Experimental and theoretical study of the pyrolysis of trichlorosilane

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Pyrolysis of trichlorosilane (TCS) and copyrolysis of TCS with 1,3-butadiene were studied. The enthalpies and activation energies for the reactions of the products of TCS pyrolysis were found by quantum-chemical calculations. A direct study of the pyrolysis of TCS by mass spectrometry was carried out. Based on the thermochemical parameters found by quantum-chemical calculations and on the results of GLC and mass spectrometry concerning the composition of the pyrolysis products, it was concluded that the pyrolysis of TCS follows a scheme that includes formation of radicals and silylenes.

Key words: trichlorosilane, pyrolysis; silylenes; radicals.

At present, vast experimental information on the pyrolysis of organochlorosilicon hydrides and trichlorosilane (TCS) has been accumulated; however, no generally accepted scheme for this process has yet been developed. Experimental results have been interpreted in terms of several mechanisms that have been discussed in the literature.

A scheme including the generation of dichlorosilylene from TCS and from organochlorosilicon hydrides has been often used to explain the mechanism of the formation of organosilicon heterocyclic compounds.[1—5] At the same time, in many studies dealing with the synthesis of organosilicon compounds, the formation of the trichlorosilyl radical (**1**) during pyrolysis of TCS has been assumed.[6—8] The statement of some authors that the radical decomposition of TCS according to Scheme 1 is the limiting step of the process is based on the fact that HCl was not detected in the products of its pyrolysis.

Scheme 1

$$HSiCl_3 \longrightarrow {}^{\cdot}H + {}^{\cdot}SiCl_3$$

1

However, experimental thermochemical data attest to the initial formation of dichlorosilylene[9] (**2**) according to Scheme 2.

Scheme 2

$$HSiCl_3 \longrightarrow HCl + :SiCl_2$$

2

The absence of HCl in the products of pyrolysis of TCS has been explained[10] by assuming that HCl is involved in secondary reactions.

It is clear that choosing between various schemes for the decomposition of TCS would require additional data obtained using the most perfect experimental and theoretical methods. Therefore, the purpose of this work was to study the pyrolysis of TCS in a wide temperature range using GLC, mass spectrometry, and quantum-chemical methods.

Pyrolysis of $HSiCl_3$ was carried out in a flow-type setup under atmospheric pressure, at 350—600 °C, and with a residence time (τ) of TCS in the reaction zone equal to 30 s. The results of these studies (Table 1) indicate that the condensate obtained after pyrolysis contains $SiCl_4$ and disilanes in addition to the starting TCS; possible pathways to these products are shown in Scheme 3.

Since none of the thermochemical data needed to calculate the enthalpies and activation energies for the reactions of the products of pyrolysis of TCS have been reported in the literature, we found them by quantum-chemical calculations. In Table 2, the results of calculations are compared with the available experimental data.

Table 1. Effect of temperature on pyrolysis of TCS (quartz reactor, τ = 30 s)

T/°C	Composition of the condensate from the pyrolysis of TCS (%)				
	$HSiCl_3$	$SiCl_4$	**3**	**4**	Si_2Cl_6
350	97.7	1.4	0.4	0.5	—
400	96.8	2.0	0.5	0.7	—
450	95.8	2.2	0.7	1.3	—
500	94.6	2.8	1.0	1.6	—
550	94.0	3.4	0.7	1.9	—
575	92.0	4.4	0.6	2.5	0.5
600	89.7	7.7	0.4	1.4	0.8

