DISPROPORTIONATION OF CHLORODISILANES CONTAINING VINYL, DIETHYLAMINO OR PHENYL SUBSTITUENTS

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Abstract
The base catalyzed disproportionation of the disilanes ClMeSi-SiMeClR, ClMeRSi-SiMeClR, MeRSi-SiMeClR (R = (CH=CH₂), NEt₂) and ClPPhSi-SiClPh was investigated. The formation of the observed mono- as well as oligosilanes with up to five silicon atoms is discussed applying a mechanism via Lewis-base stabilized silylenes and their subsequent insertion into Si-Cl bonds of another disilane or oligosilane molecule.

Introduction
Chlorosubstituted disilanes are able to undergo disproportionation reactions in the presence of a Lewis-base catalyst. As already discussed in [1,6,7] in the initial step the disilane is cleaved into a monosilane and a donor-stabilized silylene species which can insert into a Si-Cl bond of another chlorosilane molecule to form oligosilanes and finally polysilanes. In dependence on the substitution pattern of the educt disilane, linear or branched oligosilanes are formed (scheme 1).

The disproportionation reaction can be carried out "homogeneously": the Lewis base catalyst is added to the disilane. HMPT or N-heterocycles like N-methylimidazole, 3,5-dimethylpyrazole or p-dimethyloxypyridine are highly effective catalysts. Here, the disadvantage is that the catalyst remains in the oligosilane mixture. This can cause an undesired continuation of the disproportionation if the resulting oligosilane or polysilane is reheated. We have also succeeded in the preparation of fixed catalysts: trialkoxysilanes bearing a catalytic active side group (N-heterocycles or a HMPT like unit) were cast onto a silicate carrier [2,7]. Hereby it is possible to heat the disilane to reflux and to react the vapour with the solid catalyst. Applying this "heterogeneous" regime the resulting mixture or polysilane is catalyst-free and does not disproportionate again if it is reheated for further processing.

Previous investigations have been focused on disilanes bearing methyl and chloro substituents, but for various applications of the resulting polymer it is of great interest to introduce functional groups, into the polysilane e. g. phenyl, vinyl or diethylamino units. For example, the ceramic yield of silicon carbide generated from polysilanes can be increased by introducing vinyl substituents into the preceramic precursor [3]. On the other hand the introduction of phenyl substituents improves the spinability of polysilanes. This is very important in the fabrication of silicon carbide fibers. Earlier attempts to improve the spinability of a methylchloropolysilane precursor used a polymer blend with polystyrene [6], but with a decrease of the ceramic yield of the spun fibers.

Results and discussion
Disproportionation of vinylchloromethyl disilanes
In order to introduce vinyl groups into oligosilanes, disilanes containing one, two or three vinyl groups besides methyl and chloride substituents have been prepared. Starting from 1,1,2,2-tetrachlorodimethyl disilane one up to three chlorine substituents were exchanged against diethylamino groups. The remaining chlorine atoms were reacted with vinylmagnesium bromide to form the corresponding vinyl(diethylamino)methyl disilanes. Subsequent treatment with dry HCl gives a resubstitution of the diethylamino units by chlorine [4] (scheme 2).

Because 1-chloro-1,2-dimethyltrivinyldisilane (IIa) bears only one chlorine atom, the molecule does not disproportionate at ambient temperature; however the disproportionation can be initiated in a "homogeneous" reaction by N-methylimidazole at temperatures of about 140°C. The cleavage of the disilane molecule results in a donor-stabilized vinylmethyl silylene which inserts into the Si-Cl bond of IIa to form the unsymmetric trisilane VI(CMeSi-SiMeVi₂ (VI = CH=CH₂) (IIIB, see scheme 3). A further insertion step into the Si-Cl bond of IIIB yields the linear tetrasilane IVa. Both, tri- and tetrasilane can be identified by NMR spectroscopy, but the two different organic substituents at each silicon cause an increasing number of stereoisomers of the oligomers. Because of this fact the NMR spectra show complex signals, especially for the middle vinylvinylsilyl groups, no unambiguous assignment for oligomers with more than 4 silicon atoms is possible. MeVi₂CISi (IC) was found as monosilane by-product. The 29Si NMR resonance of IC was observed at 5.2 ppm.

