1,1,1-Trimethyl-3,3,3-trichlorodisiloxane as a source and a trapping agent for silanones

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The pyrolysis of 1,1,1-trimethyl-3,3,3-trichlorodisiloxane (**1**) was studied and its mechanism involving the formation of dichloro- and dimethylsilanones was proposed. The composition of the condensate from the co-pyrolysis of siloxane **1** and hexamethyldisiloxane indicated that under the pyrolysis conditions the simplest siloxanes can be both the sources and the trapping agents of silanones.

Key words: silanones, intermediates, siloxanes, pyrolysis.

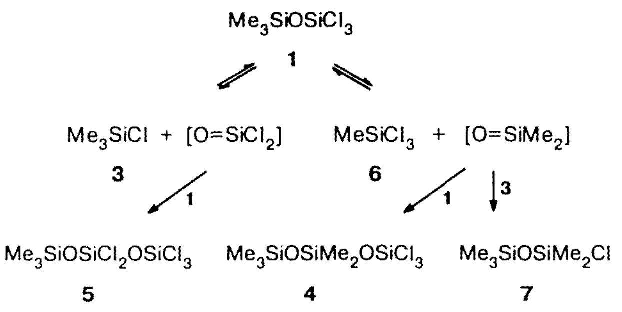
The formation of highly reactive intermediates, silanones, is postulated for many reactions involving organosilicon compounds.[1—4]

The pyrolylsis of 1,1,1-trimethyl-3,3,3-trichlorodisiloxane (**1**) and its co-pyrolysis with hexamethyldisiloxane (**2**), used as a chemical trap for the intermediate, have been studied in this work. The process was carried out at a temperature higher than 650 °C in a hollow quartz tube; the contact time of the starting components in the reaction zone was 30—40 s.

Trimethylchlorosilane (**3**), the initial siloxane **1**, 1,1,1,3,3-pentamethyl-5,5,5-trichlorotrisiloxane (**4**), 1,1,1-trimethyl-3,3,5,5,5-pentachlorotrisiloxane (**5**), trichloromethylsilane (**6**), and 1,1,1,3,3-pentamethyl-3-chlorodisiloxane (**7**) were found in the condensate after the pyrolysis of compound **1** (650 °C, 30—40 s). Compounds **6** and **7** were present as traces.

The formation of compounds **4** and **5** can be explained by the insertion of dichloro- and dimethylsilanones generated from siloxane **1** into the Si—O and Si—Cl bonds of initial siloxane **1** (Scheme 1).

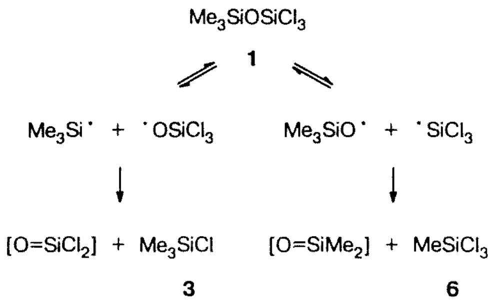
Scheme 1



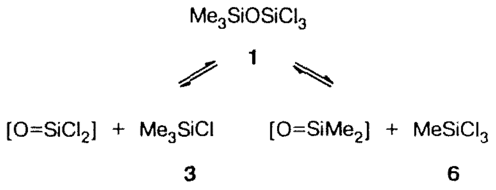
According to the GLC analysis data, compounds **3** and **5** are the main reaction products, *i.e.*, the pyrolysis of siloxane **1** at 650 °C affords primarily dichlorosilanone and trimethylchlorosilane.

The formation of silanones in the pyrolysis can proceed by the following schemes: (a) homolytic decomposition of compound **1** into silyl and oxasilyl radicals followed by their disproportionation to afford dimethyl- and dichlorosilanones and the corresponding chlorosilanes (Scheme 2); (b) elimination of silanones from initial siloxane **1** with the simultaneous cleavage of the Si—O and Si—Cl bonds (Scheme 3).

Scheme 2



Scheme 3



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Scheme 2 is supported by the presence of a minor amount (according to the mass spectrometry data) of the product of the recombination of trimethyl- and trichlorosilyl radicals, *i.e.*, trichlorotrimethyldisilane in the condensate.

$$Me_3Si^{\cdot} + Cl_3Si^{\cdot} \longrightarrow Me_3SiSiCl_3$$

The data obtained in the studies of the behavior of compound **1** under the action of electron impact indicate the possibility of the realization of Scheme 3. The mass spectrum of siloxane **1** contains a peak at *m/z* 207 with an intensity of 57 % corresponding to the $[M-Me]^+$ ion, but the main peak is at *m/z* 93 (100 %) and belongs to the Me_2SiCl^+ ion. The peak of the $[SiMe_3]^+$ ion at *m/z* 73 is absent in the mass spectrum. The peak at *m/z* 133 with an intensity of 35 % may correspond to the $[M-Me]^+$ ion of chlorosilane **6**. Thus, generation of silanones occurs most probably according to both Schemes 2 and 3.