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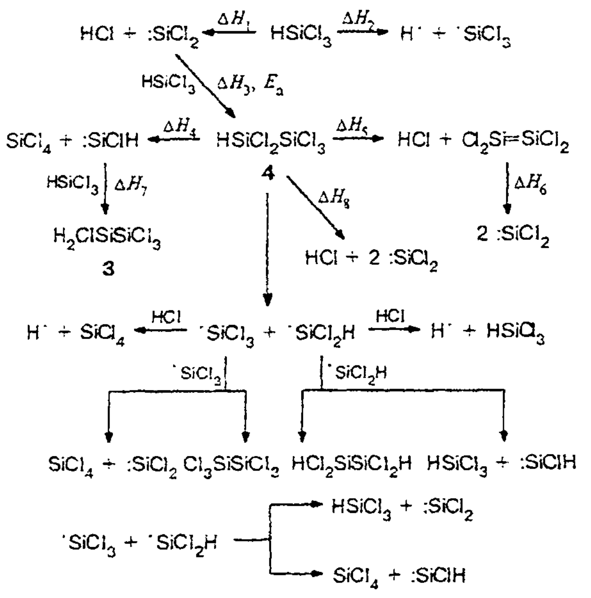
Scheme 3



ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔH_5	ΔH_6	ΔH_7	ΔH_8	E_a
kJ mol^{-1}								
239.9	387.1	−62.7	164.3	301.0	317.7	149.6	297.6	140.4

The assumption that pyrolysis of TCS affords $SiCl_2$ and HCl is supported by the fact that HCl was directly detected by mass spectrometry at the instant of its formation. This was accomplished using a procedure for withdrawing the products of pyrolysis (occurring at a pressure of 10^{-1}—10^{-2} Torr) through a heated diaphragm located in the reaction zone into a vessel with a pressure of 10^{-6}—10^{-7} Torr. It was found that after heating to 600 °C, the proportion of HCl in the products of pyrolysis increases only slightly; however, starting at 700 °C, it increases appreciably (by a factor of approximately 100). Simultaneously, the proportion of $SiCl_4$ in the reaction mixture also increases, as indicated by an increase in the ratio of the intensity of the peak of the ion with m/z 168 ($SiCl_4$) to the peak of the ion with m/z 133 ($[SiCl_3]^+$). The formation of disilanes in the reaction zone is very difficult to observe, because their proportion in the condensate obtained is low and their reactivity is high. Therefore, to detect disilanes, we used their tendency to be converted in the presence of O_2 into disiloxanes, which are stable under these experimental conditions. For this purpose, oxygen (as air) was introduced into the reaction zone in a quantity smaller than the quantity of the reaction products. The ratio of the intensities of the peaks of ions with m/z 247 ($[Cl_2SiOSiCl_3]^+$) and m/z 133 ($[SiCl_3]^+$) was 6.7 at 400 °C, 7.48 at 600 °C, 21.0 at 700 °C, and 40.0 at 800 °C. This indicates that the proportion of siloxanes in the reaction mixture increases as the temperature in the reaction zone increases.

Table 2. Calculated and experimental enthalpies of formation of TCS and the compounds formed from it

Compound	$\Delta_f H^{25}$/kJ mol^{-1}	
	calculated	experimental[11—13]
$HSiCl_3$	−494.9	−481.5
HCl	−64.6	−92.3
$:SiCl_2$	−195.6	−157.3
$^{\cdot}SiCl_3$	−378.3	−320.0
$HCl{-}{-}{-}:SiCl_2$*	−255.4	—
$HSiCl_2SiCl_3$	−756.6	—
$:SiCl_2{-}{-}{-}HSiCl_3$*	−550.1	—
$:SiClH$	28.4	—
$SiCl_4$	−619.5	−656.3
$^{\cdot}SiCl_2H$	−223.6	—
$Cl_2Si{=}SiCl_2$	−377.0	—

* Transition state.

The data presented in Table 1, together with the results of quantum-chemical calculations and the experimental thermochemical parameters, suggest that pyrolysis of TCS occurs by Scheme 3. According to thermochemical and theoretical results, at high temperatures, decomposition of TCS to give dichlorosilylene (see Scheme 2) with an activation energy E_a = 244.1 kJ mol^{-1} is more favorable (E_a for radical decomposition according to Scheme 1 is 387.1 kJ mol^{-1}).