The vinyl substituents are thermally stable up to about 200 °C. At higher temperatures the double bonds break up which leads to a crosslinking and the formation of an insoluble polymer.
Scheme 1: disproportionation of chloromethyl disilanes

The disproportionation of the symmetric 1,2-dichloro-1,2-dimethyldivinyl disilane (IIb) may be compared with that of 1,2-dichlorotetramethyl disilane [1]. While IIb did not disproportionate using a "heterogeneous" reaction-regime, in a "homogeneously" catalysed process with N-methylimidazole as catalyst, linear α,ω-dichlorooligosilanes with up to five silicon atoms were formed besides vinylmethyl dichlorosilane (see scheme 4). This is in exact agreement with the structures of the observed products in the disproportionation of 1,2-dichlorotetramethyl disilane, but because the presence of the two different organyl substituents at each silicon atom an increasing number of stereoisomers is formed when the increasing chain length. Therefore the NMR spectra of the oligosilane mixture are much more complex.

Scheme 2: preparation pathway of chloromethylvinyl disilanes
Scheme 3: disproportionation of 1-chloro-1,2-dimethyltrivinyldisilane (IIa)

\begin{align*}
\text{Me Me} & \quad \text{Me Si} \quad \text{Me Do} \\
\text{Cl} & \quad \text{Me Si} \quad \text{Cl Me} \\
\text{Me Si} \quad \text{Me Do} & \quad \text{Me Si} \quad \text{Me Do} \\
\text{Ic} & \quad \text{IIa} \\
\end{align*}

Even if the amount of catalyst is increased and the reaction time is extended, no oligosilanes containing more than five silicon atoms were observed by NMR spectroscopy.

1,1,2-Trichloro-1,2-dimethylvinylsilane (IIc) undergoes a disproportionation reaction under "heterogeneous" as well as "homogeneous" conditions (scheme 5). The cleavage of the disilane results in vinylchloromethylsilane and a donor-stabilized chloromethylsilylene species which inserts into the Si-Cl bond of both, the vinylchloromethylsilil group as well as the dichloromethylsilyl group of another molecule of IIc. Applying the "homogeneous" reaction regime with N-methylimidazole as catalyst, both expected trisilanes bearing vinylsilyl units as terminal or middle groups, respectively, could be detected while the trisilane bearing the vinyl substituent at a terminal silicon atom was formed exclusively via the "heterogeneous" reaction pathway. The tetrasilane containing a terminal vinylchlorosilyl group was found in both cases. The possibly primarily formed linear tetrasilane derived from the insertion of methylchlorosilylene into the trisilane IIIId seems to undergo a rearrangement to the branched structure IVc. Dichloromethylvinylsilane(Id) has been identified as monosilane by-product exclusively.

Scheme 4. disproportionation of 1,2-dichloro-1,2-dimethyldivinyldisilane (IIb)

\begin{align*}
\text{Me Me} & \quad \text{Me Si} \quad \text{Me Si} \quad \text{Me Do} \\
\text{Cl} & \quad \text{Me Si} \quad \text{Me Si} \quad \text{Cl Me} \\
\text{Me Si} \quad \text{Me Do} & \quad \text{Me Si} \quad \text{Me Do} \\
\text{Id} & \quad \text{IIb} \\
\end{align*}
Scheme 5: disproportionation of 1,1,2-trichloro-1,2-dimethylvinylsilane (IIc)

\[
\begin{align*}
\text{Cl} & \quad \text{Me} \\
\text{Me} & \quad \text{Si} & \quad \text{Si} & \quad \text{Me} \\
\text{Cl} & \quad \text{Me} & \quad \text{Si} & \quad \text{Si} & \quad \text{Cl} & \quad \text{Do} & \quad \text{Cl} & \quad \text{Me} & \quad \text{Cl} \\
\text{Me} & \quad \text{Si} & \quad \text{Si} & \quad \text{Me} & \quad \text{Cl} & \quad \text{Do} & \quad \text{Cl} & \quad \text{Me} & \quad \text{Cl} \\
\text{IIc} & \quad \text{Id} & \quad \text{IIIc} & \quad \text{IVc}
\end{align*}
\]

