Siloxanes as sources of silanones

E. A. Chernyshev, T. L. Krasnova,* A. P. Sergeev, and E. S. Abramova

M. V. Lomonosov Moscow State Academy of Fine Chemical Technology, 86 prosp. Vernadskogo, 117571 Moscow, Russian Federation. Fax: 007 (095) 430 7983

Pyrolysis of hexamethyldisiloxane (HMDS) and its copyrolysis with chlorotrimethylsilane and tetrachlorosilane were studied. Based on the data of GLC analysis and on the mass spectrum of the condensate obtained after the pyrolysis of HMDS, it was concluded that HMDS acts as a source of dimethylsilanone. The results of the copyrolysis of HMDS with chlorotrimethylsilane used as a trapping reagent indicate that the dimethylsilanone generated from HMDS can be inserted into the Si-Cl and Si-O bonds. In the copyrolysis of HMDS with tetrachlorosilane serving as a trapping reagent for dimethylsilanone, both dimethylsilanone and dichlorosilanone are generated.

Key words: silanones; siloxanes, pyrolysis; intermediates.

In 1952, it was suggested¹ that thermal transformations of polysiloxanes involve the formation of silanones, *viz.*, molecules with an Si=O double bond.

We were the first to find out (see the previous communication²) that under conditions of pyrolysis at temperatures >675 °C, hexamethyldisiloxane (HMDS) acts as a source of dimethylsilanone.

In fact, GLC and mass-spectrometric analyses of the condensate resulting from the pyrolysis of HMDS carried out in a hollow quartz reactor at 650-720 °C under atmospheric pressure and at a residence time of the reactants in the reaction zone (τ) of 30 s have shown the presence of octamethyltrisiloxane (1), decamethyltetrasiloxane (2), hexamethylcyclotrisiloxane (3), octamethylcyclotetrasiloxane (4), tetramethylsilane, and hexamethyldisilane.

Scheme 1

 $Me_{3}SiOSiMe_{3} \longrightarrow Me_{4}Si + Me_{3}SiOSiMe_{2}OSiMe_{3} + 1$ $+ Me_{3}Si(OSiMe_{2})_{2}OSiMe_{3} + Me + Si - O + Si - Me + O + Me_{3}SiSiMe_{3}$ $Me - Si - O - Si - Me + Me_{3}SiSiMe_{3}$ $Me - Si - O - Si - Me + Me_{3}SiSiMe_{3}$ $Me - Si - O - Si - Me + Me_{3}SiSiMe_{3}$ $Me - Si - O - Si - Me + Me_{3}SiSiMe_{3}$ $Me - Si - O - Si - Me + Me_{3}SiSiMe_{3}$ $Me - Me - Me + Me_{3}SiSiMe_{3}$

The formation of these products (Scheme 1) can be explained within the framework of transformations of the dimethylsilanone generated from HMDS during the pyrolysis, namely, by its homocyclization to cyclosiloxanes 3 and 4 and by insertion into the Si-O bond of the starting HMDS to yield compounds 1 and 2 (Scheme 2).

Scheme 2

$$Me_{3}SiOSiMe_{3} \longrightarrow Me_{4}Si + [O=SiMe_{2}] \longrightarrow 1 + 2$$

The highest total content of siloxanes 1, 2, 3, and 4 in the condensate obtained after pyrolysis at 675 °C and $\tau = 30$ s is 8%, and the yield of tetramethylsilane is 3% based on the starting HMDS.

The data on the composition of the condensate, together with the results of a mass spectrometric investigation of HMDS, made it possible to propose a possible mechanism for its thermal decomposition (Scheme 3). Apparently, radical decomposition of HMDS to give trimethylsilyl and trimethylsilyloxyl radicals is the predominant pathway under the conditions of pyrolysis.

Scheme 3



Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 9, pp. 1663-1666, September, 1997.

1066-5285/97/4609-1586 \$18.00 © 1997 Plenum Publishing Corporation

The validity of this scheme is supported by the formation of hexamethyldisilane and also by the data obtained in a study of the behavior of HMDS under electron impact. The mass spectrum of HMDS contains a peak with m/z 147 and with an intensity of 100%, which corresponds to the $[M-Me]^+$ ion. The peak with m/z 73 corresponding to the $[Me_3Si]^+$ ion is the second in intensity (27.8%).