As the temperature increases, insertion of dichlorosilylene into the Si—H bond of trichlorosilane becomes possible (Scheme 4); the energy barrier to this process is relatively high (E_a = 140.4 kJ mol^{-1}). The reaction product **4** can decompose with equal probabilities by two pathways: (1) radical cleavage at the Si—Si bond (Scheme 5); (2) decomposition with elimination of chlorosilylene (Scheme 6).

Scheme 4

$$HSiCl_3 + :SiCl_2 \longrightarrow \underset{\mathbf{4}}{HSiCl_2SiCl_3}$$

Scheme 5

$$\underset{\mathbf{4}}{HSiCl_2SiCl_3} \longrightarrow {}^{\cdot}SiCl_2H + {}^{\cdot}SiCl_3$$

(ΔH = 149.0 kJ mol^{-1})

Scheme 6

$$\underset{\mathbf{4}}{HSiCl_2SiCl_3} \longrightarrow :SiClH + SiCl_4$$

(ΔH = 164.3 kJ mol^{-1})

The resulting silyl radicals $^{\cdot}SiCl_3$ and $^{\cdot}SiCl_2H$ as well as chlorosilylenes $:SiCl_2$ and $:SiClH$ undergo subsequent transformations to give the products listed in Table 1. The decomposition of compound **4** according to Scheme 7 is energetically less favorable.

Scheme 7

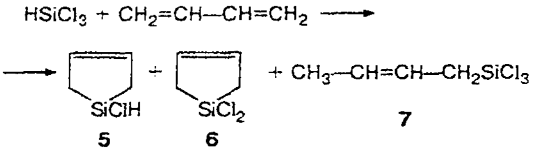
$$\underset{\mathbf{4}}{HSiCl_2SiCl_3} \longrightarrow HCl + 2\ :SiCl_2$$

(ΔH = 297.6 kJ mol^{-1})

It should be mentioned that the possibility of the formation of $:SiClH$ in the pyrolysis of TCS (according to Scheme 6) is noted for the first time. The evolution of chlorosilylene is confirmed by the presence of $H_2ClSiSiCl_3$ (**3**) resulting from the reaction of $:SiClH$ with TCS among the products of pyrolysis and also by the formation of monochlorosilacyclopentene in the gas-phase interaction of TCS with 1,3-butadiene.

The reaction of 1,3-butadiene with hexachlorodisilane at 480—500 °C is known to give 1,1-dichloro-1-silacyclopent-3-ene (**6**) in a yield of 90%. The gas-phase reaction of TCS with 1,3-butadiene (in a 1 : 2 ratio) at 470—650 °C yields a mixture of mono- and dichlorosilacyclopentenes along with the addition products (Scheme 8).

Scheme 8



The maximum overall yield of silacyclopentenes **5** and **6** (~17% based on the TCS) is attained at 560 °C. Silacyclopentene **5** is formed at a lower temperature (~510 °C), and its maximum yield is ~6%. The mass spectrum of the products of pyrolysis exhibits peaks for ions with *m/z* 152 and 118 and for other fragment ions derived from mono- and dichlorosilacyclopentene. When the ionizing potential decreases to 20 eV, only molecular ions with *m/z* 118 and 152 corresponding to mono- and dichlorosilacyclopentenes remain in the mass spectra.

Thus, using synthetic methods, quantum-chemical calculations of thermochemical parameters, and mass spectrometry, we have shown that the course of the pyrolysis of TCS depends substantially on the temperature: at lower temperatures, pyrolysis occurs predominantly by a radical mechanism, whereas at higher temperatures, it leads to the elimination of dichlorosilylene. The latter is inserted into the Si—H bond of the starting TCS yielding disilanes, which serve as sources of radicals and silylenes.

Experimental

Quantum-chemical calculations were carried out using the AMPAC 6.0 and HYPER CHEM 4.0 program packages within the framework of semiempirical AM1 and PM3 SCF LCAO methods. The geometric parameters of stable molecules, carbenes, silylenes, and radicals were found by minimization of the total energies, and the parameters of transition states (TS) of the insertion reactions were obtained by minimization of the modulus of the energy gradient with respect to inner coordinates. The calculations for radicals were carried out using the unrestricted Hartree—Fock formalism. The "quality" of the transition state thus constructed was checked by the eigenvalues of the matrix of the second derivatives of energy with respect to all inner coordinates (one negative eigenvalue).

