

Mechanism of thermal decomposition of allyltrichlorosilane with formation of three labile intermediates: dichlorosilylene, allyl radical, and atomic chlorine*

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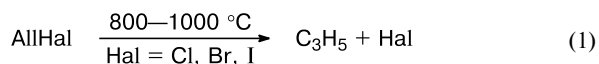
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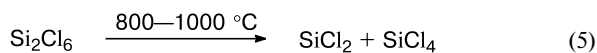
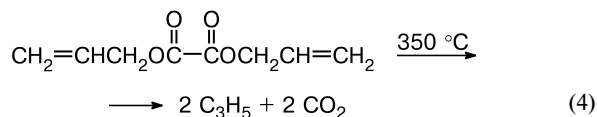
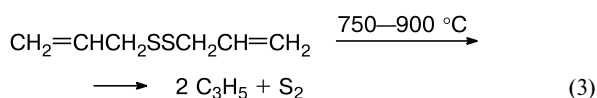
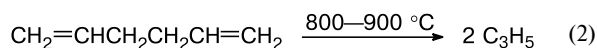
It is experimentally found that allyltrichlorosilane dissociates under vacuum pyrolysis ($\sim 10^{-2}$ Torr) at temperatures above 1100 K to form three labile intermediates: allyl radical, dichlorosilylene, and monoatomic chlorine. On the basis of experimental and theoretical data obtained, it is shown that the decomposition reaction proceeds in two steps. The first step is a typical reaction of homolytic decomposition to two radicals (C_3H_5 and $SiCl_3$) at the weakest Si—C bond. Due to weakness of the Si—Cl bond in the $SiCl_3$ radical, the energy of which is even somewhat lower than the dissociation energy of the Si—C bond in starting $AllSiCl_3$, this radical undergoes further dissociation to $SiCl_2$ and Cl, thus resulting in three intermediates of different classes of highly reactive species formed from $AllSiCl_3$.

Key words: allyltrichlorosilane, allyl radical, dichlorosilylene, trichlorosilyl radical, matrix IR spectroscopy, quantum chemical calculations, G4(MP2) level.

Matrix isolation¹ is one of the most widely used techniques for studying highly reactive intermediates of chemical reactions. The decomposition of compound-precursors under thermal action, various types of radiation, and a flow of charged or excited particles is most frequently used for the generation of labile intermediates. When organic radicals (*i.e.*, species with unpaired electrons) are generated from organic compounds characterized by only closed electron shells, two radical particles are formed,² although a stable accompanying product is often formed along with the radicals.² When such labile intermediates as nitrenes,^{3–5} carbenes,^{4,6} and their analogs (silylenes,⁷ germlylenes, and stannylenes⁸) bearing an even number of electrons on the outer shell are generated, a labile intermediate is eliminated from the precursor molecule to form one or several molecules of stable products. The examples (Eqs (1)–(5)) of the generation of allyl radical^{9–15} (C_3H_5) and dichlorosilylene¹⁶ ($SiCl_2$), used in matrix isolation studies and illustrating the above described general schemes of decomposition of precursor molecules are given below.

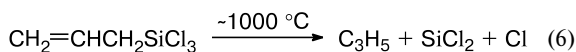


* Dedicated to Academician of the Russian Academy of Sciences O. G. Sinyashin on the occasion of his 60th birthday.



Undoubtedly, the formation of minimally possible number of labile species upon stable precursor decomposition is not a law but it has a clear physical sense. In the general case, the formation of labile molecules implies a significant increase in the energy of the molecular system. The more labile molecules are formed by the decomposition, the stronger is the increase in the energy of the system and the more energy should be transferred to the precursor molecule, which, in turn, increases the probability of secondary processes to occur. Therefore, a good precursor mainly decomposing to a target intermediate should

be a compound generating a minimum number of labile molecules for its decomposition to require minimum energy. In this respect, the thermal decomposition of allyltrichlorosilane (AllSiCl_3) turned out to be quite untypical. The formation of almost only allyl radical and SiCl_2 , two labile species belonging to different classes of highly reactive intermediates, was detected by matrix IR spectroscopy upon vacuum pyrolysis of AllSiCl_3



This work deals with the study of the mechanism of this unusual process.

