}^4-15]^+$	–	0.2	2.3	5.3
	54	$\text{C}_4\text{H}_6^{++}$	–	4.1	41	110
	43.972	SiO^{++}	6.4	6.9	10	24
	15	CH_3^+	2.5	2.4	10	33
2	156	$[\text{M}^2]^{++} + [\text{M}^4]^{++}$	3.5	3.8	4.6	8.6
	141	$[\text{M}^2-15]^+ + [\text{M}^4-15]^+$	100	100	100	100
	123	$[\text{M}^2-15-18]^+$ $+ [\text{M}^4-15-18]^+$	24	26	71	170
	133	$[\text{D}^2-15]^+$	–	2.2	48	38
	207	$[\text{D}^3-15]^+$	–	0.8	11	25
	281	$[\text{D}^4-15]^+$	–	0.5	8	14
	82	$\text{C}_6\text{H}_{10}^{++}$	–	7.7	140	210
	43.972	SiO^{++}	6.8	7.5	36	120
	15	CH_3^+	3.8	4.5	43	150



took place which was indicated by the appearance of an m/z 128 ion at higher temperatures, and by the significant and characteristic differences in the metastable daughter ion spectra of m/z 113 ions obtained at high and low temperatures of the pyrolyzer (Table 2). In addition to the characteristic ions of these stable products, those of the starting compound 1, at higher temperatures of the pyrolyzer an ion at m/z 133, and the ions SiO^+ and CH_3^+ were observed in significant abundance.

The pyrolytic decomposition of 2 was very similar to that of 1 and took place to an even greater extent (see Table 1). The isomerization of 2 probably to form 4 was indicated by the increasing abundance of m/z 156 ion at higher temperatures, as well as by significant differences in the metastable daughter ion spectra of m/z 141 ions recorded at 25°C and at 950°C of the pyrolyzer (Table 2).

It is noteworthy, that the abundance ratios of the characteristic ions of various compounds listed in Table 1 for 1 and 2 changed very little even when the pressure in the pyrolyzer was increased five-fold. The m/z 133 ion was studied in detail. Its exact mass and elemental composition were found to be m/z 133.014 and $\text{C}_3\text{H}_9\text{Si}_2\text{O}_2^+$, respectively, thus corresponding to $[\text{D}^2 - \text{CH}_3]^+$ ion. Accordingly, measurements at low electron energies showed an appearance energy very close to that of the $[\text{D}^3 - \text{CH}_3]$ and $[\text{D}^4 - \text{CH}_3]^+$ ions. This fact, together with our observation that D^3 , D^4 and D^5 gave no significant single-charge ions at m/z 133 when the temperature of the pyrolyzer was kept at 25 or at 950°C, excluded the possible formation of the majority of these ions from D^3 or higher homologues either by electron impact or by pyrolysis.

The metastable daughter ion spectra of m/z 133 and that of $[\text{D}^3 - \text{CH}_3]^+$ and (partly) of $[\text{D}^4 - \text{CH}_3]^+$ ions (Table 2) recorded under comparable conditions showed decomposition processes common to these ions; namely competing losses of small molecules such as CH_4 , H_2O and C_2H_4 .

The above-mentioned results seem to provide clear evidence that the vast majority of ions at m/z 133 observed in our experiments correspond to $[\text{D}^2 - \text{CH}_3]^+$ ions and that they originate from D^2 and are present in the gas phase as a separate entity.

Our attempt to detect dimethylsilanone (D^1) by monitoring its M^+ (m/z 74) and $[M - 15]^+$ (m/z 59) ions at 70 and 15 eV was unsuccessful, which indicates that there was a very low stationary concentration of D^1 . This is probably due to its ability to form D^2 in a very fast cyclodimerization reaction which has no activation barrier according to calculation [5]. Nevertheless, our effort to identify the cyclo-dimer D^2 did provide indirect evidence for primary formation of D^1 from 1 and 2 via pyrolysis.

Very recently, in fact, matrix isolation has been used successfully to collect dimethylsilanone (D^1) together with other pyrolysis products of 1 in inert matrix in sufficient quantities, to enable its IR spectrum [6–8] to be recorded.

Table 2
The metastable daughter ion (B/E scan) spectra of some selected ions at 70 eV

m/z 133 $[D^2-15]^+$		m/z 207 $[D^3-15]^+$		m/z 281 $[D^4-15]^+$		m/z 113 $[M^1-15]^+$		m/z 141 $[M^2-15]^+$		m/z 128 $[M^3]^+$	
m/z	$I(\%)^b$	m/z	$I(\%)^{a,b}$	m/z	$I(\%)^{a,b}$	m/z	$I(\%)^a$	m/z	$I(\%)^a$	m/z	$I(\%)^b$
119	100	191	100	265	100	111	100	139	35	113	100
115	5	189	4	253	5	95	2.5	126	100	110	9
105	11	179	7	207	15	87	3	115	70	98	2
						85	8	101	14	75	3
						71	16	99	6		7

^a The temperature of the pyrolyser was kept at 25 °C. ^b 950 °C.

It is very probable, that the SiO^+ and CH_3^+ ions which appear as abundant peaks in the mass spectra at higher temperatures (Table 1) are mainly due to the pyrolytic decomposition of D^1 , in accord with earlier observations [6–8] (eq. 2).



Experimental

Compounds **1** and **2** were synthesized by published procedures [9] and purified by preparative GLC. The starting materials and, in the initial stages, the pyrolysis products were analysed by a monopole MKh-7303 mass spectrometer (resolution power ~ 200). In the latter stages of the experiments, and for detailed mass spectroscopy of the products an AEI MS-902 type double focussing mass spectrometer equipped with linked scanning facilities was used.

Pyrolysis of **1** and **2** was carried out in a ceramic pyrolyzer tube of 2 mm internal diameter with a 20–25 mm heated zone ending near the electron beam (~ 10 mm). The pressure of the samples in the pyrolyzer varied between 1×10^{-4} and 5×10^{-4} Torr.

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