# Pyrolysis of trichlorosilane in the presence of chloroform

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The pyrolysis of trichlorosilane in the presence of different amounts of chloroform and the copyrolysis of $HSiCl_3$ with buta-1,3-diene in the presence of 1 mol.% chloroform were studied. The enthalpies of formation of products resulting from the pyrolysis of $HSiCl_3$ in the presence of chloroform were calculated by the quantum chemical method. Based on the thermochemical data as well as data from GLC and mass spectrometry, it was concluded from the condensate composition that introduction of chloroform into the zone of pyrolysis of $HSiCl_3$ favors generation of silylenes.

**Key words:** pyrolysis, silylenes, carbenes, radicals, trichlorosilane.

To increase the degree of conversion and the yields of the desired products in the pyrolysis of trichlorosilane, compounds easily decomposable into radicals and halocarbenes are usually introduced into the reaction zone.[1—9] Halogen derivatives ($CHF_2Cl$, $CH_2Cl_2$, $CH_3Cl$, $CHCl_3$) are the strongest initiating agents, when added in concentrations varying from 0.5 to 10 mol.%.

In the present work, the pyrolysis of trichlorosilane in the presence of chloroform was studied. It was interesting to determine how the amount of chloroform and the temperature of the reaction zone affect the composition of pyrolysis products.

## Experimental

A mass-spectrometric analysis of the final products was performed with an MKh-1303 spectrometer. The quantitative composition of pyrolysis products was determined by GLC with an LKhM-72 chromatograph equipped with a katharometer (12.8% PMS on an INZ-600 substrate as a stationary phase; He as carrier gas).

Copyrolysis of $HSiCl_3$ with chloroform in the molar ratios 100 : 1 and 1 : 1 was studied at 350—600 °C and with a residence time (τ) of the reagents in the reaction zone of 30 s.

Pyrolysis and copyrolysis were performed in a hollow quartz tube (inner diameter 28 mm, reaction zone length 400 mm).

**Pyrolysis of trichlorosilane in the presence of 1 mol.% chloroform.** A mixture of trichlorosilane (27.1 g, 0.2 mol) and chloroform (0.24 g, 0.002 mol) was passed through a hollow quartz tube (heated to 575 °C) with a velocity sufficient for the reagents to stay in the reaction zone for 30 s. The resulting condensate (26.1 g) contained (GLC and mass spectrometry) $HSiCl_3$ (65.1%, *m/z* 133 $[SiCl_3]^+$), $SiCl_4$ (25.8%, *m/z* 168 $[SiCl_4]^+$), tetrachlorodisilane (**1**) (1.7%, *m/z* 197 $[SiCl_2SiCl_2H]^+$), pentachlorodisilane (**2**) (5.1%, *m/z* 231 $[SiCl_2SiCl_3]^+$), hexachlorodisilane (**3**) (1.6%, *m/z* 266 $[Cl_3SiSiCl_3]^+$), and trichloro(dichloromethyl)silane (**4**) (0.7%). The pyrolysis of trichlorosilane in the presence of 1 mol.% chloroform at other temperatures as well as the copyrolysis of trichlorosilane with chloroform (in the ratio 1 : 1) at different temperatures were carried out in a similar way.

**Copyrolysis of trichlorosilane with buta-1,3-diene (5).** A mixture of trichlorosilane (27.1 g, 0.2 mol), buta-1,3-diene (21.6 g, 0.4 mol), and chloroform (0.24 g, 0.002 mol) was passed through a hollow quartz tube (heated to 560 °C) with a velocity sufficient for the reagents to stay in the reaction zone for 30 s. The resulting condensate (39.9 g) contained (GLC and mass spectrometry) buta-1,3-diene (10%), $HSiCl_3$ (25.6%), $SiCl_4$ (6.5%), disilane **1** (4.1%), disilane **2** (4.9%), but-2-enyltrichlorosilane (**6**) (11.1%), 1,1-dichloro-1-silacyclopent-3-ene (**7**) (19.1%), and 1-chloro-1-silacyclopent-3-ene (**8**) (5.7%).[10] The copyrolysis of $HSiCl_3$ with buta-1,3-diene in the presence of 1 mol.% chloroform at other temperatures was carried out in the same fashion.

## Results and Discussion

Table 1 presents data on the compositions of condensates obtained upon pyrolysis of trichlorosilane in the presence of 1 mol.% chloroform. A comparison with the published results[10] shows that the pyrolysis of $HSiCl_3$ starts at ~350 °C, regardless of the presence of $CHCl_3$. Introduction to the pyrolysis zone of 1 mol.% $CHCl_3$ increases the degree of conversion of $HSiCl_3$. The pyrolysis condensate contains silicon tetrachloride, tetrachlorodisilane (**1**), pentachlorodisilane (**2**), and hexachlorodisilane (**3**).