Experimental

A setup for matrix isolation was constructed on the basis of a Displex CSW-208R closed-cycle refrigeration system (APD Cryogenics). The matrices were formed on a cooled mirror copper plate located inside a standard vacuum cryostat (APD Cryogenics) with optical KBr windows (for IR measurements) and CaF_2 windows (for UV and visible irradiation of matrices). The temperature of the copper plate during matrix deposition and IR spectra recording was 10–12 K, and the matrices were annealed at the temperatures specified in a range of 24–41 K. The temperature was measured using a DT-470-SD12 silicon diode fixed on the plate with a Lake Shore Model 330-11 controller (Lake Shore Cryotronics). The cryostat was evacuated with a CVL-100 diffusion pump through a liquid nitrogen trap to a residual pressure of $\sim 10^{-6}$ Torr.

Argon (99.998%, OAO Moskoks) served as a matrix gas. An Ar flow was passed over P_2O_5 to remove water traces, supplied to the cryostat along the non-heated line with a rate of 7–9 mmol h^{-1} , and condensed on the copper plate together with pyrolysis products. The pyrolysis of AllSiCl_3 (97%, ABCR GmbH) or allyl chloride (AllCl , Acros Organics, 99%) was carried out in a quartz reactor connected to the cryostat. The reactor was a quartz tube with the external and internal diameters equal to 6 and 4 mm, respectively, and the heated zone length equal to 100 mm. The outlet hole of the reactor was remote at a distance of ~ 50 mm from the copper plate. The reactor was heated with a nichrome coil to 900–1000 $^\circ\text{C}$. The temperature was measured with a chromel–alumel thermocouple connected to an IRT 5301 digital meter (Elemer Company). The pressure of the reactant in the flow through the reactor was monitored using a PMT-4M manometric converter and maintained not higher than 10^{-2} Torr to provide the dilution of the reactant with argon (in mol) in a ratio of at least 1 : 600. The typical time of matrix deposition was 1.5–2 h.

A DRSh-500 high-pressure mercury lamp (500 W) equipped with a water filter to absorb IR radiation served as a light source for the photolysis of matrices.

IR spectra were recorded in a range of 4000–400 cm^{-1} with a resolution of 0.5 cm^{-1} via the reflection scheme on an IFS 113v FT-IR spectrometer (Bruker) with a DTGS/KBr detector.

Quantum chemical calculations were performed at the G4(MP2) level of theory¹⁷ using the Gaussian 09, revision D.01 program package.¹⁸ The character of the found stationary points (a minimum or a first order saddle point) was monitored by the

calculation of the eigenvalues of the matrix of the second derivatives of the energy. The structures related to the transition states were established using IRC.^{19,20} The thermodynamic functions were calculated in the harmonic oscillator–rigid rotor approximation.

Results and Discussion

The matrix IR spectrum of allyltrichlorosilane (AllSiCl_3) earlier non-described in literature is presented in Fig. 1. The detected vibration frequencies of AllSiCl_3 and their most probable assignment to normal modes, which is based on the calculation of fundamental vibrations by the B3LYP/6-31G(2df,p) method (a part of the G4(MP2) calculations) are presented in Table 1.

The pyrolytic decomposition of AllSiCl_3 started at ~ 850 $^\circ\text{C}$. As the temperature increased, the conversion of AllSiCl_3 increased and reached $\sim 50\%$ at ~ 1000 $^\circ\text{C}$ (see Fig. 1, *b*). The bands of the pyrolysis products observed in the IR spectra are presented in Table 2. The most part of them is easily identified on the basis of literature data and the matrix IR spectra of individual compounds and labile intermediates detected previously at our laboratory. The bands of SiCl_2 (see Table 2) near 500 cm^{-1} having a characteristic splitting on the Cl isotopes are most intense.^{16,21} The band of radical C_3H_5 at 801 cm^{-1} is almost of the same intensity. In addition to this band, 15 bands belonging to radical C_3H_5 , whose matrix IR spectrum is well known,^{9–15} were revealed in the spectra of the products.