Mass spectrometric analysis of the final products was accomplished on an MX-1305 mass spectrometer (the energy of ionizing radiation was 50 eV, and the emission currents were 0.5 and 0.1 mA). The quantitative composition of the products of pyrolysis was found by GLC on a LKhM-72 chromatograph with a heat-conductivity detector (12.8% PMS on INZ-600 as the stationary phase; He as the carrier gas).

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

Pyrolysis of trichlorosilane. TCS (27.1 g, 0.2 mol) was passed through a quartz reactor heated to 575 °C at such a rate as to ensure a residence time of TCS in the reaction zone of 30 s. The pyrolysis afforded 26.0 g of a condensate that consisted (according to GLC and mass spectrometry) of 92.0% TCS (*m/z* 133 $[SiCl_3]^+$), 4.4% $SiCl_4$ (*m/z* 168 $[SiCl_4]$), 0.6% 3 (*m/z* 197 $[SiCl_3SiClH]^+$), 2.5% **4** (*m/z* 231 $[SiCl_2SiCl_3]^+$), and 0.5% Si_2Cl_6 (*m/z* 266 $[Cl_3SiSiCl_3]$).

Table 3. Effect of the temperature on the copyrolysis of TCS with 1,3-butadiene (1 : 2) (quartz reactor, τ = 30 s)

T/°C	Composition of the condensate from copyrolysis (%)								
	$CH_2=CHCH=CH_2$	$HSiCl_3$	$SiCl_4$	3	**4**	**5**	**6**	**7**	HB*
470	45.2	46.8	1.7	—	0.1	5.4	0.3	0.3	0.2
510	39.6	43.9	2.1	—	0.3	5.9	3.3	2.2	2.7
560	13.4	31.0	2.6	2.5	1.3	5.0	12.0	11.2	21.0
610	12.3	24.4	3.8	4.8	1.9	4.3	11.1	8.4	29.0
650	1.1	23.1	6.0	6.0	2.3	3.9	10.6	5.4	41.6

* High-boiling components of the mixture of products.

Copyrolysis of trichlorosilane and 1,3-butadiene. A mixture of TCS (27.1 g, 0.2 mol) and 1,3-butadiene (21.6 g, 0.4 mol) was passed through a quartz reactor heated to 560 °C at such a rate as to ensure a residence time of the reagents in the reaction zone of 30 s. The pyrolysis gave 39.6 g of the condensate containing (according to GLC and mass spectrometry) 13% 1,3-butadiene, 31% TCS, 2.6% $SiCl_4$, 2.5% **3** (*m/z* 197 $[SiCl_3SiClH]^+$), 1.3% **4** (*m/z* 231 $[SiCl_2SiCl_3]^+$), 5% **5**, 12% **6**, and 11.2% **7**.

Mass spectrometric analysis of the products of pyrolysis of trichlorosilane. TCS was injected through a valve into a 1.5-L steel cylinder maintained at 100 °C until the pressure in the cylinder was 10^{-1}—10^{-2} Torr. The cylinder was connected through a heated valve to a reactor in which pyrolysis of TCS was carried out. The reactor was a hollow steel tube 50 mm in length and 3 mm in diameter equipped with an electric heater. The heated area in the reactor was separated by a diaphragm (60 mm) in a ratio of 3 : 2. Pyrolysis of TLC occurred in the larger section of the reactor at 10^{-1}—10^{-2} Torr and at a specified temperature. The products migrated through the heated diaphragm to the smaller section of the reactor with a pressure of 10^{-6}—10^{-7} Torr. This section was connected to the ionizing chamber of the mass spectrometer in which the mass spectra of the products were recorded.

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