

The Formation of a Solid from the Reaction $\text{SiCl}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{s}) + 2\text{Cl}_2(\text{g})$

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Dedicated to Prof. Dr. Heinrich Vahrenkamp on the occasion of his 60th birthday

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The formation of a solid by the reaction of small gaseous molecules during a CVD or CVT experiment is a highly complicated process. In the case of the combustion of silicon(IV) chloride in oxygen, which leads to solid silicon dioxide, hundreds of intermediate chlorosiloxanes have been detected. On the basis of their compositions, structures, and stabilities,

growth mechanisms of Si–O networks can be derived. The stepwise formation of solid SiO₂ can be described in terms of three basic reactions: (i) formation of highly reactive O=SiCl₂, (ii) insertion of O=SiCl₂ into an Si–Cl bond, and (iii) thermally induced elimination of SiCl₄ from the resulting chlorosiloxanes.

1. Introduction

Although solid-state chemistry has been largely concerned with the structures, physical and chemical properties, and broad applications of solids, over the past 30 years solid-state chemists have become increasingly interested in their formation and in the intermediates involved during

the formation process. Nowadays, cluster compounds are considered and discussed as connecting links between molecules and solids. Whereas these were considered as rare exceptions in the 1960s,^[1] more and more examples have been found, in particular as a result of the impressive development in the area of X-ray analysis, of substances that can be classified as cluster compounds. The principle of condensed clusters^[2] accounts for their role as links between molecules and solids. Colloids, as examples of giant clusters with 10³ to 10⁹ atoms, are also included in the discussion.^[3] In general, clusters represent small fragments of the structures of solids. From the present viewpoint, it can be stated that the traditional separation between molecules and solids is nei-

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Michael Binnewies studied chemistry in Münster/Westfalen, where he received his Diploma in 1971 and his Dr. rer. nat. in 1973. He worked on solid-gas equilibria in metal halide systems under the direction of Harald Schäfer. Further work involved the mass spectrometric characterization of highly reactive molecules containing main group elements. In 1988, he took up a professorship in Freiburg/Br. Since 1992, he has been Professor of Inorganic Chemistry at the University of Hannover. His current research interests lie in the fields of chemical vapour transport reactions and main group chemistry.

Karl Jug studied physics in Frankfurt/Main, where he received his Diploma in physics in 1964 and his Dr. phil. nat. in physical chemistry in 1965. His research work, under the direction of Hermann Hartmann, was on quantum chemical modelling of the spectra of inorganic and



organic compounds. From 1965 to 1967, he was head of staff of Theoretica Chimica Acta in Frankfurt/M., before he moved to the IIT in Chicago to work with Peter Lykos. He was Assistant Professor in 1969 and Associate Professor in 1971 at St. Louis University. He returned to Germany in 1975 to take up a position as Professor of Theoretical Chemistry at the University of Hannover. His research interests have focussed on semiempirical methods and the theoretical basis of chemical concepts (charge, bonding, diradicals, aromaticity). In applied work, he has been concerned with thermal and photochemical reactions of organic compounds, the structures and reactivities of organic and inorganic compounds and clusters, the cluster simulation of solid-state surfaces, and heterogeneous catalysis.



MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

ther up to date nor scientifically substantiated. While the structural borderline between molecules and solids has become largely indistinct, the physical properties of compounds in this transition range are becoming increasingly interesting. Typical co-operative phenomena, such as electrical conductivity, do not appear abruptly, but change continuously over a certain range.

Whereas solid compounds have generally been characterized after their formation, in the transition range between molecules and solids the relevant formation pathways and mechanisms have not been so well investigated. In the case of the title reaction, i.e. the formation of solid SiO₂ from SiCl₄ and oxygen, this chemically – from the viewpoint of substance change – interesting question has now been investigated and is largely understood. This subject is reviewed here.

2. Thermodynamic Aspects

Reactions of chlorides of elements with oxygen to give the corresponding oxides and chlorine are found to be exothermic for almost all elements. The Gibbs energy ΔG_R^0 is almost always negative. The reaction equilibrium generally lies on the side of the oxide, as is the case with silicon. At 298 K, a reaction enthalpy of -248.2 kJ/mol and a reaction entropy of 48.3 J/(Kmol)^[4,5] are calculated for the title reaction and consequently $\Delta G_R^0(298) = -233$ kJ/mol. The equilibrium at 298 K therefore lies close to the product SiO₂. This also holds true for temperatures of 1000 or 2000 K, although the equilibrium constant decreases with increasing temperature. In spite of this extreme equilibrium situation, if an oxygen flow containing SiCl₄ is passed through a heated tube about 30 cm in length, noticeable reaction only occurs at temperatures above 700–800 °C. In the temperature range 800–1000 °C, the resulting product is, however, not the SiO₂ that would be expected from a thermodynamic point of view. Instead, a multitude of chlorosiloxanes Si_xO_yCl_z are formed. In these compounds, the chlorine atoms of the starting SiCl₄ are only partially replaced by oxygen atoms. The compounds are considered as intermediates that are formed in the course of the reaction. Their investigation allows an insight into the mode of formation of the solid silicon dioxide and the individual steps involved. If the reaction temperature is increased to above 1000 °C, the reaction rate becomes considerably enhanced. The title reaction proceeds very quickly without noticeable by-product formation to give the final products SiO₂ and Cl₂. Under these conditions, the experimental possibility of trapping the intermediates in order to learn more about the reaction process is lost. For a better understanding of the reaction process, the temperature range between 700 and 1000 °C, in which the chlorosiloxanes are formed, is therefore of special interest.

3. Chlorosiloxanes

3.1 Literature Survey

3.1.1 Experimental Facts

In the following, a tabular survey of the literature on perchlorosiloxanes^[6–34] with up to 10 silicon atoms per molecule and their mode of formation is given (Table 1).

Beyond the listed compounds, the title reaction leads to the formation of numerous other higher chlorosiloxanes with molar weights up to 7000 D. These contain between 11 and about 70 silicon atoms per molecule, and have quite different oxygen and chlorine contents. The formulae of about 250 other chlorosiloxanes with molar weights up to 5000 D have been reported following mass spectrometric investigations, which are listed below. Details can be found in the literature.^[34]