After the reaction of compound **1** with hexamethyldisiloxane **2** used as a trapping agent, (650 °C; the contact time of the reagents was 30—40 s, [**1**] : [**2**] = 1 : 2), tetramethylsilane, 1,1,1,5,5,5-hexamethyl-3,3-dichlorotrisiloxane (**8**), and octamethyltrisiloxane (**9**), along with the products of the pyrolysis of **1**, were found in the condensate.

The presence of compounds **8** and **9** in the condensate indicates that under conditions of the co-pyrolysis of disiloxanes **1** and **2**, dimethyl- and dichlorosilanones are introduced at the Si—O bond of compound **2**.

$$\underset{\mathbf{2}}{Me_3SiOSiMe_3} + [O{=}SiCl_2] \longrightarrow \underset{\mathbf{8}}{Me_3SiOSiCl_2OSiMe_3}$$

$$\mathbf{2} + [O{=}SiMe_2] \longrightarrow \underset{\mathbf{9}}{Me_3SiOSiMe_2OSiMe_3}$$

The formation of tetramethylsilane and trisiloxane **9**, as well as the increase in the content of compounds **4** and **7** in the condensate as compared with their amounts in the products of the pyrolysis of **1**, indicate the generation of dimethylsilanone from siloxane **2** at 650 °C.

Based on these data one may conclude that under the pyrolysis conditions, disiloxanes **1** and **2** themselves are both sources and trapping agents for silanones and their behavior is determined by the reaction temperature and the nature of the substituent at the Si atom.

Experimental

Mass spectra were obtained on a MX-1303 mass spectrometer with an ionization energy of 70 eV. The composition of the pyrolysis products was determined by GLC on a LKhM-72 chromatograph with a heat conductivity detector; the stationary phase was PMS-100 (12.8 %) at INZ-600, and helium was the carrier gas.

Pyrolysis of 1,1,1-trimethyl-3,3,3-trichlorodisiloxane (1). The pyrolysis of compound **1** (8.8 g) at 650 °C afforded 7.3 g of a condensate. The conversion of **1** under these conditions was 49.1 % (including the losses). The following fractions were distilled off from the condensate: fraction (5.2 g) with boiling points below 120 °C, which was (according to the GLC and mass spectral data) a mixture of Me_3SiCl (*m/z* 93), Me_2SiCl_2 (*m/z* 113), $MeSiCl_3$ (*m/z* 133), and in part the initial **1** (*m/z* 207); fraction (2.2 g) with boiling points below 200 °C containing the initial **1** and two trisiloxanes, $Me_3SiOSiMe_2OSiCl_3$ (**4**) (*m/z* 281 $[M-Me]^+$ and 261 $[M-Cl]^+$) and $Me_3SiOSiCl_2OSiCl_3$ (**5**) (*m/z* 321 $[M-Me]^+$ and 301 $[M-Cl]^+$). Compounds with higher boiling points were present in the condensate in insignificant amounts; cyclic siloxanes were not found.

Co-pyrolysis of 1,1,1-trimethyl-3,3,3-trichlorodisiloxane (1) and hexamethyldisiloxane (2). The co-pyrolysis of compound **1** (10.3 g) and compound **2** (8.4 g) at 650 °C afforded 15.1 g of a condensate. The conversion of **1** in this case was ~50 %. A fraction with boiling point below 120 °C, which was (according to the GLC and mass spectral data) a mixture of Me_3SiCl (*m/z* 93 $[M-Me]^+$), Me_4Si (*m/z* 73 $[M-Me]^+$), **2** (*m/z* 147 $[M-Me]^+$), and $Me_3SiOSiCl_3$ (**1**) (*m/z* 207 $[M-Me]^+$), was distilled off from the condensate. Compound **1**, $Me_3SiOSiMe_2Cl$ (**7**) (*m/z* 167 $[M-Me]^+$), $Me_3SiOSiMe_2OSiCl_3$ (**4**) (*m/z* 281 $[M-Me]^+$), $Me_3SiOSiCl_2OSiCl_3$ (**5**) (*m/z* 321 $[M-Me]^+$), and $Me_3SiOSiMe_2OSiMe_3$ (**9**) (*m/z* 221 $[M-Me]^+$) were present in the bottoms.

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