The constitutions of the formed branched tetrasilane IVc as well as the formed monosilane are in agreement with the products observed in the disproportionation of 1,1,2-trichlorotrimethyldisilane (carried out with N-methylimidazole) [1]. In that case only one trisilane with a structure comparable to that of IIIc has been observed, but only in very small amounts.

Disproportionation of (diethylamino)chloromethylsilanes

Due to the kinetic instability of diethylamino substituents at silicon, the disproportionation of (diethylamino)chlorodisilanes is a complex reaction. Diethylamino and chloro substituents can be exchanged easily by one another. Thus, as described in [5] for the synthesis of aminosilanes, always the thermodynamically favoured product has been obtained. That means, that the primarily formed disproportionation products can equilibrate with other aminosubstituted mono- or oligosilanes.

Table 1 $^{29}$Si NMR data of the vinyl substituted oligosilanes

<table>
<thead>
<tr>
<th>compound</th>
<th>A</th>
<th>$\delta_{\text{Si}}$/ppm</th>
<th>B</th>
<th>$^{1}J_{\text{Si-Si}}$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClViMeSi$^{A}$-Si$^{B}$MeVi$_{2}$ IIa</td>
<td>9.0</td>
<td>-29.7</td>
<td></td>
<td>96.9</td>
</tr>
<tr>
<td>ClViMeSi-SiMeClIV IIb</td>
<td>4.4/4.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ClViMeSi$^{A}$-Si$^{B}$MeCl$_{2}$ IIc</td>
<td>1.8</td>
<td>23.5</td>
<td></td>
<td>129.3</td>
</tr>
<tr>
<td>(NEt$<em>{2}$)ViMeSi$^{A}$-Si$^{B}$MeVi$</em>{2}$</td>
<td>-10.3</td>
<td>-31.8</td>
<td></td>
<td>97.5</td>
</tr>
<tr>
<td>Vi$<em>{2}$MeSi-SiMeVi$</em>{2}$</td>
<td>-29.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ClViMeSi$^{A}$-Si$^{B}$MeVi-Si$^{C}$MeVi$_{2}$ IIIa</td>
<td>12.8</td>
<td>-27.3</td>
<td>-49.3</td>
<td>81.4 (Si$^{A}$-Si$^{B}$) 77.0 (Si$^{B}$-Si$^{C}$)</td>
</tr>
<tr>
<td>ClViMeSi$^{A}$-Si$^{B}$MeVi-SiMeViCl IIIb</td>
<td>11.4</td>
<td>-47.9</td>
<td></td>
<td>81.1</td>
</tr>
<tr>
<td>ClViMeSi$^{A}$-Si$^{B}$MeCl-Si$^{C}$MeCl$_{2}$ IIIc</td>
<td>-2.8/-25.2</td>
<td>5.8/6.2</td>
<td>25.7</td>
<td></td>
</tr>
<tr>
<td>Cl$<em>{2}$MeSi$^{A}$-Si$^{B}$ViMe-SiMeCl$</em>{2}$ IIIId</td>
<td>23.7</td>
<td>-42.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ClViMeSi$^{A}$-(Si$^{B}$MeVi)$<em>{2}$-Si$^{C}$MeVi$</em>{2}$ IVa</td>
<td>12.8</td>
<td>-48.74/-48.63</td>
<td>-26.5/-26.4</td>
<td>-46.1/-46.04</td>
</tr>
<tr>
<td>[ClViMeSi$^{A}$-Si$^{B}$MeVi$_{2}$] IVb</td>
<td>12.5</td>
<td>-46.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ClViMeSi$^{A}$-Si$^{B}$Me-[Si$^{C}$MeCl$<em>{2}$]$</em>{2}$ IVc</td>
<td>11.3</td>
<td>-66.7</td>
<td>33.13/33.07</td>
<td>75.3 (Si$^{A}$-Si$^{B}$) 82.1 (Si$^{B}$-Si$^{C}$)</td>
</tr>
<tr>
<td>[ClViMeSi$^{A}$-Si$^{B}$MeVi$<em>{2}$]$</em>{2}$Si$^{C}$MeVi Va</td>
<td>12.6</td>
<td>-45.3</td>
<td>-46.1</td>
<td></td>
</tr>
</tbody>
</table>
Table 2. $^{13}$C and $^1$H NMR data of the Si-Me groups of the vinyl substituted oligomers