**Table 1.** Influence of temperature on the pyrolysis of trichlorosilane in the presence of 1 mol.% chloroform

| *T** /°C | Condensate composition (%) | | | | | |
|---|---|---|---|---|---|---|
| | $HSiCl_3$ | $SiCl_4$ | **1** | **2** | **3** | **4** |
| 350 | 91.5 | 6.5 | 0.6 | 1.2 | | 0.2 |
| 400 | 86.8 | 8.9 | 0.8 | 2.7 | 0.5 | 0.3 |
| 450 | 82.6 | 11.8 | 0.9 | 3.4 | 0.8 | 0.5 |
| 500 | 76.0 | 14.2 | 1.6 | 5.1 | 2.1 | 1.0 |
| 550 | 66.2 | 22.7 | 2.1 | 6.4 | 1.8 | 0.8 |
| 575 | 65.1 | 25.8 | 1.7 | 5.1 | 1.6 | 0.7 |
| 600 | 64.9 | 27.8 | 1.1 | 4.8 | 0.9 | 0.5 |

* Temperature of the reaction zone.

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[†] Deceased.

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**Table 2.** MNDO-calculated (calc) and experimental (exp)[12—14] enthalpies of formation ($\Delta H_f$) of compounds and intermediates discussed

| Compound, intermediate | $\Delta H_f$/kJ mol$^{-1}$ calc | exp |
|---|---|---|
| $HSiCl_3$ | −494.9 | −481.5 |
| $HCl$ | −64.6 | −92.3 |
| $:SiCl_2$ | −195.6 | −157.3 |
| ${}^{\cdot}SiCl_3$ | −378.3 | −320.0 |
| $HSiCl_2SiCl_3$ | −756.6 | – |
| $:SiClH$ | 28.4 | – |
| $SiCl_4$ | −619.5 | −656.3 |
| ${}^{\cdot}SiCl_2H$ | −223.6 | – |
| $HCCl_3$ | −121.2 | −104.5 |
| $:CCl_2$ | 239.5 | 224.9 |
| ${}^{\cdot}CCl_3$ | −78.4 | −79.4 |
| $HCCl_2SiCl_3$ | −581.0 | – |
| ${}^{\cdot}CCl_2H$ | −8.8 | – |

To estimate the probability of one or another mechanism operative in the formation of the products, we calculated the enthalpies of formation ($\Delta H_f^{\circ}$) of some chlorosilanes and organochloric compounds. In this work, the $\Delta H_f^{25}$ values were calculated by the semiempirical MNDO method with the ChemOffice Pro program complex. As can be seen from Table 2, the calculated and experimental enthalpies of formation in most cases are in a good agreement. Hereafter, whenever possible, we will use the experimental values.

From comparison of the experimental and thermochemical data, a conclusion can be made that the pyrolysis of trichlorosilane proceeds through the formation of highly active dichlorosilylene.

$$HSiCl_3 \longrightarrow HCl + :SiCl_2 \qquad (1)$$

$$\Delta H_f^{\circ} = 231.9 \text{ kJ mol}^{-1}$$

Like trichlorosilane, chloroform starts to decompose at 350 °C to give dichlorocarbene.[11]

$$CHCl_3 \longrightarrow HCl + :CCl_2 \qquad (2)$$

$$\Delta H_f^{\circ} = 237.0 \text{ kJ mol}^{-1}$$

The formation of disilanes **1** and **2** may be explained by generation of mono- and dichlorosilylenes and their insertion at the Si—H bond of trichlorosilane under the pyrolysis conditions.[10]

$$HSiCl_3 + :SiCl_2 \longrightarrow \underset{\mathbf{2}}{HSiCl_2SiCl_3} \qquad (3)$$

$$\Delta H_f^{\circ} = -62.7 \text{ kJ mol}^{-1}$$

$$HSiCl_2SiCl_3 \longrightarrow :HSiCl + SiCl_4 \qquad (4)$$

$$\Delta H_f^{\circ} = 164.3 \text{ kJ mol}^{-1}$$

$$:HSiCl + HSiCl_3 \longrightarrow \underset{\mathbf{1}}{H_2ClSiSiCl_3} \qquad (5)$$

$$\Delta H_f^{\circ} = 149.6 \text{ kJ mol}^{-1}$$

At the same time, the insertion of the dichlorocarbene generated from $CHCl_3$ under the pyrolysis conditions at the Si—H bond of trichlorosilane results in trichloro(dichloromethyl)silane.