Si ₁₁ O ₁₂ Cl ₂₀ ,	Si ₁₁ O ₁₃ Cl ₁₈ ,	Si ₁₁ O ₁₄ Cl ₁₆ ,	Si ₁₁ O ₁₅ Cl ₁₄ ,	Si ₁₂ O ₁₃ Cl ₂₂ ,
Si ₁₂ O ₁₄ Cl ₂₀ ,	Si ₁₂ O ₁₅ Cl ₁₈ ,	Si ₁₂ O ₁₆ Cl ₁₆ ,	Si ₁₂ O ₁₇ Cl ₁₄ ,	Si ₁₃ O ₁₄ Cl ₂₄ ,
Si ₁₃ O ₁₅ Cl ₂₂ ,	Si ₁₃ O ₁₆ Cl ₂₀ ,	Si ₁₃ O ₁₇ Cl ₁₈ ,	Si ₁₃ O ₁₈ Cl ₁₆ ,	Si ₁₃ O ₁₉ Cl ₁₄ ,
Si ₁₃ O ₂₀ Cl ₁₂ ,	Si ₁₄ O ₁₆ Cl ₂₄ ,	Si ₁₄ O ₁₇ Cl ₂₂ ,	Si ₁₄ O ₁₈ Cl ₂₀ ,	Si ₁₄ O ₁₉ Cl ₁₈ ,
Si ₁₄ O ₂₀ Cl ₁₆ ,	Si ₁₅ O ₁₇ Cl ₂₆ ,	Si ₁₅ O ₁₈ Cl ₂₄ ,	Si ₁₅ O ₁₉ Cl ₂₂ ,	Si ₁₅ O ₂₀ Cl ₂₀ ,
Si ₁₅ O ₂₁ Cl ₁₈ ,	Si ₁₅ O ₂₂ Cl ₁₆ ,	Si ₁₆ O ₁₉ Cl ₂₆ ,	Si ₁₆ O ₂₀ Cl ₂₄ ,	Si ₁₆ O ₂₁ Cl ₂₂ ,
Si ₁₆ O ₂₂ Cl ₂₀ ,	Si ₁₆ O ₂₃ Cl ₁₈ ,	Si ₁₆ O ₂₄ Cl ₁₆ ,	Si ₁₇ O ₂₀ Cl ₂₈ ,	Si ₁₇ O ₂₁ Cl ₂₆ ,
Si ₁₇ O ₂₂ Cl ₂₄ ,	Si ₁₇ O ₂₃ Cl ₂₂ ,	Si ₁₇ O ₂₄ Cl ₂₀ ,	Si ₁₇ O ₂₅ Cl ₁₈ ,	Si ₁₈ O ₂₁ Cl ₃₀ ,
Si ₁₈ O ₂₂ Cl ₂₈ ,	Si ₁₈ O ₂₃ Cl ₂₆ ,	Si ₁₈ O ₂₄ Cl ₂₄ ,	Si ₁₈ O ₂₅ Cl ₂₂ ,	Si ₁₈ O ₂₆ Cl ₂₀ ,
Si ₁₈ O ₂₇ Cl ₁₈ ,	Si ₁₈ O ₂₈ Cl ₁₆ ,	Si ₁₉ O ₂₂ Cl ₃₂ ,	Si ₁₉ O ₂₃ Cl ₃₀ ,	Si ₁₉ O ₂₄ Cl ₂₈ ,
Si ₁₉ O ₂₅ Cl ₂₆ ,	Si ₁₉ O ₂₆ Cl ₂₄ ,	Si ₁₉ O ₂₇ Cl ₂₂ ,	Si ₁₉ O ₂₈ Cl ₂₀ ,	Si ₂₀ O ₂₃ Cl ₃₄ ,
Si ₂₀ O ₂₄ Cl ₃₂ ,	Si ₂₀ O ₂₅ Cl ₃₀ ,	Si ₂₀ O ₂₆ Cl ₂₈ ,	Si ₂₀ O ₃₀ Cl ₂₀ ,	Si ₂₁ O ₂₅ Cl ₃₄ ,
Si ₂₁ O ₂₆ Cl ₃₂ ,	Si ₂₁ O ₂₇ Cl ₃₀ ,	Si ₂₁ O ₂₈ Cl ₂₈ ,	Si ₂₁ O ₂₉ Cl ₂₆ ,	Si ₂₂ O ₂₆ Cl ₃₆ ,
Si ₂₂ O ₂₇ Cl ₃₄ ,	Si ₂₂ O ₂₈ Cl ₃₂ ,	Si ₂₂ O ₂₉ Cl ₃₀ ,	Si ₂₂ O ₃₀ Cl ₂₈ ,	Si ₂₂ O ₃₁ Cl ₂₆ ,
Si ₂₂ O ₃₂ Cl ₂₄ ,	Si ₂₃ O ₂₇ Cl ₃₈ ,	Si ₂₃ O ₂₈ Cl ₃₆ ,	Si ₂₃ O ₂₉ Cl ₃₄ ,	Si ₂₃ O ₃₀ Cl ₃₂ ,
Si ₂₃ O ₃₁ Cl ₃₀ ,	Si ₂₃ O ₃₂ Cl ₂₈ ,	Si ₂₃ O ₃₃ Cl ₂₆ ,	Si ₂₃ O ₃₄ Cl ₂₄ ,	Si ₂₄ O ₂₈ Cl ₄₀ ,
Si ₂₄ O ₂₉ Cl ₃₈ ,	Si ₂₄ O ₃₀ Cl ₃₆ ,	Si ₂₄ O ₃₁ Cl ₃₄ ,	Si ₂₄ O ₃₂ Cl ₃₂ ,	Si ₂₄ O ₃₃ Cl ₃₀ ,
Si ₂₄ O ₃₄ Cl ₂₈ ,	Si ₂₄ O ₃₅ Cl ₂₆ ,	Si ₂₄ O ₃₆ Cl ₂₄ ,	Si ₂₅ O ₂₉ Cl ₄₂ ,	Si ₂₅ O ₃₀ Cl ₄₀ ,
Si ₂₅ O ₃₁ Cl ₃₈ ,	Si ₂₅ O ₃₂ Cl ₃₆ ,	Si ₂₅ O ₃₃ Cl ₃₄ ,	Si ₂₅ O ₃₄ Cl ₃₂ ,	Si ₂₅ O ₃₅ Cl ₃₀ ,
Si ₂₅ O ₃₆ Cl ₂₈ ,	Si ₂₅ O ₃₇ Cl ₂₆ ,	Si ₂₆ O ₃₁ Cl ₄₂ ,	Si ₂₆ O ₃₂ Cl ₄₀ ,	Si ₂₆ O ₃₃ Cl ₃₈ ,
Si ₂₆ O ₃₄ Cl ₃₆ ,	Si ₂₆ O ₃₅ Cl ₃₄ ,	Si ₂₆ O ₃₇ Cl ₃₀ ,	Si ₂₆ O ₃₈ Cl ₂₈ ,	Si ₂₆ O ₃₉ Cl ₂₆ ,
Si ₂₇ O ₃₂ Cl ₄₄ ,	Si ₂₇ O ₃₃ Cl ₄₂ ,	Si ₂₇ O ₃₄ Cl ₄₀ ,	Si ₂₇ O ₃₅ Cl ₃₈ ,	Si ₂₇ O ₃₆ Cl ₃₆ ,
Si ₂₈ O ₃₃ Cl ₄₆ ,	Si ₂₈ O ₃₄ Cl ₄₄ ,	Si ₂₈ O ₃₅ Cl ₄₂ ,	Si ₂₈ O ₃₆ Cl ₄₀ ,	Si ₂₈ O ₃₇ Cl ₃₈ ,
Si ₂₈ O ₄₃ Cl ₂₆ ,	Si ₂₉ O ₃₅ Cl ₄₆ ,	Si ₂₉ O ₃₆ Cl ₄₄ ,	Si ₂₉ O ₃₇ Cl ₄₂ ,	Si ₂₉ O ₃₈ Cl ₄₀ ,
Si ₂₉ O ₃₉ Cl ₃₈ ,	Si ₂₉ O ₄₀ Cl ₃₆ ,	Si ₂₉ O ₄₁ Cl ₃₄ ,	Si ₃₀ O ₃₆ Cl ₄₈ ,	Si ₃₀ O ₃₇ Cl ₄₆ ,
Si ₃₀ O ₃₈ Cl ₄₄ ,	Si ₃₀ O ₃₉ Cl ₄₂ ,	Si ₃₀ O ₄₀ Cl ₄₀ ,	Si ₃₀ O ₄₁ Cl ₃₈ ,	Si ₃₀ O ₄₂ Cl ₃₆ ,
Si ₃₀ O ₄₃ Cl ₃₄ ,	Si ₃₀ O ₄₄ Cl ₃₂ ,	Si ₃₁ O ₃₇ Cl ₅₀ ,	Si ₃₁ O ₃₈ Cl ₄₈ ,	Si ₃₁ O ₃₉ Cl ₄₆ ,
Si ₃₁ O ₄₀ Cl ₄₄ ,	Si ₃₁ O ₄₁ Cl ₄₂ ,	Si ₃₁ O ₄₂ Cl ₄₀ ,	Si ₃₁ O ₄₃ Cl ₃₈ ,	Si ₃₁ O ₄₄ Cl ₃₆ ,
Si ₃₁ O ₄₅ Cl ₃₄ ,	Si ₃₁ O ₄₇ Cl ₃₀ ,	Si ₃₂ O ₃₉ Cl ₅₀ ,	Si ₃₂ O ₄₀ Cl ₄₈ ,	Si ₃₂ O ₄₁ Cl ₄₆ ,
Si ₃₂ O ₄₂ Cl ₄₄ ,	Si ₃₂ O ₄₃ Cl ₄₂ ,	Si ₃₂ O ₄₄ Cl ₄₀ ,	Si ₃₂ O ₄₅ Cl ₃₈ ,	Si ₃₂ O ₄₆ Cl ₃₆ ,
Si ₃₂ O ₄₇ Cl ₃₄ ,	Si ₃₂ O ₄₈ Cl ₃₂ ,	Si ₃₂ O ₄₉ Cl ₃₀ ,	Si ₃₃ O ₃₉ Cl ₅₄ ,	Si ₃₃ O ₄₀ Cl ₅₂ ,
Si ₃₃ O ₄₁ Cl ₅₀ ,	Si ₃₃ O ₄₂ Cl ₄₈ ,	Si ₃₃ O ₄₃ Cl ₄₆ ,	Si ₃₃ O ₄₄ Cl ₄₄ ,	Si ₃₃ O ₄₅ Cl ₄₂ ,
Si ₃₃ O ₄₆ Cl ₄₀ ,	Si ₃₃ O ₄₇ Cl ₃₈ ,	Si ₃₃ O ₄₈ Cl ₃₆ ,	Si ₃₃ O ₄₉ Cl ₃₄ ,	Si ₃₃ O ₅₀ Cl ₃₂ ,
Si ₃₄ O ₄₁ Cl ₅₄ ,	Si ₃₄ O ₄₂ Cl ₅₂ ,	Si ₃₄ O ₄₃ Cl ₅₀ ,	Si ₃₄ O ₄₄ Cl ₄₈ ,	Si ₃₄ O ₄₅ Cl ₄₆ ,
Si ₃₄ O ₄₆ Cl ₄₄ ,	Si ₃₄ O ₄₇ Cl ₄₂ ,	Si ₃₄ O ₄₉ Cl ₃₈ ,	Si ₃₄ O ₅₀ Cl ₃₆ ,	Si ₃₄ O ₅₁ Cl ₃₄ ,
Si ₃₄ O ₅₂ Cl ₃₂ ,	Si ₃₅ O ₄₂ Cl ₅₆ ,	Si ₃₅ O ₄₃ Cl ₅₄ ,	Si ₃₅ O ₄₄ Cl ₅₂ ,	Si ₃₅ O ₄₅ Cl ₅₀ ,
Si ₃₅ O ₄₆ Cl ₄₈ ,	Si ₃₅ O ₄₇ Cl ₄₆ ,	Si ₃₅ O ₄₈ Cl ₄₄ ,	Si ₃₅ O ₅₀ Cl ₄₀ ,	Si ₃₅ O ₅₁ Cl ₃₈ ,
Si ₃₅ O ₅₂ Cl ₃₆ ,	Si ₃₅ O ₅₃ Cl ₃₄ ,	Si ₃₅ O ₅₄ Cl ₃₂ ,	Si ₃₆ O ₄₃ Cl ₅₈ ,	Si ₃₆ O ₄₄ Cl ₅₆ ,
Si ₃₆ O ₄₅ Cl ₅₄ ,	Si ₃₆ O ₄₆ Cl ₅₂ ,	Si ₃₆ O ₄₇ Cl ₅₀ ,	Si ₃₆ O ₄₈ Cl ₄₈ ,	Si ₃₆ O ₄₉ Cl ₄₆ ,
Si ₃₆ O ₅₂ Cl ₄₀ ,	Si ₃₆ O ₅₄ Cl ₃₆ ,	Si ₃₆ O ₅₅ Cl ₃₄ ,	Si ₃₆ O ₅₆ Cl ₃₂ ,	Si ₃₇ O ₄₄ Cl ₆₀ ,
Si ₃₇ O ₄₅ Cl ₅₈ ,	Si ₃₇ O ₄₆ Cl ₅₆ ,	Si ₃₇ O ₄₇ Cl ₅₄ ,	Si ₃₇ O ₄₈ Cl ₅₂ ,	Si ₃₇ O ₄₉ Cl ₅₀ ,
Si ₃₇ O ₅₂ Cl ₄₄ ,	Si ₃₇ O ₅₃ Cl ₄₂ ,	Si ₃₇ O ₅₄ Cl ₄₀ ,	Si ₃₇ O ₅₆ Cl ₃₆ ,	Si ₃₇ O ₅₇ Cl ₃₄ ,