<table>
<thead>
<tr>
<th>compound</th>
<th>$\delta_{C}$/ppm</th>
<th>$\delta_{H}$/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NEt$_2$)ViMe$^A$Si-Si$^B$MeVi$_2$</td>
<td>-2.19/2.24</td>
<td>-5.34/-5.38</td>
</tr>
</tbody>
</table>
| ClViMe$^A$Si-Si$^B$MeCl$_2$ IIc | -1.0 | 5.9 | A: 0.68  
| | | B: 0.89 |
| ClViMeSi-SiMeClVi Ilb | -0.4 | A: 0.62/0.60 |
| Cl ViMe$^A$Si-Si$^B$MeVi$_2$ IIa | 1.0 | -6.2 | A: 1.12  
| | | B: 0.92 |
| Vi$_2$Me-Si-SiMeVi$_2$ | -5.7 | A: 0.83 |
| Cl$_2$MeSi$^A$-Si$^B$MeVi-SiMeCl$_2$ | 8.0 | -9.9 |
| ClViMeSi$^A$-Si$^B$MeCl-Si$^C$MeCl$_2$ IIIc | 1.0 | -2.2 | 6.8 |
| ClViMeSi$^A$-Si$^B$MeVi-SiMeViCl IIIa | 1.5/1.6 | -9.9 |
| [ClViMeSi$^A$-Si$^B$MeVi-]$_2$ IVb | 1.17/1.22/1.30/1.34 | -8.9/-8.8 |
| ClViMeSi$^A$-Si$^B$Me-[Si$^C$MeCl$_2$]$_2$ IVc | 2.1 | -12.6 | 9.4 | A: 0.79  
| | | B: 0.51  
| | | C: 1.019/1.026 |
| [ClViMeSi$^A$-Si$^B$MeVi-]$_2$Si$^C$MeVi Va | 1.6/2.4 | -8.5/-8.7 | 7.3/-7.4/  
| | | 7.5/-7.7 |

Starting with 1,1,2-trichloro-1-(diethylamino)-dimethylsilane (IId) the Lewis base catalyzed disproportionation yields trichloromethylsilane and dichloro(diethylamino)methylsilane as volatile monosilanes (scheme 6). Formation of these compounds seems possible via two reaction pathways. Most likely the cleavage of the Si-Si bond of IId leads to a donor-stabilized chloromethylsilylene and dichloro(diethylamino)methylsilane that equilibrates in further steps with other chlorosilanes into trichloromethylsilane. On the other hand, a cleavage of IId into methyltrichlorosilane and a (diethylamino)methylsilylene may be also possible. From the oligomer mixture the trisilane MeClSi[SiClMe(NEt$_2$)]$_2$ IIIf and two tetrasilanes MeSi(SiCl$_2$Me)$_2$[SiMeCl(NEt$_2$)] IVd and MeSi(SiCl$_2$Me)[SiMeCl(NEt$_2$)]$_2$ IVe could be detected by NMR spectroscopy (scheme 6).