$$HSiCl_3 + :CCl_2 \longrightarrow \underset{\mathbf{4}}{CHCl_2SiCl_3} \qquad (6)$$

$$\Delta H_f^{\circ} = -300.0 \text{ kJ mol}^{-1}$$

Under pyrolysis conditions, compound **4** can undergo both radical and silylene decomposition.

$$\mathbf{4} \longrightarrow {}^{\cdot}CHCl_2 + {}^{\cdot}SiCl_3 \qquad (7)$$

$$\Delta H_f^{\circ} = 193.7 \text{ kJ mol}^{-1}$$

$$\mathbf{4} \longrightarrow CHCl_3 + :SiCl_2 \qquad (8)$$

$$\Delta H_f^{\circ} = 264.2 \text{ kJ mol}^{-1}$$

The enthalpies of formation and quantum-chemical (MNDO) results[12—15] summarized in Tables 2 and 3 provide evidence in favor of primary carbene decomposition of chloroform and penetration of dichlorocarbene at the Si—H bond of trichlorosilane (reactions (2) and (6)), followed by radical decomposition of **4** at the Si—C bond (reaction (7)).

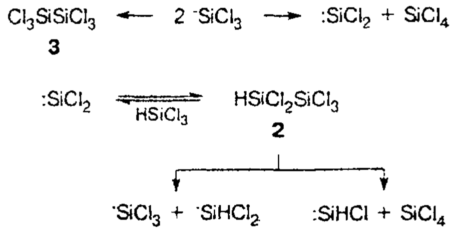
If one assumes that the equilibrium mixture resulting from the decomposition of trichlorosilane and chloroform is composed of ${}^{\cdot}H$, ${}^{\cdot}MCl_3$, HCl, and $:MCl_2$ (M = C or Si), then $\log\{[:CCl_2]/[{}^{\cdot}CCl_3]\} = 9.51$ and $\log\{[:CCl_2]/[:SiCl_2]\} = 0.87$ for equimolar mixtures at 500 °C.[16] This means that the relative concentrations of unstable particles at 500 °C are sufficient to initiate a reaction and participate in secondary processes.

Thus, it can be assumed that chloroform, when added to $HSiCl_3$, initiates its pyrolysis and facilitates the formation of a trichlorosilyl radical. In this case, the chain process leads to pentachlorodisilane (**2**) as a predominant product, which, in turn, also generates silylenes and radicals (Scheme 1).

**Table 3.** MNDO-calculated enthalpies of pyrolytic decomposition of compounds formed upon insertion of dichlorocarbene and dichlorosilylene at the Si—H bond of trichlorosilane and the C—H bond of chloroform

| Compound | Products of radical and molecular decomposition | $\Delta H$ /kJ mol$^{-1}$ |
|---|---|---|
| $CHCl_2CCl_3$ | ${}^{\cdot}CHCl_2 + {}^{\cdot}CCl_3$ | 120.9 |
| | $CCl_4 + :CHCl$ | 310.0 |
| | $CHCl_3 + :CCl_2$ | 256.4 |
| $HSiCl_2CCl_3$ | ${}^{\cdot}SiHCl_2 + {}^{\cdot}CCl_3$ | 215.6 |
| | $CHCl_3 + :SiCl_2$ | 264.2 |
| | $CCl_4 + :SiHCl$ | 369.2 |
| | $HSiCl_3 + :CCl_2$ | 191.9 |
| | $SiCl_4 + :CHCl$ | 166.2 |
| $CHCl_2SiCl_3$ | ${}^{\cdot}CHCl_2 + {}^{\cdot}SiCl_3$ | 193.7 |
| | $CCl_4 + :SiHCl$ | 502.9 |
| | $SiCl_4 + :CHCl$ | 299.9 |
| $HSiCl_2SiCl_3$ | ${}^{\cdot}SiHCl_2 + {}^{\cdot}SiCl_3$ | 154.7 |
| | $HSiCl_3 + :SiCl_2$ | 66.1 |
| | $SiCl_4 + :SiHCl$ | 164.0 |

**Scheme 1**



It follows from Table 1 that the content of compound **4** in the condensate obtained by the pyrolysis of trichlorosilane (in the presence of 1 mol.% chloroform) remains virtually constant over the whole temperature range studied and does not exceed 1%. At the same time, the pyrolysis of compound **4** itself occurs nearly completely at 500 °C (Fig. 1). The appearance of **4** in the condensate upon pyrolysis of trichlorosilane in the presence of 1 mol.% chloroform at temperatures >500 °C can be explained only by the fact that dichlorocarbene is continuously generated from $CHCl_3$ (reaction (2)) and inserted into the Si—H bond of trichlorosilane. Introduction of compound **4** in a concentration of 0.5 mol.% into the pyrolysis zone of $HSiCl_3$ also initiates the thermal decomposition of trichlorosilane.