It is known³ that alkyl and silyl radicals are similar in many respects. The carbon analogs of silyloxyl and silyl radicals either recombine or disproportionate to give stable products and unsaturated or carbenoid type compounds. Thus, it can be assumed that in the pyrolysis of HMDS, trimethylsilyl and trimethylsilyloxyl radicals disproportionate to yield stable tetramethylsilane and dimethylsilanone.

Dimethylsilanone could also result from the thermal destruction of the trimethylsilyloxyl radical according to the scheme of decomposition of silyloxyl radicals proposed previously.⁴ One-act elimination of dimethyl-silanone from HMDS also cannot be ruled out.

One of the reactions typical of dimethylsilanone is its insertion into the Si-Cl bond of chlorotrimethylsilane (CTMS); the latter is used as a trapping reagent and is thus converted into chloropentamethyldisiloxane (5). We studied the reaction of HMDS with CTMS in the gas phase at 675 °C, $\tau = 30$ s, and at a HMDS/CTMS

ratio of 1: 1. The degree of conversion of HMDS under these conditions was 10%. In addition to the products of the homopyrolysis of HMDS (see Scheme 1), the condensate obtained after copyrolysis contained compound 5 and chloroheptamethyltrisiloxane (6).

These results indicate that silanone can insert into both the Si-Cl and Si-O bonds in the starting and intermediate compounds (Scheme 4).

Scheme 4

$$Me_{3}SiOSiMe_{3} \longrightarrow [O=SiMe_{2}] \xrightarrow{Me_{3}SiCl} Me_{3}SiOSiMe_{2}Cl \xrightarrow{[O=SiMe_{2}]} Me_{3}Si(OSiMe_{2})_{2}Cl \xrightarrow{6}$$

Tetrachlorosilane (TCS) was also used as a trapping reagent for dimethylsilanone. Copyrolysis of HMDS with TCS was carried out in a hollow quartz reactor at 600-700 °C, $\tau = 30$ or 60 s, and HMDS/TCS ratios of 2 : 1, 1 : 1, or 1 : 4. The data on the effect of the reaction conditions on the composition of the condensate are presented in Tables 1-3. In addition to the compounds formed in the pyrolysis of HMDS, this condensate contained CTMS, compounds 5 and 6,

τ/S	Degree of	Composition of the condensate (%)										
	of HMDS (%)	CTMS + TCS	HMDS	1	5	3 + 7	6	8	9	4 + 11	HCDS	
30	8.4	43.0	50.1	0.4	2.2	2.7		0.6		1.0		
60	20.0	40.8	43.8	0.7	4.6	6.5	0.3	1.2	0.2	1.7	0.2	

Table 1. Dependence of the composition of the condensate obtained after copyrolysis of HMDS with TCS on the residence time of the reactants in the reaction zone at 700 °C and at a HMDS/TCS ratio of 1 ± 1

Table 2. Dependence of the composition of the condensate obtained after the copyrolysis of HMDS with TCS on the temperature in the reaction zone at a HMDS/TCS ratio of l : 1 and $\tau = 30$ s

T∕°C	Degree of	Composition of the condensate (%)									
	of HMDS (%)	CTMS + TCS	HMDS	1	5	6	3 + 7	8	9	4 + 11	
500	2.7	45.7	53.8		0.4	_	0.2				
550	3.5	43.1	52.7	0.1	0.9		2.2	0.4		0.6	
575	5.5	42.0	51.7	0.2	2.3		2.0	0.8	-	1.0	
700	8.4	43.0	50.1	0.4	2.2	-	2.7	0.6		1.0	
/20	18.3	44.0	44.7	1.0	1.9	1.2	4.9	0.5	0.8	1.0	

Table 3. Dependence of the composition of the condensate obtained after the copyrolysis of HMDS with TCS on the ratio of the starting components at 675 °C and $\tau = 30$ s

HMDS/TCS	Degree of	Composition of the condensate (%)								
	of HMDS (%)	CTMS + TCS	HMDS	1	5	3 + 7	8	4 + 11		
2:1	6.9	26.8	67.6	0.7	3.1	1.8		_		
1:1	3.5	42.0	51.7	0.2	2.3	2.0	0.8	1.0		
1:4	68.5	86.9	12.4	0.1	0.1	0.2	0.1	0.2		

3,3,3-trichloro-1,1,1-trimethyldisiloxane (7), 1,3,3,3-tetrachloro-1,1-dimethyldisiloxane (8), 3,3-dichloro-1,1,1,5,5,5-hexamethyltrisiloxane (9), hexachlorodisiloxane (HCDS), 3,3,5,5,5-pentachloro-1,1,1-trimethyltrisiloxane (10), 5,5,5-trichloro-1,1,1,3,3-pentamethyltrisiloxane (11), etc. The formation of these compounds can be explained by intermediate generation of dichlorosilanone in the reaction zone.