The disproportionation of the symmetrical 1,2-dichloro-1,2-(diethylamino)dimethylsilane (IIe) yields a volatile mixture of dichloro(diethylamino)methylsilane and chlorobis(diethylamino)methylsilane as well as a oligomer mixture of the trisilane MeClSi(SiClMe(NEt$_2$))$_2$ (IIIh) and the tetrasilane MeSi(SiClMe(NEt$_2$))$_3$ (IVg). Applying a "homogeneous" reaction regime the tetrasilane IVg is obtained exclusively besides the same two monosilanes as mentioned above. Thus, this reaction is an effective way to synthesize the branched tetrasilane IVg that can be converted into MeSi(SiCl$_2$Me)$_3$ by subsequent treatment with HCl.
The heterogeneous disproportionation of 1-chloro-1,2,2-tris(diethylamino)-dimethyldisilane (IIIf) gave the monosilanes tris(diethylamino)methylsilane and chloro-bis(diethylamino)methylsilane (scheme 8). Any trisilanes could not be detected, but the oligomer mixture contained the three branched tetaasilanes $\text{SiMe(SiMeCl(NEt}_2)_3}$ (IVj), $\text{SiMe(SiMeCl(NEt}_2)_2(SiMe(NEt}_2)_2)$ (IVi), and $\text{SiMe(SiMeCl(NEt}_2))(SiMe(NEt}_2)_2$ (IVh). The tetaasilane IVh bearing five diethylamino groups was not available via the amination of MeSi(SiMeCl$_2)_3$ with diethylamine. The NMR spectroscopic data of all formed aminochlorotri- and tetrasilanes have already been reported in [5] and are in good agreement with our results.
Scheme 7: disproportionation of $[(\text{NEt}_2)\text{MeClSi-}]_2$ (compounds in parentheses are not observed)

Disproportionation of 1,1,2,2-tetrachlorodiphenyldisilane (IIg)

1,1,2,2-Tetrachlorodiphenyldisilane (IIg) has been synthesized starting from phenyltrichlorosilane via PhSi(NEt$_2$)$_2$Cl and Ph(ET$_2$N)$_2$Si(NEt$_2$)$_2$Ph as published in [8]. Addition of N-methylimidazole to a solution of IIg in C$_6$D$_6$ resulted after one hour at 100°C in a disproportionation of IIg into phenyltrichlorosilane and the new branched tetrasilane IVk besides small amounts of the trisilane IIIj (ascheme 9). The $^29$Si NMR data of the latter have already been published in [9].

This reaction pathway can be compared with that of 1,1,2,2-tetrachlorodimethyldisilane where methyltrichlorosilane is formed besides the corresponding methylchlorooligosilanes, see scheme 1. Oligosilanes with up to seven silicon atoms have been identified in that case [1]. In comparison with Cl$_2$MeSi-SiMeCl$_2$ IIg is less reactive towards disproportionation catalyzed by Lewis bases, but the reaction leads to the analogous products.
Scheme 8: disproportionation of (NEt₂)MeClSi-SiMe(NEt₂)₂ (IIf) (compounds in parentheses are not observed)

**Scheme 9: disproportionation of Cl₂PhSi-SiPhCl₂**

<table>
<thead>
<tr>
<th>Compound</th>
<th>A</th>
<th>δ&lt;sub&gt;Si&lt;/sub&gt;/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhSiCl₃</td>
<td>-0.50</td>
<td></td>
</tr>
<tr>
<td>PhSiCl₂-SiCl₂Ph</td>
<td>2.63</td>
<td></td>
</tr>
<tr>
<td>PhSi&lt;sup&gt;A&lt;/sup&gt;Cl₂-Si&lt;sup&gt;B&lt;/sup&gt;ClPh-Si&lt;sup&gt;A&lt;/sup&gt;Cl₂Ph</td>
<td>7.47</td>
<td>-15.02</td>
</tr>
<tr>
<td>PhSi&lt;sup&gt;A&lt;/sup&gt;(Si&lt;sup&gt;C&lt;/sup&gt;Cl₂Ph)₃</td>
<td>-63.06</td>
<td>-14.28&lt;sup&gt;1&lt;/sup&gt;J&lt;sub&gt;SiSi&lt;/sub&gt;: 88.9 Hz</td>
</tr>
</tbody>
</table>
Experimental

Synthesis of olefinic substituted chlorodisilanes

1-chloro-1,2-dimethyltrivinyldisilane \( \text{IIa} \), 1,2-dichloro-1,2-dimethylvinylidisilane \( \text{IIb} \) and 1,1,2-trichloro-1,2-dimethylvinylidisilane \( \text{IIc} \) were synthesized in analogy to the method described in [4].