Table 1. Survey of chlorosiloxanes with up to 10 Si atoms with mode of formation, characterization, and references

Chlorosiloxane	Formation ^[‡]	Characterization method	References
SiOCl_2	9	[c][g]	[6][40][42]
Si_2OCl_6	1–8	[a][b][c][d][e][g][h]	[6–29][42]
$\text{Si}_2\text{O}_2\text{Cl}_4$	4	[g][h]	[17][42]
Si_3OCl_8	3, 4, 7	[h]	[7][18]
$\text{Si}_3\text{O}_2\text{Cl}_8$	1–4, 7, 8	[a][b][c][d][h]	[7][11–17][20–22][27][30–32][42]
$\text{Si}_3\text{O}_3\text{Cl}_6$	1–4, 8	[a][b][c][d][e][g][h]	[7][12–15][17][27][31–33][42]
$\text{Si}_4\text{OCl}_{10}$	4	[h]	[7]
$\text{Si}_4\text{O}_2\text{Cl}_{10}$	4	[h]	[7]
$\text{Si}_4\text{O}_3\text{Cl}_{10}$	1–4, 7, 2a	[a][b][c][d][g][h]	[7][10–14][16][17][20][22][27][30–32][42]
$\text{Si}_4\text{O}_4\text{Cl}_8$	1–4, 6, 7	[a][b][c][d][e][g][h]	[7][9–14][27][29][31–34][43]
$\text{Si}_4\text{O}_5\text{Cl}_6$	1, 3, 4	[g][h]	[7][17][31][34][42]
$\text{Si}_5\text{O}_3\text{Cl}_{12}$	4	[h]	[7]
$\text{Si}_5\text{O}_4\text{Cl}_{12}$	1–4, 7	[a][b][h]	[7][11][13][17][20][22][27][30][32][43]
$\text{Si}_5\text{O}_5\text{Cl}_{10}$	1, 3, 4	[a][b][g][h]	[7][12][14][17][27][31][32][42]
$\text{Si}_5\text{O}_6\text{Cl}_8$	1, 3, 4	[b][g][h]	[7][14][17][31][32][34][43]
$\text{Si}_5\text{O}_7\text{Cl}_6$	1	[h]	[31][34][43]
$\text{Si}_6\text{O}_2\text{Cl}_{14}$	1, 2, 2a, 4, 7	[a][b][h]	[7][11][13][17][22][27][29][32]
$\text{Si}_6\text{O}_6\text{Cl}_{12}$	1, 3, 4	[h]	[7][17][31][32][43]
$\text{Si}_6\text{O}_7\text{Cl}_{10}$	1, 3, 4	[a][b][h]	[7][17][27][31][32][34][43]
$\text{Si}_6\text{O}_8\text{Cl}_8$	1	[a][b][h]	[7][17][27][31][32][34][43]
$\text{Si}_6\text{O}_9\text{Cl}_6$	1	[h]	[31][34]
$\text{Si}_7\text{O}_6\text{Cl}_{16}$	1, 2, 4, 7	[a][b][h]	[7][11][13][22][32]
$\text{Si}_7\text{O}_7\text{Cl}_{14}$	1, 4	[h]	[7][32][34]
$\text{Si}_7\text{O}_8\text{Cl}_{12}$	1, 3	[a][b][h]	[7][31][32][43]
$\text{Si}_7\text{O}_9\text{Cl}_{10}$	1, 3	[h]	[7][31][32][43]
$\text{Si}_7\text{O}_{10}\text{Cl}_8$	1	[h]	[31][34]
$\text{Si}_8\text{O}_7\text{Cl}_{18}$	1	[h]	[32]
$\text{Si}_8\text{O}_8\text{Cl}_{16}$	1	[h]	[28][32][34]
$\text{Si}_8\text{O}_9\text{Cl}_{14}$	1	[h]	[28][32][34]
$\text{Si}_8\text{O}_{10}\text{Cl}_{12}$	1	[a][h]	[10][31][34][43]
$\text{Si}_8\text{O}_{11}\text{Cl}_{10}$	1	[a][b][g][h]	[31][34][42]
$\text{Si}_8\text{O}_{12}\text{Cl}_8$	1	[a][d][h]	[10][31][34–36][43]
$\text{Si}_8\text{O}_{14}\text{Cl}_4$	1	[a][h]	[10]
$\text{Si}_9\text{O}_8\text{Cl}_{20}$	1	[h]	[32]
$\text{Si}_9\text{O}_9\text{Cl}_{18}$	1	[h]	[32][34]
$\text{Si}_9\text{O}_{10}\text{Cl}_{16}$	1	[h]	[32][34]
$\text{Si}_9\text{O}_{11}\text{Cl}_{14}$	1	[h]	[32][34]
$\text{Si}_9\text{O}_{12}\text{Cl}_{12}$	1	[h]	[34]
$\text{Si}_9\text{O}_{13}\text{Cl}_{10}$	1	[h]	[34]
$\text{Si}_{10}\text{O}_9\text{Cl}_{22}$	1	[h]	[32]
$\text{Si}_{10}\text{O}_{10}\text{Cl}_{20}$	1	[h]	[32]
$\text{Si}_{10}\text{O}_{11}\text{Cl}_{18}$	1	[h]	[32][34]
$\text{Si}_{10}\text{O}_{12}\text{Cl}_{16}$	1	[h]	[34][43]
$\text{Si}_{10}\text{O}_{13}\text{Cl}_{14}$	1	[h]	[34][43]
$\text{Si}_{10}\text{O}_{14}\text{Cl}_{12}$	1	[h]	[34]
$\text{Si}_{10}\text{O}_{15}\text{Cl}_{10}$	1	[g]	[43]

[‡] Methods of formation and conditions: 1: $\text{SiCl}_4 + \text{O}_2$, ΔT ; 2: $\text{SiCl}_4 + \text{H}_2\text{O}$; 2a: $\text{Si}_2\text{OCl}_6 + \text{H}_2\text{O}$; 2b: $\text{Si}_4\text{O}_4\text{Cl}_8 + \text{H}_2\text{O}$; 3: Si_2OCl_6 , ΔT ; 4: Si_2OCl_6 , plasma; 5: $\text{SiCl}_4 + \text{SO}_3$, ΔT ; 6: $\text{SiCl}_4 + \text{NO}_3$, ΔT ; 7: $\text{Si} + \text{O}_2 + \text{Cl}_2$, ΔT ; 7a: $\text{SiC} + \text{O}_2 + \text{Cl}_2$, ΔT ; 8: SiCl_3OBz (Bz = Benzyl), ΔT ; 9: $\text{SiO} + \text{Cl}_2$, h.v. – [a] Analytical determination of the composition. – [b] ^{29}Si NMR spectroscopy. – [c] Infrared spectroscopy. – [d] Raman spectroscopy. – [e] Electron diffraction. – [f] X-ray diffraction. – [g] Quantum chemical calculations. – [h] Mass spectrometry.