A study of the reaction of $HSiCl_3$ with buta-1,3-diene (**5**) in the gaseous phase at 470—610 °C in the presence of 1 mol.% chloroform confirms that chlorosilylenes (:$SiCl_2$ and :SiHCl) can be generated under pyrolytic conditions at a ratio of diene **5** to trichlorosilane of 2 : 1.

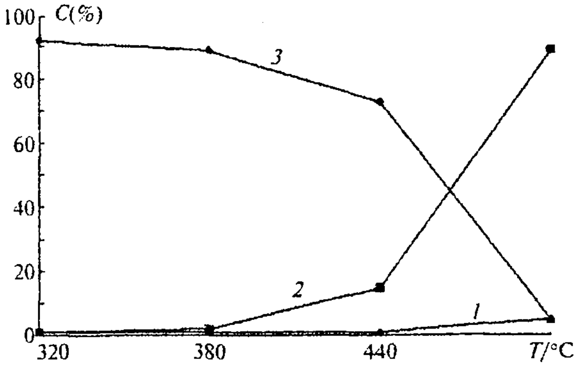
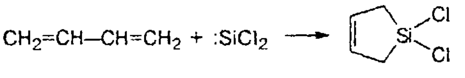


**Fig. 1.** Influence of temperature on the yield of products of the pyrolysis of trichloro(dichloromethyl)silane: $CCl_4$ (*1*); $SiCl_4$ (*2*); and $HCCl_2SiCl_3$ (*3*).

It is known[10] that the gas-phase reaction of trichlorosilane with diene **5** at 560 °C gives but-2-enyltrichlorosilane (**6**) in ~11% yield.

$$\underset{\mathbf{5}}{CH_2{=}CH{-}CH{=}CH_2} + HSiCl_3 \longrightarrow \underset{\mathbf{6}}{CH_3{-}CH{=}CH{-}CH_2SiCl_3} \qquad (9)$$

The gas-phase reaction of hexachlorodisilane **3** with buta-1,3-diene (ratio 2 : 1, 500 °C, τ = 30 s) affords 1,1-dichloro-1-silacyclopent-3-ene (**7**) in ~95% yield. Apparently, under these conditions, dichlorosilylene generated from disilane **3** undergoes 1,4-cycloaddition to diene **5**.[17]



(10)

**7**

The composition of the condensate produced upon copyrolysis of trichlorosilane with buta-1,3-diene, obtained in the presence of 1 mol.% chloroform at 470—610 °C and a $HSiCl_3$ : diene **5** ratio = 1 : 2, are given in Table 4. It can be seen that the condensate contains, apart from silane **6** (which is a product of the thermal addition of diene **5** to $HSiCl_3$), $SiCl_4$, disilanes **1** and **2**, dichlorosilacyclopentene **7**, and monochlorosilacyclopentene **8**. Hence, one can conclude that silylenes formed under copyrolysis conditions are involved in an insertion reaction along the Si—H bond of trichlorosilane and in 1,4-cycloaddition to diene **5** (Scheme 2).

The maximum amount of heterocycles **7** and **8** in the reaction mixture (~24.8%) was obtained at 560 °C. Above this temperature, the overall yield of silacyclopentenes decreases because of their thermal destruction and an increase in the content of disilanes **1** and **2**.

When the trichlorosilane : chloroform ratio in the initial mixture is equal to 1 : 1, the main copyrolysis products are $SiCl_4$ and methylene chloride, which are more thermodynamically stable under these conditions

**Table 4.** Influence of temperature on the copyrolysis of trichlorosilane with buta-1,3-diene (**5**) (in the 1 : 2 ratio) in the presence of 1 mol.% chloroform

| *T* | Condensate composition (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| /°C | **5** | $HSiCl_3$ | $SiCl_4$ | **1** | **2** | **8** | **7** | **6** | ΣX* |
| 470 | 22.5 | 71.6 | 2.1 | | 0.3 | 3.2 | 0.3 | | |
| 510 | 15.9 | 51.1 | 5.7 | 0.9 | 0.9 | 11.4 | 4.7 | 4.1 | 5.3 |
| 560 | 10.0 | 25.6 | 6.5 | 4.1 | 4.9 | 5.7 | 19.1 | 11.1 | 13.0 |
| 580 | 7.5 | 18.1 | 6.9 | 9.0 | 6.4 | 4.7 | 17.2 | 12.4 | 17.8 |
| 610 | 1.0 | 10.0 | 7.1 | 8.6 | 9.1 | 3.8 | 14.3 | 10.3 | 35.8 |

* ΣX are high-boiling components.