1,2-dichloro-1,2-dimethylvinylidisilane \( \text{IIb} \). To a mixture of 63.5 g (0.278 mol) tetrachlorodimethyldisilane in 800 ml n-hexane 81.8 ml (1.12 mol) HNEt\( _2 \) were added with stirring. The reaction started immediately and HNEt\( _2 \)·HCl precipitated as a white solid. After stirring over night, the ammonium salt was filtered off and the solvent was evaporated. The crude product that yielded about 85% of \( \text{IIb} \) was added dropwise to 440 ml 1M vinylmagnesium bromide / thf solution. After the addition was complete the mixture was kept under reflux for 6 h. Slow cooling caused a good crystallisation of the magnesium salt, thus the solution could be decanted and after stirring with n-hexane the remaining salt could be filtered off. After removal of the solvents the remaining crude product was collected and dissolved in 400 ml CCl\( _4 \). HCl was bubbled through the solution until the white precipitate forms an oily second phase. The lower phase containing the vinylchlorosilane can be separated easily, and CCl\( _4 \) is distilled off. After the distillation in vacuo 22 g (37% related to tetrachlorodimethyldisilane) of pure \( \text{IIb} \) were obtained.

1,1,2-trichloro-1,2-dimethylvinyldisilane \( \text{IIc} \): The procedure was the same as described for \( \text{IIa} \) but the amounts of HNEt\( _2 \) and vinylmagnesium bromide were varied. 161 g HNEt\( _2 \) and 300 ml of an 1 M solution of vinylmagnesiumbromide in thf were used. 24 g pure \( \text{IIc} \) (35% in relation to tetrachlorodimethyldisilane) were obtained.

1-chloro-1,2-dimethyl-1,2,2-trivinyldisilane \( \text{IIa} \): The same method described for \( \text{IIb} \) and \( \text{IIc} \) was used, but the purification of 1(diethylamino)-1-chloro-1,2-dimethyldisilane as well as \( \text{IIa} \) from by-products by distillation is more difficult than for \( \text{IIb} \) and \( \text{IIc} \). Therefore small amounts of 1,2-dimethyltetra vinylidisilane were detected in the product \( \text{IIa} \). But 1,2-dimethyltetravinylidisilane did not undergo any disproportionation reactions and was removed from the oligosilanes of the disproportionation mixture of \( \text{IIa} \) by distillation.

Disproportionation reactions

Homogeneous disproportionation: Homogeneously catalyzed reactions were carried out without solvents. The catalyst (1-methylimidazole) was added to the pure disilane in the ratio 1:10. Precipitated 1-imidazole-monosilane adducts were filtered off and the reaction mixtures were fractionated into mono- and disilanes, trisilanes and tetrasilanes, higher oligomers were comprised in the residue.

In the case of 1,1,2,2-tetrachlorodiphenyldisilane \( \text{IIg} \) 0.35 g (1 mmol) \( \text{IIg} \) were dissolved in 0.3 ml \( \text{C}_6\text{D}_6 \) and 0.04 g (0.5 mmol) N-methylimidazole were added. The reaction mixture was heated up to 100 °C for one hour in a sealed tube before NMR spectra were recorded.

Heterogeneous disproportionation: The experimental procedure of the heterogeneous disproportionation of chlorodisilanes was already described in detail [1,2,7]. The preparation of the catalyst used was published in [7]. All NMR spectra were recorded on a Bruker DPX 400 in CDC\( _3 \) solution and TMS as internal standard for \( ^1\text{H} \), \( ^{13}\text{C} \) and \( ^{29}\text{Si} \).

References


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