$\text{Si}_{38}\text{O}_{46}\text{Cl}_{60}$, $\text{Si}_{38}\text{O}_{47}\text{Cl}_{58}$, $\text{Si}_{38}\text{O}_{48}\text{Cl}_{56}$, $\text{Si}_{38}\text{O}_{49}\text{Cl}_{54}$, $\text{Si}_{38}\text{O}_{50}\text{Cl}_{52}$,
 $\text{Si}_{38}\text{O}_{51}\text{Cl}_{50}$, $\text{Si}_{38}\text{O}_{55}\text{Cl}_{42}$, $\text{Si}_{38}\text{O}_{57}\text{Cl}_{38}$, $\text{Si}_{38}\text{O}_{58}\text{Cl}_{36}$, $\text{Si}_{39}\text{O}_{47}\text{Cl}_{62}$,
 $\text{Si}_{39}\text{O}_{48}\text{Cl}_{60}$, $\text{Si}_{39}\text{O}_{49}\text{Cl}_{58}$, $\text{Si}_{39}\text{O}_{50}\text{Cl}_{56}$, $\text{Si}_{39}\text{O}_{51}\text{Cl}_{54}$, $\text{Si}_{39}\text{O}_{58}\text{Cl}_{40}$,
 $\text{Si}_{39}\text{O}_{59}\text{Cl}_{38}$, $\text{Si}_{39}\text{O}_{61}\text{Cl}_{34}$, $\text{Si}_{39}\text{O}_{62}\text{Cl}_{32}$, $\text{Si}_{40}\text{O}_{47}\text{Cl}_{66}$, $\text{Si}_{40}\text{O}_{48}\text{Cl}_{64}$,
 $\text{Si}_{40}\text{O}_{50}\text{Cl}_{60}$, $\text{Si}_{40}\text{O}_{51}\text{Cl}_{58}$, $\text{Si}_{40}\text{O}_{52}\text{Cl}_{56}$, $\text{Si}_{40}\text{O}_{53}\text{Cl}_{54}$, $\text{Si}_{41}\text{O}_{49}\text{Cl}_{66}$,
 $\text{Si}_{41}\text{O}_{50}\text{Cl}_{64}$, $\text{Si}_{41}\text{O}_{51}\text{Cl}_{62}$, $\text{Si}_{41}\text{O}_{52}\text{Cl}_{60}$, $\text{Si}_{41}\text{O}_{53}\text{Cl}_{58}$, $\text{Si}_{41}\text{O}_{54}\text{Cl}_{56}$,
 $\text{Si}_{41}\text{O}_{64}\text{Cl}_{36}$, $\text{Si}_{42}\text{O}_{50}\text{Cl}_{68}$, $\text{Si}_{42}\text{O}_{51}\text{Cl}_{66}$, $\text{Si}_{42}\text{O}_{52}\text{Cl}_{64}$, $\text{Si}_{42}\text{O}_{53}\text{Cl}_{62}$,
 $\text{Si}_{42}\text{O}_{54}\text{Cl}_{60}$, $\text{Si}_{43}\text{O}_{53}\text{Cl}_{66}$, $\text{Si}_{43}\text{O}_{54}\text{Cl}_{64}$, $\text{Si}_{43}\text{O}_{55}\text{Cl}_{62}$, $\text{Si}_{43}\text{O}_{56}\text{Cl}_{60}$,
 $\text{Si}_{43}\text{O}_{57}\text{Cl}_{58}$, $\text{Si}_{44}\text{O}_{56}\text{Cl}_{64}$, $\text{Si}_{44}\text{O}_{57}\text{Cl}_{62}$, $\text{Si}_{44}\text{O}_{58}\text{Cl}_{60}$, $\text{Si}_{44}\text{O}_{59}\text{Cl}_{58}$,
 $\text{Si}_{45}\text{O}_{59}\text{Cl}_{62}$, $\text{Si}_{45}\text{O}_{60}\text{Cl}_{60}$.

To give a complete survey of chlorosiloxanes, we have also listed in Table 1 such compounds that are not formed by the title reaction. In the following, however, only the thermally formed chlorosiloxanes are discussed. The present compounds can be classified as belonging to a homo-

logous series of the general formula $\text{Si}_n\text{O}_{n+x}\text{Cl}_{2(n-x)}$ ($x = -1$ to 24). We observe that particularly oxygen-rich chlorosiloxanes (large x) are favoured in the case of large molecules (large n). This is to be expected, because x cannot exceed n . For $x = n$, the limit of Si_nO_{2n} , i.e. SiO_2 is obtained. The composition of a chlorosiloxane closely corresponds to its structure. This will be demonstrated in Section 3.2.

As can be seen, the reaction of SiCl_4 with oxygen results in the formation of an unusual multitude of chlorosiloxanes. The number of Si atoms ranges from 1 up to about 70 per molecule. With just a few exceptions, all of the aforementioned chlorosiloxanes can be prepared in significant amounts, although often not in pure form. In particular, the higher molecular weight siloxanes [$n(\text{Si}) > 10$] can only be characterized in mixtures owing to separation difficult-

ies. Whereas the lower homologues can be separated by distillation^[13] and the medium weight homologues by gas chromatography,^[32] separation of the high molecular weight compounds has proved insurmountable. The sensitivity of chlorosiloxanes to hydrolysis makes separation even more difficult, although it should also be noted that this is reduced with increasing oxygen content. However, with increasing oxygen content the molar weight increases accordingly. Adjacent compounds become more and more similar with respect to their physical and chemical properties and hence separation becomes more difficult.

3.1.2 Theoretical Methods

A difficulty in evaluating the experimental results is the structural characterization of the chlorosiloxanes described by the general molecular formula $\text{Si}_n\text{O}_{n+x}\text{Cl}_{2(n-x)}$. Whereas for a few Si atoms it is possible to obtain an appropriate structure by application of simple valence rules, this is no longer the case for larger systems due to the sharp increase in the number of possible isomers. Moreover, structural data such as bond lengths and bond angles, as well as the relative stabilities of the isomers, cannot be experimentally determined in a simple way. Here, quantum chemical methods can offer additional information to complement that obtained in the experimental investigations. So-called ab initio methods are mainly based on the Hartree–Fock method in the self-consistent field (SCF) approximation. Here, the electrons are described by one-electron functions, the molecular orbitals (MOs), where each MO for an electron is calculated in the field of the nuclei and the average field of all the other electrons. This one-electron approximation can be improved by the inclusion of the correlation between the electrons. This is achieved by applying configuration interaction (CI) or perturbation theory (MP2). Since ab initio calculations are very demanding in terms of computer time due to the increased basis sets and the inclusion of correlation, their application is restricted to systems with a few dozen atoms.

For comparative studies, which are necessary in the case of siloxanes because of the multitude of compounds, semiempirical methods are more appropriate. Here, one also starts from the SCF method and tries to considerably reduce the computer time by applying approximations. In this way, the differential overlaps of the atomic orbitals are neglected (ZDO approximation) and the remaining integrals are in part empirically adjusted. The first procedure can be justified by the orthogonalization of the atomic orbitals. The second leads to an implicit inclusion of correlation and therefore often to substantial improvements in the prediction of structures and stabilities. As a result of the continuous improvements of semiempirical methods, large systems with more than a hundred atoms can now be reliably calculated, once smaller systems have been tested by making comparisons with experimental data or highly accurate ab initio calculations. Semiempirical methods suitable for the calculation of larger molecules with first and second row atoms are

AM1,^[35] PM3,^[36] MNDO/d,^[37] and SINDO1^[38] or its improved version MSINDO.^[39]

Siloxanes were at first studied only sporadically.^[40] Here, the basic system SiOCl_2 played a special role. As a single molecule it is undoubtedly stable, but is extremely reactive. It is possible that it is formed from Si_2OCl_6 , which is easily accessible experimentally. Relevant calculations were performed ab initio with large basis sets and correlation.^[41] SINDO1 calculations were first performed for small systems with up to eight Si atoms. The emphasis was on structure and stability with the aim of deriving rules for predicting the preferred formation of isomers.^[42] These selected systems were $\text{Si}_n\text{O}_{n-1}\text{Cl}_{2(n+1)}$ ($n = 2-4$), $\text{Si}_n\text{O}_n\text{Cl}_{2n}$ ($n = 2-5$), $\text{Si}_n\text{O}_{n+1}\text{Cl}_{2(n-1)}$ ($n = 4, 5$), and $\text{Si}_n\text{O}_{n+3}\text{Cl}_{2(n-3)}$ ($n = 8$). In order to gain insight into the growth mechanism, the palette of these small systems was extended to $\text{Si}_n\text{O}_{n-1}\text{Cl}_{2(n+1)}$ ($n = 5$), $\text{Si}_n\text{O}_n\text{Cl}_{2n}$ ($n = 6$), $\text{Si}_n\text{O}_{n+1}\text{Cl}_{2(n-1)}$ ($n = 6, 7$), $\text{Si}_n\text{O}_{n+2}\text{Cl}_{2(n-2)}$ ($n = 5-8, 10$), and $\text{Si}_n\text{O}_{n+3}\text{Cl}_{2(n-3)}$ ($n = 10, 12$).^[43] In order to understand the growth mechanism, additional calculations were needed, which introduced interesting new aspects, in particular with regard to the silsesquioxanes $\text{Si}_2n\text{O}_{3n}\text{Cl}_{2n}$ ($n = 2-8, 10, 12, 18, 24, 30$) and polycycles $\text{Si}_2n\text{O}_{3n-3}\text{Cl}_{2(n+3)}$ ($n = 9, 15$).

3.2 Structures of Chlorosiloxanes

Mainly on the basis of ^{29}Si NMR studies, but also by crystal structure analyses, the structures of a substantial number of chlorosiloxanes have been determined.^[13,14,27,28,31,44-46] For the characterization of such species, the chlorosiloxanes have first been prepared and then derivatized (esterified) with retention of the Si–O backbone, and the derivatives have been structurally characterized. In the following, only the siloxanes formed by the title reaction will be discussed. A compilation of the experimentally determined connection patterns is presented in Table 2 in the form of structure diagrams. For completeness, the atomic connections of chlorosiloxanes prepared in a different way are additionally listed in Table 3.

From the survey, the relationship between the structures of the molecules and their compositions can be seen. The chlorosiloxanes $\text{Si}_n\text{O}_{n+x}\text{Cl}_{2(n-x)}$ with $x = -1$ form chains and both unbranched and branched catenated structures are found.^[13] For $x = 0$, Si–O monocyclic rings are observed, which often bear side groups^[31] of the same composition. It should be mentioned that among the prepared chlorosiloxanes there are no four-membered rings of the Si_2O_2 type. This is in agreement with the structural chemistry of silicon dioxide and silicates, as well as with the results of quantum chemical calculations.^[42] Three-dimensional polycyclic Si–O structures are formed when $x \geq 1$. Increasing oxygen content leads to an increase in the three-dimensional character of the Si–O framework. The largest chlorosilsesquioxane with an experimentally determined structure is $\text{Si}_8\text{O}_{12}\text{Cl}_8$,^[46] which has a cubane-like cage structure. The compound $\text{Si}_8\text{O}_{12}(\text{OCH}_3)_8$ has in fact been studied previously.^[47] However, this structure was obtained in a different way and will not be discussed here.