Since TCS does not undergo any changes during homopyrolysis under these conditions, it can be assumed that the trimethylsilyl radical resulting from the decomposition of HMDS is stabilized by abstracting a Cl atom from SiCl₄ to give CTMS and a trichlorosilyl radical (Scheme 5).

Scheme 5

The trimethylsilyl, trimethylsilyloxyl, and trichlorosilyl radicals present in the reaction zone can either recombine to yield siloxanes or disproportionate to give silanones and silanes (Scheme 6).

Scheme 6



The relative quantities of dichloro- and dimethylsilanones and of the products of their insertion into the Si-Cl and Si-O bonds are determined by the conditions of the copyrolysis: the temperature in the reaction zone, the residence time of the starting compounds in the reaction zone, and their ratio in the initial mixture (see Tables 1-3). For example, when the temperature is increased from 675 to 720 °C (HMDS/TCS = 1 : 1, $\tau = 30$ s), the degree of conversion of HMDS increases from 3.5 to 18% (see Table 2).

A twofold increase in the time (till 60 s) the components spend in the reaction zone at 700 °C and at an HMDS/TCS ratio of 1 : 1 results in an increase in the degree of conversion and, as a consequence, in the yields of all the products of copyrolysis (see Table 1).

When the proportion of HMDS in the initial mixture increases (HMDS/TCS = 2 : 1), the reaction at 675 °C and $\tau = 30$ s yields mostly compounds 1, 2, 3, 4, 5, and CTMS, which result from the insertion of dimethyl-silanone into the Si-Cl and Si-O bonds, as well as products of its homocyclization.

An increase in the proportion of TCS in the reaction mixture (HMDS/TCS = 1 : 4) leads to a decrease in the temperature of the onset of the reaction to 590 °C. At 675 °C, the degree of conversion of HMDS is 68%; in this case, the process affords compounds whose appearance can be explained by the insertion of dimethyland dichlorosilanones into the Si-Cl and Si-O bonds in the starting compounds and in the compounds arising during the process (see Table 3).

Thus, when TCS is used as a trapping reagent for dimethylsilanone, dichlorosilanone is generated; it can be formed not only according to Scheme 6 but also in the pyrolysis of the linear siloxanes resulting from the copyrolysis of HMDS with TCS (Scheme 7).

Scheme 7

It should be noted that HCDS arising in the copyrolysis of HMDS with TCS is extremely thermally stable. It is known⁴ that HCDS does not undergo any transformations below 950 °C; its pyrolysis occurs only at temperatures of >1000 °C and gives TCS and octachlorotrisiloxane as the major products (Scheme 8).

Scheme 8

Apparently, during the pyrolysis, HCDS undergoes homolytic cleavage to give trichlorosilyl and trichlorosilyloxyl radicals; disproportionation of these species results in the generation of dichlorosilanone and the formation of TCS. The dichlorosilanone is inserted into the Si-O bond of the starting compound to give octachlorotrisiloxane (Scheme 9).

Scheme 9

$$Cl_3SiOSiCl_3 \longrightarrow Cl_3SiO^+ SiCl_3 \longrightarrow [O=SiCl_2] + SiCl_4$$

 $\downarrow cl_3siOSiCl_2OSiCl_3$
 $Cl_3SiOSiCl_2OSiCl_3$

Pyrolysis of octachlorotrisiloxane affords TCS, HCDS, and also higher linear and cyclic siloxanes (Scheme 10).

Scheme 10

$$Cl_{3}SiOSiCl_{2}OSiCl_{3} \longrightarrow SiCl_{4} + Cl_{3}Si(OSiCl_{2})_{n}OSiCl_{3} + + (Cl_{2}SiO)_{k}$$

n = 0 to 2; k = 3 to 6

Thus, at temperatures >600 °C, linear siloxanes with various substituents at the Si atom act as sources and traps of silanones. The latter can be inserted into the Si-O bonds of the starting and formed siloxanes and can also undergo homocyclization into cyclic siloxanes.