**Scheme 2**

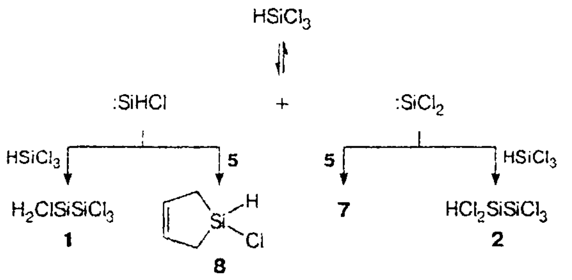


**Table 5.** Influence of temperature on the composition of the condensate of copyrolysis of trichlorosilane with chloroform (1 : 1)

| $T$ | Condensate composition (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| /°C | $HSiCl_3$ | $CH_2Cl_2$ | $SiCl_4$ | $CHCl_3$ | **1** | **2** | **3** |
| 350 | 59.2 | — | 1.5 | 39.2 | 0.1 | — | — |
| 400 | 59.0 | — | 4.1 | 36.5 | 0.4 | — | — |
| 450 | 41.5 | 9.2 | 12.2 | 34.6 | 1.0 | 1.5 | — |
| 500 | 18.6 | 17.7 | 40.9 | 19.0 | 1.5 | 1.8 | 0.5 |
| 550* | 16.9 | 16.7 | 46.7 | 15.5 | 1.3 | 1.9 | 1.0 |
| 575** | 1.9 | 14.9 | 76.6 | 2.9 | 1.0 | 1.3 | 1.4 |

* Elemental carbon is formed on the walls of the reaction vessels.

** Elemental carbon is formed in the bulk solution.

(Table 5). In addition, elemental carbon is formed on the walls of the reaction vessel. The degree of conversion of $HSiCl_3$ increases to 60% at 450 °C and up to 100% at 475 °C. $CHCl_3$ is completely converted at 575 °C, and the highest total content of disilanes **1—3** does not exceed 4%. The data in Table 3 suggest that noticeable amounts of radicals $^{\cdot}CHCl_2$, $^{\cdot}CCl_3$, $^{\cdot}SiCl_3$, and $^{\cdot}SiHCl_2$, of carbenes $:CCl_2$, and $:CHCl$, and of silylenes $:SiCl_2$ and $:SiHCl$ can be present simultaneously in the reaction zone. Further transformations of carbon-containing radicals predominantly involve the abstraction of hydrogen from trichlorosilane and chloroform

$$HSiCl_3 + {}^{\cdot}CHCl_2 \longrightarrow CH_2Cl_2 + {}^{\cdot}SiCl_3, \tag{11}$$

$$HSiCl_3 + {}^{\cdot}CCl_3 \longrightarrow CHCl_3 + {}^{\cdot}SiCl_3, \tag{12}$$

$$CHCl_3 + {}^{\cdot}CHCl_2 \longrightarrow CH_2Cl_2 + {}^{\cdot}CCl_3, \tag{13}$$

while those of silicon-containing radicals involve the detachment of chlorine from chloroform

$$CHCl_3 + {}^{\cdot}SiCl_3 \longrightarrow SiCl_4 + {}^{\cdot}CHCl_2, \tag{14}$$

$$CHCl_3 + {}^{\cdot}SiCl_2H \longrightarrow HSiCl_3 + {}^{\cdot}CHCl_2. \tag{15}$$

The formation of elemental carbon in the copyrolysis of trichlorosilane with chloroform may be due to the disproportionation of $:SiCl_2$ and $:CCl_2$.

$$:SiCl_2 + :CCl_2 \longrightarrow SiCl_4 + C \tag{16}$$

Thus, the introduction of 1 mol.% chloroform in the reaction zone initiates the thermal decomposition of trichlorosilane and favors the generation of silylenes, whereas the copyrolysis of an equimolar mixture of $HSiCl_3$ and chloroform predominantly yields elemental carbon, $SiCl_4$, and methylene chloride, which are thermodynamically stable at the copyrolysis temperature.

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