Table 2. Survey of structures of thermally formed chlorosiloxanes; M: silicon atom bonded to one oxygen atom; D: silicon atom bonded to two oxygen atoms; T: silicon atom bonded to three oxygen atoms; Q: silicon atom bonded to four oxygen atoms

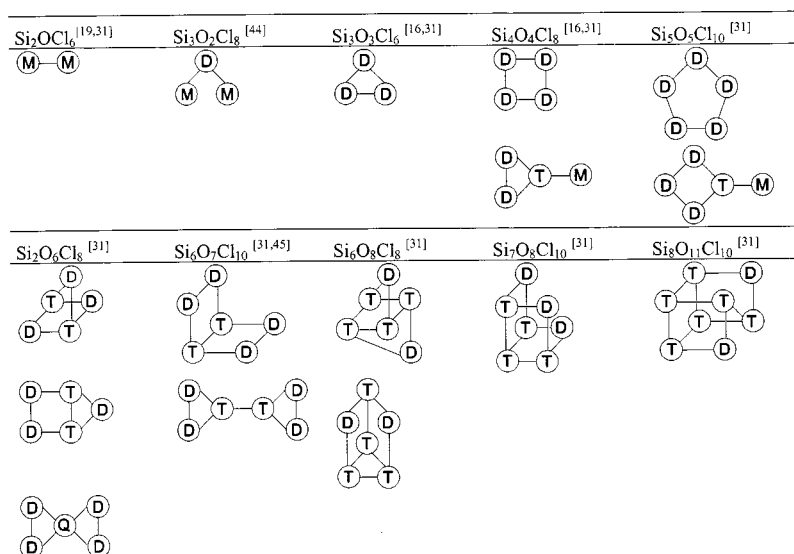
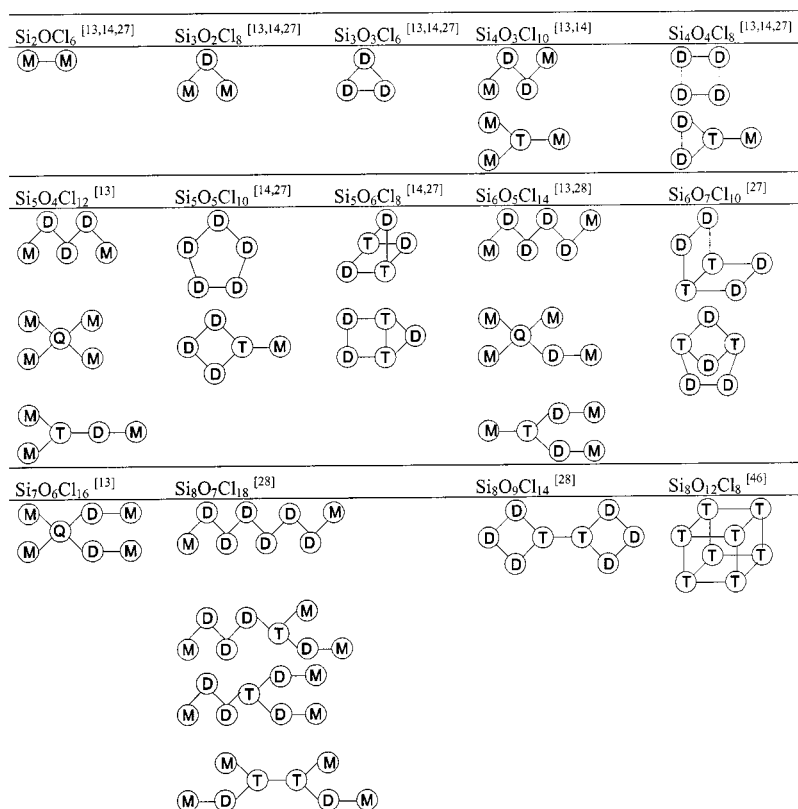


Table 3. Survey of structures of other chlorosiloxanes not thermally formed



Larger molecules have to date eluded experimental structure determination for the aforementioned reasons, but the results of quantum chemical calculations are available, on the basis of which cage-like structures can be expected for siloxanes with up to 40 Si atoms.^[43,48] Particularly comprehensive information is available for hydridosilsesquioxanes $\text{Si}_{2n}\text{O}_{3n}\text{H}_{2n}$,^[48] which are built up analogously to the chloro-

silsesquioxanes $\text{Si}_{2n}\text{O}_{3n}\text{Cl}_{2n}$. In Figure 1, the expected structures of a few representative compounds are presented.

A common feature of all the structures, determined both experimentally and theoretically, is that they contain differently connected six-, eight-, ten-, and twelve-membered rings. The preferred ring size can be established from stabilization curves and the growth patterns.^[43,48] The findings

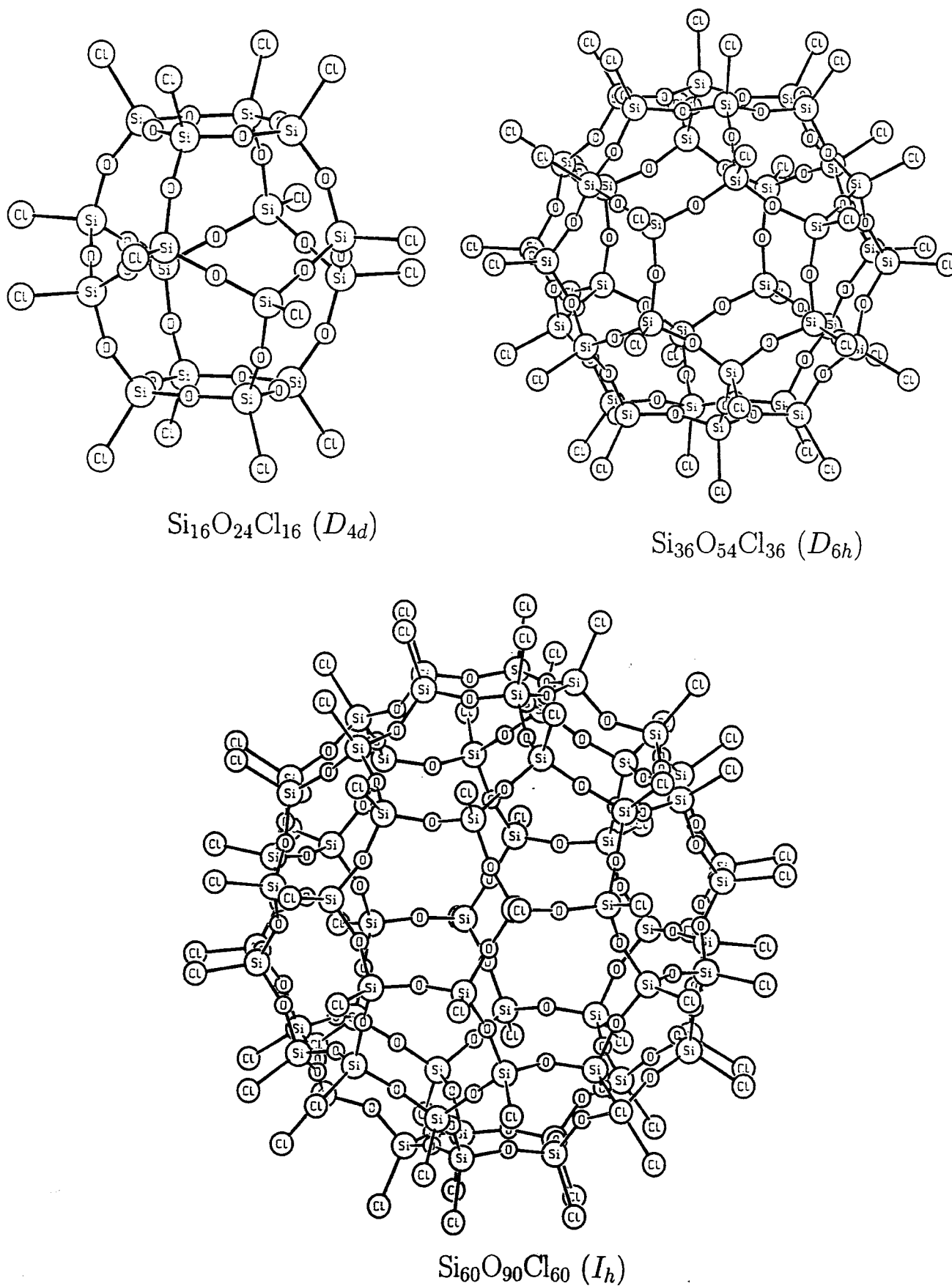


Figure 1. Quantum chemically calculated structures of some silsesquioxanes

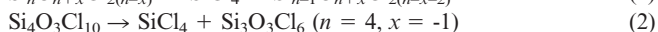
are in agreement with studies on the stabilities of monocyclic chlorosiloxanes, which led us to expect very similar stabilities for rings of different sizes,^[43] although with larger rings being somewhat more stabilized. However, with a further increase in ring size, the energy decreases once more so that a saturation is reached for twelve-membered rings. A balanced combination of rings (ten- and twelve-membered) is more stable than a combination of small (six- and eight-membered) and large (twelve- and higher-membered) rings.