Experimental

Mass spectrometric analysis of the final products was carried out on an MX-1303 spectrometer (the energy of ionizing radiation was 50 eV). The quantitative composition of the products of pyrolysis was determined by GLC using an LKhM-72 chromatograph with a heat-conductivity detector (12.8% PMS on INZ-600 as the stationary phase; He as the carrier gas).

A hollow quartz tube with an internal diameter of 28 mm and a length of the reaction zone of 400 mm served as the reactor for pyrolysis and copyrolysis.

Pyrolysis of hexamethyldisiloxane. HMDS (20 g) was passed through a quartz reactor heated to 675 °C at such a rate as to ensure its residence time in the reaction zone of 30-40 s. This gave 15.7 g of a condensate. Upon distillation, 10.9 g of a fraction with a boiling point of 30-100 °C was isolated; according to GLC, it contained tetramethylsilane (0.32 g, 2.9%) and the starting HMDS. According to GLC and mass spectrometry, the bottom residue (4.1 g), consisted of HMDS (3.05 g, 74.4%, m/z 147 [M-Me]⁺); 1 (0.6 g, 14.6%, m/z 221 [M-Me]⁺); 2 (0.26 g, 6.3%, m/z 295 [M-Me]⁺); 3 (0.13 g, 3.2%, m/z 207 [M-Me]⁺); 4 (0.06 g, 1.5%, m/z 281 [M-Me]⁺); and Me₃SiSiMe₃ (m/z 131 [M-Me]⁺; a peak that is second in intensity in the mass spectrum emerges in the chromatogram together with HMDS).

Copyrolysis of hexamethyldisiloxane with chlorotrimethylsilane. A mixture of HMDS (16.4 g) and CTMS (11 g) (HMDS/CTMS = 1 : 1) was passed through a quartz reactor heated to 675 °C at such a rate as to ensure a residence time in the reaction zone of 30-40 s. This gave 21.7 g of a condensate. Upon distillation, 7.2 g of a fraction with a boiling point of >100 °C was isolated; according to GLC and mass spectrometry, it was a mixture of HMDS (4.66 g, 63%, m/z 147 $[M-Me]^+$); 1 (0.57 g, 7.8%, m/z 221 $[M-Me]^+$); 2 (0.2 g, 2.7%, m/z 295 $[M-Me]^+$); 5 (0.96 g, 13%, m/z 167 $[M-Me]^+$); 6 (0.76 g, 10.2%, m/z 241 $[M-Me]^+$); 3 (0.17 g, 2.3%, m/z 207 $[M-Me]^+$); and 4 (0.08 g, 1.0%, m/z 281 $[M-Me]^+$).

Copyrolysis of hexamethyldisiloxane with tetrachlorosilane. A mixture of HMDS (33.7 g) and TCS (68.6 g) was passed through a quartz reactor heated to 600 °C at such a rate as to ensure a residence time of the mixture in the reaction zone of 30-40 s. The process gave 91.7 g of a condensate; its distillation yielded 73.4 g of a fraction with a boiling point of 32–101 °C, which (GLC data) contained the initial reactants and CTMS; 10 g of a fraction with a boiling point of 101 °C, which (according to GLC and mass spectrometry) consisted of HMDS (m/z 147 [M-Me]⁺); 4.86 g of a fraction boiling at 127–129 °C, which was (GLC data and mass spectrum) disiloxane 7 (m/z 207 [M-Me]⁺); and 3.44 g of a bottom residue containing compounds 9 (m/z 261 [M-Me]⁺) and 10 (m/z 331 [M-Me]⁺).

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 96-03-33268).

References

- 1. K. A. Andrianov and N. N. Sokolov, Dokl. Akad. Nauk SSSR [Comm. USSR Acad. Sci.], 1952, 82, 909 (in Russian).
- T. L. Krasnova, E. A. Chernyshev, and A. P. Sergeev, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1299 [*Russ. Chem. Bull.*, 1996, 45, 1238 (Engl. Transl.)].
- 3. D. C. Nonhebel and J. C. Walton, *Free-Radical Chemistry*, Cambridge University Press, Cambridge, 1974.
- N. D. Kagramanov, I. O. Bragilevskii, V. A. Yablokov, A. V. Tomadze, and A. K. Mal'tsev, *Izv. Akad. Nauk SSSR,* Ser. Khim., 1987, 1109 [Bull. Acad. USSR, Div. Chem. Sci., 1987, 36, 1024 (Engl. Transl.)].

Received February 12, 1997; in revised form April 7, 1997