RAMAN-SPECTRUM INVESTIGATION OF THE C-H BONDS OF CHLORO SILA-
AND DISILA-HYDROCARBONS CONTAINING SILICON-ATTACHED CHLORINE
AND THEIR CHLORO DERIVATIVES IN CONNECTION WITH PECULIARITIES
OBSERVED IN THE CHLORINATION OF THESE COMPOUNDS*

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Radiation-induced chlorination of chloro(methyl)- and chloro(chloromethyl) silanes was carried out for the
first time as recently as 1954 by Krieble and Elliot [2] and was later studied in special detail by Speier [3]. The
chlorination of chloro(methyl)disilanes was the subject of some other investigations [4]. Some phenomena were ob-
served which, as Speier emphasized, have an essentially specific (anomalous) character when compared with the
results of the chlorination of the corresponding carbon compounds; these were as follows. In chlorosilanes con-
taining silicon-attached chloromethyl and methyl groups, the former are much more readily chlorinated than the
latter, which is not observed in the corresponding carbon compounds.** Moreover, the tendency for the chlorina-
tion of the chloromethyl groups rather than the methyl groups in such silanes increases considerably as the number
of chlorine atoms in the molecule increases:

\[
\frac{(CH_3)_2Si}{B} - \frac{CH_2Cl}{A} \quad \text{chlorination in A > in B}
\]

\[
\frac{(CH_3)_2Si(Cl)}{B} - \frac{CH_2Cl}{A} \quad \text{chlorination in A >> in B}
\]

\[
\frac{CH_3Si(Cl)}{B} - \frac{CH_2Cl}{A} \quad \text{chlorination in A >>> in B}
\]

The preferential character of the chlorination of the chloromethyl group in chloro(chloromethyl)methyl-
silanes is clearly illustrated by the comparison of two ratios of amounts of chlorination products of (CH_3)_2XCl
(X = C or Si), calculated from the data of Table 1:

\[
\frac{(CH_3)_2C(Cl)CH_2Cl}{(CH_3)_2C(Cl)(CH_2Cl)_2} = 0.67; \quad \frac{(CH_3)_2Si(Cl)(CHCl_2)}{(CH_3)Si(Cl)(CH_2Cl)_2} = 4.9.
\]

* This paper is associated to a considerable extent with the contents of the paper [1].
** From the ratio of chlorination products obtained from (CH_3)_2Si - CH_2Cl, namely [3]:

\[
\frac{(CH_3)_2SiCHCl_2}{(CH_3)_2Si(CH_2Cl)_2} = 0.66,
\]

It might be concluded that no substantial preferential chlorination of the chloromethyl group is observed in this
compound; such an inference has been made [5]. However, the following must be taken into account: in the
compound (CH_3)_2Si - CH_2Cl the number of C-H bonds in methyl groups is 4.5 times as high as the number of
C-H bonds in chloromethyl groups and, in spite of this, the absolute number of chlorinated C-H bonds of chloro-
methy1 groups is greater than the absolute number of chlorinated C-H bonds of methyl groups. In this case, there-
fore, the greater activity of chloromethyl groups in chlorination is quite evident.
**TABLE 1**
Distribution of Chlorination Products of (CH₃)₃XC1 (moles %) [3]

<table>
<thead>
<tr>
<th>Formula of compound</th>
<th>X-C</th>
<th>X-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₃XCl</td>
<td>No data</td>
<td>41,5</td>
</tr>
<tr>
<td>(CH₃)₂XC1 (Cl) CH₂Cl</td>
<td>8,4</td>
<td>39,0</td>
</tr>
<tr>
<td>(CH₃)₂XC1 (Cl) CHCl₂</td>
<td>15,5</td>
<td>11,7</td>
</tr>
<tr>
<td>(CH₃)₂XC1 (Cl) CCl₃</td>
<td>Traces</td>
<td>1,2</td>
</tr>
<tr>
<td>(CH₃)XC1 (Cl) CH₂Cl₂</td>
<td>22,9</td>
<td>2,4</td>
</tr>
<tr>
<td>X (Cl) (CH₃)Cl₂</td>
<td>3,1</td>
<td>—</td>
</tr>
<tr>
<td>CH₃XC1 (Cl) (CH₃Cl) (CHCl₃)</td>
<td>10,9</td>
<td>Traces</td>
</tr>
</tbody>
</table>

Another notable peculiarity of the chlorination of chloro(methyl)disilanes is the great deactivation of the molecules of these compounds with respect to chlorination, which increases from compound (I) to compound (IV):

1. (CH₃)₃Si; 2. (CH₃)₂SiCl; 3. (CH₃)SiCl₂; 4. CH₃SiCl₃

It was found [3] that, for example, the rate of chlorination of (CH₃)₂SiCl is nine times as high as that of (CH₃)₃SiCl. It must be emphasized, however, that when the chlorination of the compounds (I)-(IV) has started and chloromethyl groups have made their appearance, further chlorination proceeds rapidly. Thus, in the chlorination of CH₃SiCl₃ in the liquid phase [6] the intermediate chlorination products of this compound, i.e., (CH₂Cl)SiCl₂ and (CHCl₂)SiCl₂, could not be detected, but only the final chlorination product, (CCl₃)SiCl₃. However, as we have shown, the chloromethyl groups themselves are more and more deactivated with respect to chlorination as chlorine atoms accumulate on the silicon atom. Thus, in the chlorination of an equimolecular mixture of • Cl₃Si(CH₂Cl) and Cl₂Si(CH₃)(CH₂Cl) (Table 2), of the 50% of the first compound only 7,5% was chlorinated, and of the 50% of the second 42,5% was chlorinated. In other words, the compound in which the smaller number of chlorine atoms had been replaced by methyl groups Cl₂Si(CH₃)(CH₂Cl) was indeed preferentially chlorinated; moreover, the chloromethyl group of this compound was preferentially chlorinated.

For the explanation of these regularities in chlorination it is necessary to take account of various factors determined by the structures of the reacting molecules and the reaction conditions. Our task in the present investigation consisted solely in determining, with the aid of Raman spectra, how the state of the C–H bonds reacting with chlorine changes with change in the structure of the molecule and the presence of electronegative chlorine atoms.

**EXPERIMENTAL**

The spectra were determined with a Soviet ISP-51 three-prism spectrograph with a central camera; the exciting radiation was the mercury line at 4358 Å. Before their spectra were determined all the substances were

* Chlorination of the mixture of CH₃Si(Cl₂)CH₂Cl and Cl₃SiCH₂Cl. A mixture of 54,5 g (0,3 m ole) of CH₃Si(Cl₂)CH₂Cl (b. p. 121.5°) and 61,3 g (0,3 m ole) of Cl₃SiCH₂Cl (b. p. 117°) was prepared in a flask fitted with reflux condenser, thermometer, and tube for the passage of chlorine. Chlorination was carried out at 100-105° for 57 hours under the radiation of a quartz lamp. The final boiling point of the mixture was 138°. Increase of weight 4,2 g. Fractionation through a column of 35-plate efficiency gave 45 g of a mixture (b. p. 117,5-119,5°) of unchanged reactants and 57,6 g of chlorination products. The latter were analyzed by the Raman-spectrum method. The results of the analysis are given in Table 2.