3.3 Stability of Chlorosiloxanes

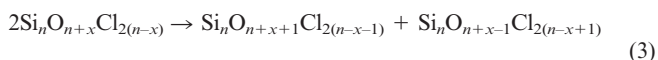
For none of the chlorosiloxanes discussed here have heats of formation or entropies been experimentally determined, hence a discussion of their thermodynamic stabilities has to rely on quantum chemical calculations, estimates, and practical experience.

The fact that these compounds are formed at temperatures slightly less than 1000 °C seems to suggest that they are thermodynamically stable. However, there are also literature reports pertaining to their thermal decomposition at similar temperatures.^[7,30] Considering the rather complicated decomposition reaction of a chlorosiloxane, it is apparent that silicon tetrachloride and a variety of oxygen-rich chlorosiloxanes will invariably be formed. In the resultant product(s) of the thermolysis, the number of silicon atoms can be either smaller (a), equally large (b), or both larger and smaller (c). Let us now consider these three possible decomposition reactions and formulate for each case one of the many possible reaction equations in a general form. In the following, we choose one example of each case and discuss its likelihood.

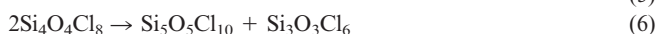
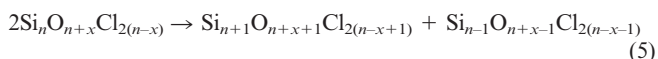
(a) Decomposition of a gaseous chlorosiloxane under cleavage of SiCl_4 :^[30]



(b) Decomposition of a chlorosiloxane with n Si atoms with formation of an oxygen-richer and an oxygen-poorer chlorosiloxane with n Si atoms in each:



(c) Decomposition of a chlorosiloxane with n Si atoms with formation of a larger ($n + 1$ Si atoms) and a smaller ($n - 1$ Si atoms) siloxane:



In all such cases, the total number of Si–O and Si–Cl bonds remains unchanged in the course of the reaction. Since one can assume that the bond energies in such chemically similar systems will have similar values, heats of reaction close to 0 kJ/mol are to be expected. The entropies of the reactions of types (a)–(c) are, however, more significant,

at least in case (a). If a chlorosiloxane decomposes into several smaller molecules [reaction type (a)], the increase in the number of molecules means that such a process will invariably proceed under entropy gain (considering the homogeneous gas-phase reaction). This reaction entropy can be expected to be of the order of 120–160 J/(Kmol) for a change in the number of molecules (Δv) of +1. If a chlorosiloxane decomposes into two comparatively equal siloxanes, distinguished only by their oxygen content [reaction type (b)], such a reaction occurs without a change in the number of molecules and hence its associated entropy will be close to 0 J/(Kmol). The same holds for a reaction of type (c). Of course, mixed forms of reactions (a)–(c) are conceivable. For case (a), a temperature-independent ($\Delta H = 0$) equilibrium constant of $e^{120/R}$ to $e^{160/R} \approx 10^6$ to 10^8 is obtained from the above considerations. Almost complete decomposition is thus to be expected from a thermodynamic point of view. For cases (b) and (c), equilibrium constants of about $e^0 = 1$ are to be expected. The decomposition products should thus be present in similar concentrations as the reactant. For each of the resulting decomposition products (other than SiCl_4), analogous considerations can be made. In summary, we can state from a thermodynamic point of view that each chlorosiloxane should undergo decomposition. The most favoured decomposition reaction is the cleavage of SiCl_4 , which should eventually lead to SiO_2 and SiCl_4 . Consideration of the discussed decomposition reactions from a molecular point of view (kinetic aspect) also leads to a clear preference for decomposition reaction (a). To bring about reaction (a), only the necessary activation energy from a collision with an energy-rich molecule or the (hot) wall of the reaction vessel has to be supplied. For reactions (b) and (c), however, a collision of two molecules of equal composition is necessary. This is rather improbable in the complex reaction mixture. Unimolecular reactions leading to the products of reactions (b) and (c) are inconceivable.

The results of these considerations clearly show that from both thermodynamic and kinetic points of view, all chlorosiloxanes must be unstable. They decompose to give SiCl_4 along with oxygen-richer siloxanes. This is consistent with all the experimental evidence.^[7,30,49,50]

4. Build-Up and Decomposition Reactions: Growth of Si–O Frameworks

In Section 3.1, it was shown that an impressive number of descendants, i.e. chlorosiloxanes of quite different composition with molar weights up to 7000 D, can be generated. We suspect that further chlorosiloxanes with even higher molar weights are formed, which remain undetected.^[50] The formation of such a wealth of reaction products in this seemingly simple reaction leads to the conjecture that a highly reactive intermediate is involved, which reacts with numerous reaction partners in a non-specific manner, thereby generating the broad spectrum of products. Recent matrix-spectroscopic studies have shown that in both the

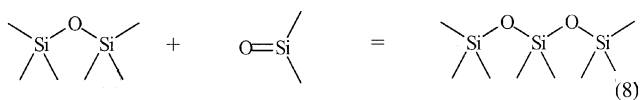
reaction of SiCl_4 with O_2 and the thermolysis of Si_2OCl_6 , the initial step at about 1000 °C leads to the formation of $\text{O}=\text{SiCl}_2$.^[51] Although silaphosgene has long been known as a molecule that can be isolated in a matrix,^[6] its presence in high-temperature vapours has now been demonstrated for the first time. Thermodynamic calculations [without consideration of $\text{SiO}_2(\text{s})$ and subsequent reactions of $\text{O}=\text{SiCl}_2$] lead us to expect that $\text{O}=\text{SiCl}_2$ should appear in the temperature range from about 1100 K to 1700 K, in concentrations peaking at 1400 K.^[51] The performed experiments support this expectation. The temperature at which $\text{O}=\text{SiCl}_2$ first appears in appreciable concentrations (about 1100 K) is identical to that at which the reaction of SiCl_4 with O_2 commences and chlorosiloxanes are formed. This can be taken as strong evidence that $\text{O}=\text{SiCl}_2$ is involved in the formation of chlorosiloxanes. The initial step in the thermolysis of Si_2OCl_6 also leads to silaphosgene,^[51] as well as to a build-up of higher chlorosiloxanes.^[7,30,49] Here, the key role of silaphosgene in the build-up of catena-siloxanes has been demonstrated.^[49] The chemical properties of $\text{O}=\text{SiCl}_2$ are not known. In view of the unusual coordination number of three at silicon and the presence of an Si–O double bond, it can be expected to be a highly reactive molecule. Although the value of its standard heat of formation is highly negative at -702.1 kJ/mol,^[40] decomposition into solid SiO_2 and SiCl_4 can be expected on the basis of literature data concerning the stabilities of other silicon compounds.^[4] In the case of the reaction of SiCl_4 with O_2 , a great excess of SiCl_4 is available as a potential reaction partner. Silaphosgene could react with it by inserting into an Si–Cl bond with the formation of Si_2OCl_6 :



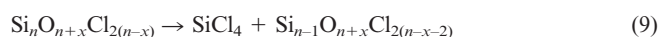
In fact, Si_2OCl_6 is also the main product when SiCl_4 and O_2 are reacted in the temperature range 700–950 °C. If Si_2OCl_6 is indeed formed, it is also available as a reaction partner for silaphosgene.

For catena-siloxanes with 4 or more silicon atoms, several isomers are formed, which can be separated, to some extent, by gas chromatography.^[50] This growth of unbranched and branched chains is terminated for chain lengths of about 10 Si atoms.^[32] Larger catena-siloxanes have not hitherto been observed.

This mechanism allows some understanding of the growth of the chains. However, it does not provide an explanation for the formation of mono- and oligocyclic siloxanes (see Table 1). In a growth reaction, $\text{O}=\text{SiCl}_2$ will invariably introduce Si and O atoms into the newly formed



siloxanes in a 1:1 ratio. In this way, no chlorosiloxanes with more oxygen than silicon atoms can be formed. Since these are, however, undoubtedly formed, the insertion of $\text{O}=\text{SiCl}_2$ cannot be the only reaction responsible for the build-up of the Si–O frameworks of oxygen-rich siloxanes and eventually therefore of solid SiO_2 . In Section 3.2, it was explained that all chlorosiloxanes must decompose for entropy reasons, preferably according to the following decomposition reaction:



For each such decomposition step, the stepwise built-up chlorosiloxane is decomposed once more, but in a stoichiometrically different way than for the build-up. Whereas in a growth reaction, the Si and O atoms are invariably introduced in equal numbers, only Si and Cl are cleaved in the decomposition process (eq. 9). All oxygen atoms are retained by the decomposing molecule. In this way, the molecules becomes smaller after each decomposition step, but concurrently oxygen-richer. Step by step, siloxanes with three-dimensional, cage-like Si–O frameworks are generated.

In Figure 2, we attempt to represent graphically the interplay between growth and decomposition. For chlorosiloxanes $\text{Si}_n\text{O}_{n+x}\text{Cl}_{2(n-x)}$, the ratio $(n+x)/n$ of the number of mol of oxygen and silicon is plotted against the number n of Si atoms per molecule for a series of x values.

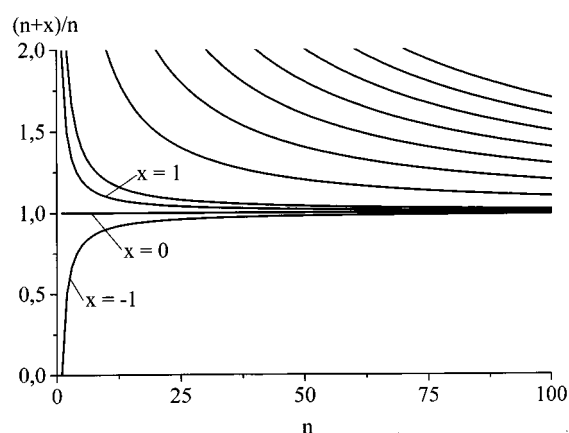


Figure 2. Dependence of the composition of homologous chlorosiloxanes on the number of silicon atoms

The generated sequences of points can be connected with hyperbola-like curves. Each of these curves corresponds to a homologous series of chlorosiloxanes; the lowest to the catena-siloxanes ($x = -1$), the next to the cyclosiloxanes ($x = 0$), etc. If growth and decomposition steps are introduced (in the form of arrows) into this diagram, Figure 3 is obtained.

Starting from SiCl_4 , first Si_2OCl_6 is formed, then a further increase in the chain length occurs, for example up to $\text{Si}_5\text{O}_4\text{Cl}_{12}$. If this decomposes with formation of SiCl_4 , $\text{Si}_4\text{O}_4\text{Cl}_8$ is formed, which can grow for example up to $\text{Si}_7\text{O}_7\text{Cl}_{14}$, before this in turn decomposes into the bicyclic

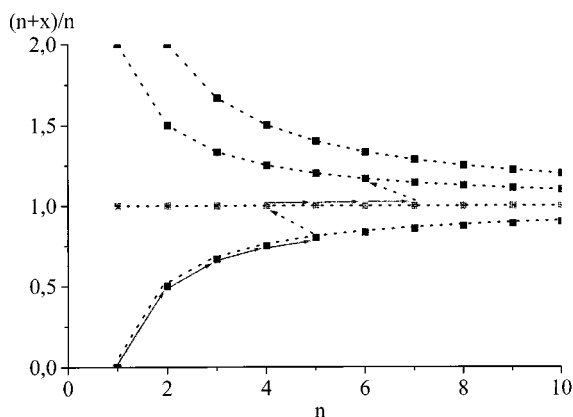


Figure 3. Growth pathways of chlorosiloxanes

$\text{Si}_6\text{O}_7\text{Cl}_7$. In this way, the stepwise transformation of SiCl_4 to SiO_2 can be followed almost continuously.

For thermolysis of Si_2OCl_6 in a closed vessel, it has been shown^[49] that the rate of the growth reaction [$v(\text{growth})$] is greater than that of the decomposition reaction [$v(\text{decomposition})$]. Therefore, at a constant temperature, more and more chlorosiloxanes are formed. In studies of the influence of temperature on the formation of chlorosiloxanes it is found that the relative amount of increasingly oxygen-rich siloxanes increases.^[30,49] This means that the rate of decomposition reaction, which leads to the formation of oxygen-rich compounds, has a higher temperature coefficient than that of the growth reaction. The following inequalities hold:

$$v(\text{growth}) > v(\text{decomposition}), \\ dv(\text{growth})/dT < dv(\text{decomposition})/dT$$

This means that with increasing temperature a point must be reached where the overall decomposition reaction proceeds more rapidly than the overall growth reaction. The two curves intersect at a temperature T_s . This is schematically represented in Figure 4.

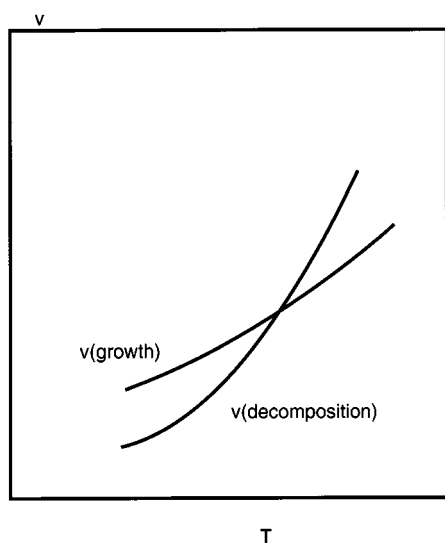


Figure 4. Temperature-dependence of the growth and decomposition rates of chlorosiloxanes

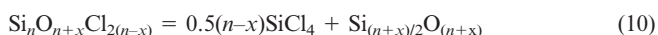
This temperature is at first unknown. Also unknown is to what (average) molar weight the molecules have grown at this point. It is certain that the reaction process discussed on the basis of the experimental results takes place below T_s .

In summary, we can say that $\text{O}=\text{SiCl}_2$ is formed in a first step of the reaction between SiCl_4 and O_2 . This is a highly reactive molecule, which reacts with all reaction partners possessing an Si–Cl bond with formation of an Si–O–Si group. This is a typical growth reaction and leads to a variety of catena-siloxanes starting from SiCl_4 . However, siloxanes with a ratio $n(\text{O})/n(\text{Si})$ greater than one cannot originate in this way. They are formed from chlorosiloxanes by entropy-driven cleavage of SiCl_4 . In this way, the molecules become smaller once more, but oxygen-richer. Their compositions approach that of the final product SiO_2 . Species with up to about 70 Si atoms and molar weights of 7000 D could be followed experimentally. As regards the further reaction, we can only speculate. However, it is unlikely that there will be any change in the fundamental reaction pattern, which is governed by the decomposition of chlorosiloxanes. If we extrapolate on the basis of the described findings, two alternative possibilities arise depending on the reaction conditions.

(a) The reaction temperature is always below T_s : As long as the formed siloxanes are at the reaction temperature and $\text{O}=\text{SiCl}_2$ is available as a reaction partner, the molecules will keep growing and become increasingly oxygen-rich. This growth cannot proceed indefinitely as the volatility of the siloxanes decreases with increasing molar weight. Eventually, condensed phases must arise. In particular, this will occur if the residence period of the siloxanes in the reaction zone, and consequently the time for molecular growth, is long. As an alternative to the condensation of high molecular weight chlorosiloxanes, the formation of aerosols, small suspended particles with diameters of 10^{-7} to 10^{-3} cm, appears likely. The formation of such an aerosol, which shows no tendency to undergo condensation, is not unusual. Indeed, in the technological processing of light-wave conductors, such aerosols present an exhaust air problem. Here, an oxygen flow loaded with SiCl_4 , GeCl_4 , BCl_3 , POCl_3 and other compounds is passed through a heated tube of very pure quartz glass so that the oxides of the aforementioned elements are deposited on the interior of the quartz tube. From this so-called “preform”, light-wave guides for optical data transfer are manufactured. This reaction, which is very similar to the one discussed, does not proceed to completion either. A portion of the introduced halogen compounds leaves the reaction tube as smoke, which is difficult to condense or filter. Whether such a suspended particle follows the same growth and decomposition mechanisms as a large siloxane molecule is not clear, but is nevertheless conceivable.

(b) The reaction temperature exceeds T_s : The decomposition reactions (in particular SiCl_4 cleavage) proceed more rapidly than the formation reactions. However, such molecules cannot completely decompose in this way. If SiCl_4 is cleaved, Si and Cl atoms are lost in a ratio of 1:4. If, in

the limiting situation, all Cl atoms are eliminated, we can formulate the following equation:



An $(\text{SiO}_2)_{(n+x)/2}$ "molecule" would have to be formed, an oligomer of the monomer SiO_2 ,^[6] i.e. an SiO_2 cluster with a molar weight not much lower than that of the chlorosiloxane from which it originated.

Since a fundamental change of the whole Si–O framework is unlikely in this process, a structural relationship between the formed SiO_2 and the high molecular weight chlorosiloxanes can be expected. Quantum chemical calculations on the structures and stabilities of SiO_2 clusters seem quite interesting in this context.

It is found experimentally that the reaction of SiCl_4 with oxygen leads to larger and larger amounts of increasingly oxygen-rich chlorosiloxanes with increasing temperature. Depending on the experimental conditions, a point just below 1000 °C is reached at which the reaction behaviour changes abruptly within a temperature interval of just a few degrees.^[50] This sudden change in the reaction behaviour could be connected with the marked intersection point T_s . No more chlorosiloxanes with typically molecular properties (relatively high fugacity, solubility in non-polar organic solvents) are formed, but rather a white, X-ray-amorphous solid, which mainly consists of "SiO₂" with variable but low chlorine content (< 5%). The globular particles have diameters of about 0.1 μm and are reminiscent of the industrial product "Aerosil" (Degussa–Hüls). This is formed in a similar way, under similar conditions. Thus, gaseous SiCl_4 is blown into an oxyhydrogen flame at temperatures of about 1000 °C. Depending on the reaction conditions, SiO_2 particles with diameters between 7 and 50 nm are formed. The reactions occurring in the flame are unknown. In principle, three reaction partners are initially available for the SiCl_4 : H_2 , O_2 , and H_2O . If H_2 and O_2 are introduced in the ratio 2:1, they should react primarily as in the oxyhydrogen reaction and water will be the primary reaction partner for SiCl_4 . In a first step, trichlorosilanol SiCl_3OH will thus be generated with elimination of HCl.^[17] This can then react in a similar manner as $\text{O}=\text{SiCl}_2$ with SiCl_4 or chlorosiloxanes with formation of Si–O–Si bonds.^[52] The interplay between growth and decomposition should be analogous to the situation discussed above. If a globular Aerosil particle with a diameter of 7 nm and densely packed oxygen atoms is considered, we can estimate that such a particle contains 10^5 O atoms. This corresponds to a formula of $\text{Si}_{50000}\text{O}_{100000}$ in molecular language. Such a giant molecule is thus separated from the chlorosiloxane with about 50 Si atoms by three orders of magnitude. Nevertheless, a continuous transition from the high molecular weight chlorosiloxanes to these solid-state particles is not unlikely. The properties and uses of Aerosil and related products are described in company reports.^[53–55]

Finally, two questions will be addressed:

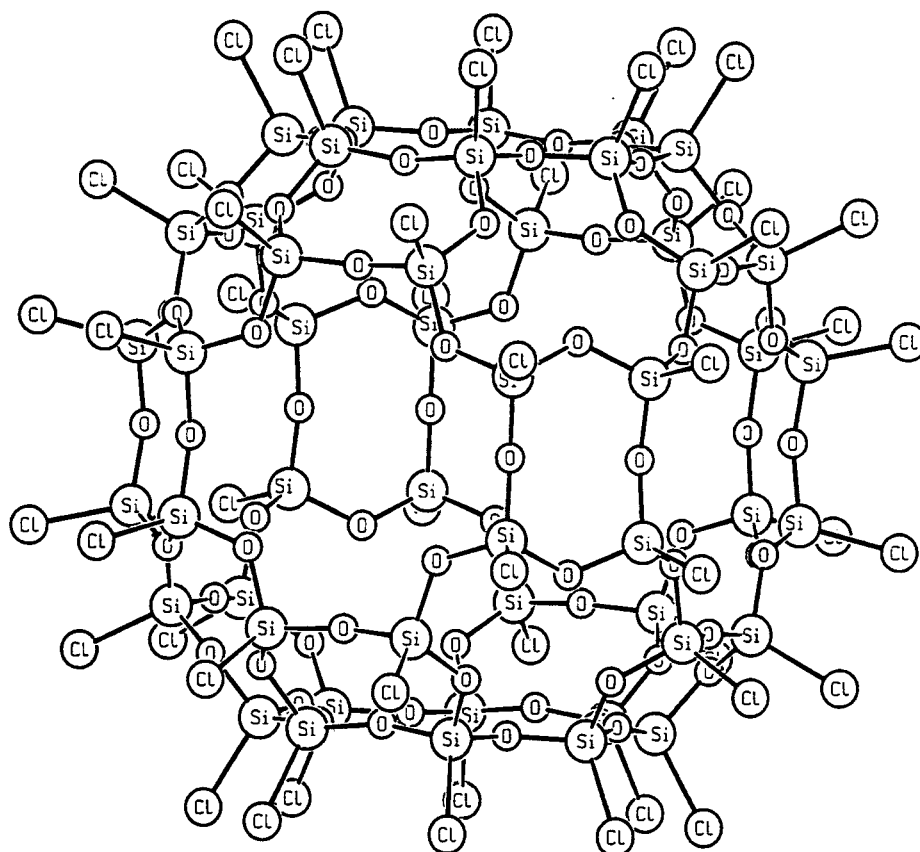
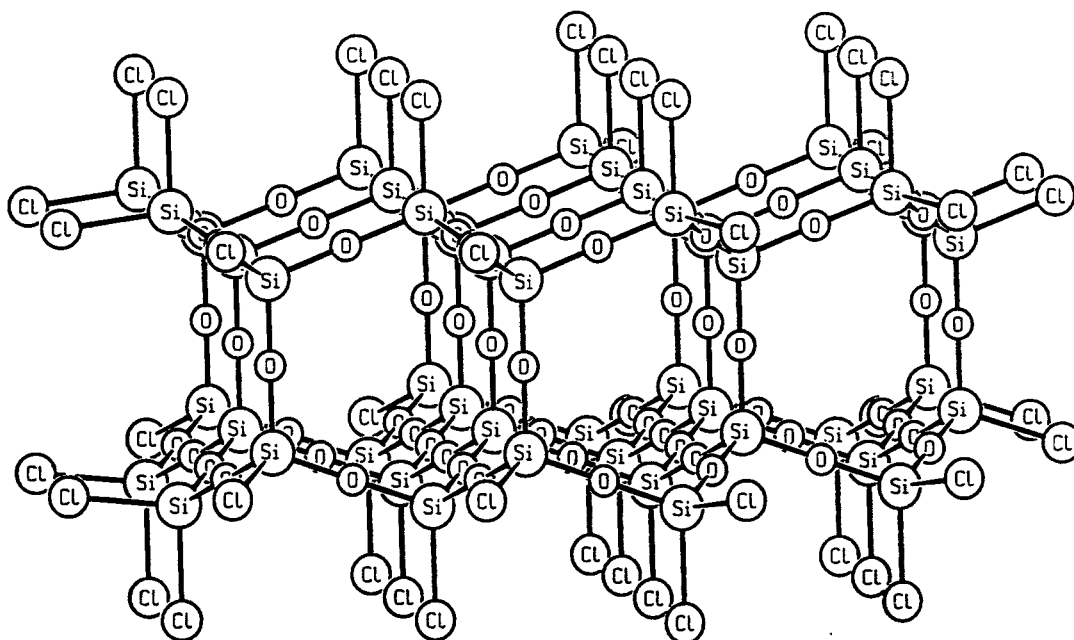
(a) Why is X-ray amorphous SiO_2 formed?

(b) Does the situation described for the system Si/O/Cl apply to elements other than silicon?

Let us start with (a): It is obvious that SiO_2 formed in fractions of a second in an oxyhydrogen flame cannot be well-ordered and crystalline. An equally amorphous product is formed if an oxygen stream loaded with SiCl_4 is passed through a heating section of about 40 cm^[50] at a relatively low flow velocity. The thermolysis of Si_2OCl_6 in a closed system for an extended time of several weeks also leads to amorphous products.^[50] This latter observation would suggest that the reaction time is of lesser importance. Although as a typical glass-forming substance, SiO_2 is a material that is normally solidified from a melt, it can be obtained in crystalline form from media of low viscosity, such as supercritical water (hydrothermolysis of α -quartz). An intrinsic property of SiO_2 is therefore probably not the reason. Thus, this phenomenon is seemingly related to the discussed reaction course. In the discussion of the structures of the initially formed chlorosiloxanes, it was pointed out that rings of different sizes arise in the monocyclic and oligocyclic siloxanes. In the course of the reaction, these rings become linked to form increasingly complicated three-dimensional structures. For the silsesquioxanes in particular, quantum chemical calculations were performed to gain insight into the stabilities of isomeric siloxanes. These showed that beyond molecular sizes of about 48 silicon atoms, structures with skeletons akin to that in crystalline SiO_2 become favoured.^[43,56] In the example shown in Figure 5, two isomers of $\text{Si}_{48}\text{O}_{72}\text{Cl}_{48}$ are depicted; the upper one is an Si–O framework corresponding to the so-called α -cage, while the lower one corresponds to the structure of β -tridymite.

The latter isomer is more stable according to new MSINDO calculations.^[56] The stability of such a bulk-like structure is also greater than that of a fullerene-like cage structure with 12 ten-membered and 14 twelve-membered rings.^[48] The growth of fullerene-like structures can occur in two steps in the presence of water and is accompanied by the elimination of HCl. The insertion mechanism has been described previously.^[48] In cases where the intermediately formed chlorosiloxanes show bulk-like structures even at the beginning of their growth, we would, of course, expect crystalline SiO_2 . However, this is not the case, as was made clear in Section 3.2. If the growth of Si–O frameworks starts in a different way than the formation and condensation of Si–O twelve-membered rings (as in crystalline SiO_2) and molecules of the type depicted in the upper portion of Figure 5 are initially formed, it is difficult to conceive that a rearrangement to a bulk-like, albeit more stable structure (Figure 5, below), would occur. It seems, therefore, that the initial growth of chlorosiloxane molecules with a few dozen Si atoms is responsible for the non-occurrence of bulk-like crystalline SiO_2 .

(b) The question arises as to whether the discussed mechanisms are also applicable to other material systems, and whether intermediates analogous to those of the present reaction are also observable for other elements. There are relatively few examples in the literature of elements that

 $\text{Si}_{48}\text{O}_{72}\text{Cl}_{48} (O_h)$  $\text{Si}_{48}\text{O}_{72}\text{Cl}_{48} (D_{3h})$ Figure 5. Quantum chemically calculated structures of two isomeric silsesquioxanes (Si_{48}); top: α -cage; bottom: tridymite structure

form molecular oxyhalides that can be discussed as intermediates of the reactions of halides with oxygen. These are mainly the metalloids and non-metals, as well as a few transition elements (fifth, sixth, and seventh subgroups). Oxyhalides of germanium, which correspond to those of silicon, but are thermally more labile, are known in somewhat larger numbers.^[57] No other element shows the variety of molecular oxyhalides as silicon. In the group of one of the authors (M.B.), analogous experiments on other systems have been attempted, most notably on the reaction of TiCl₄ with oxygen. Despite extensive efforts, the search for corresponding intermediates was in this and many other cases fruitless. Clearly, silicon represents a special situation. If we consider the similarities and differences of the material systems Si/O/Cl and Ti/O/Cl, we can say the structural chemistry of silicon is characterized by the coordination number 4 and tetrahedral coordination, whereas for titanium oxides the coordination number 6 dominates. In contrast to titanium, for silicon the transition from chloride to oxide proceeds without a change in the coordination number or geometry. Therefore, a stepwise substitution of Cl by O atoms is possible for silicon, without destruction of the short-range order. This is not possible for the transition of molecular chloride to oxide in the case of titanium. The reaction of TiCl₄ with oxygen also leads also to the oxide and may conceivably pass through similar intermediates. However, even if these are indeed formed, they are so unstable and have such a short lifetime that they cannot be isolated or observed experimentally. This argument holds true not only for titanium, but also for almost all metals.

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