The bands of such stable unsaturated hydrocarbons as allene,^{22,23} acetylene,^{24–29} methylacetylene,^{22,30,31} and especially ethylene^{32,33} are noticeably less intense. The formation of the listed hydrocarbons is characteristic of the processes of pyrolytic generation of allyl radical from various precursors^{9,11–14} and, most likely, it is predominantly a result of secondary transformations of C_3H_5 .¹⁴

According to published data,¹⁴ the weak band at 3040 cm^{-1} belongs to cyclopropyl radical ($\text{c-C}_3\text{H}_5$), an isomer allyl radical. This assignment is confirmed by the disappearance of this band under the irradiation of the matrices with the full light of a mercury lamp (230–1000 nm) due to the isomerization of this radical to C_3H_5 .³⁴ The formation of cyclopropyl radical was observed upon the thermal generation of C_3H_5 from various precursors.^{11,14} Two very weak bands at 3308 and 687 cm^{-1} were assigned to propargyl radical,^{22,30,35,36} since the first of them is characteristic of this radical.

Minor amounts of HCl were also detected in the matrices.^{37–40} However, the intensity of its bands was comparable with that of the bands of water, which is always present in the matrices because of microleakages in the vacuum system and desorption from its internal surfaces, rather than with the band intensity of other products, indicating the formation of HCl due to the side reaction of hydrolysis of the Si–Cl bonds that are very sensitive to water traces.

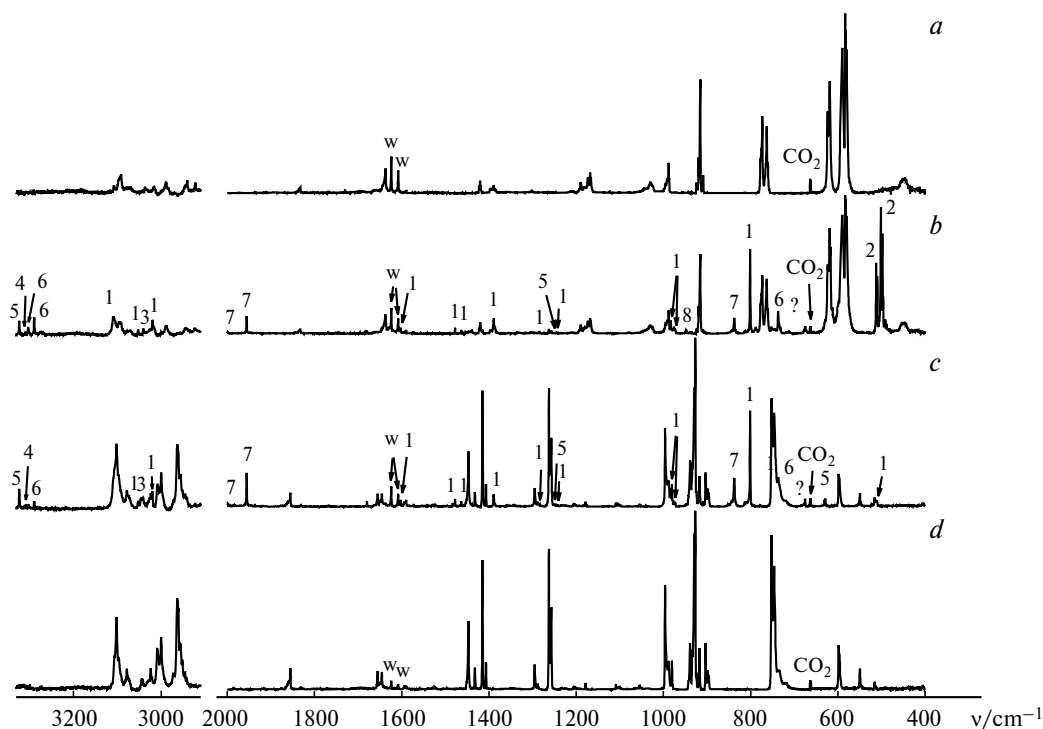


Fig. 1. Matrix IR spectra of AlSiCl_3 (a), products of pyrolysis of AlSiCl_3 (b) and AlCl (c) at $1000\text{ }^\circ\text{C}$, and unpyrolyzed AlCl (d). The bands of the following compounds are marked: 1, C_3H_5 ; 2, SiCl_2 ; 3, $c\text{-C}_3\text{H}_5$; 4, propargyl radical $\text{HC}\equiv\text{CCH}_2$; 5, $\text{HC}\equiv\text{CMe}$; 6, $\text{HC}\equiv\text{CH}$; 7, $\text{H}_2\text{C}=\text{C}=\text{CH}_2$; 8, $\text{H}_2\text{C}=\text{CH}_2$; ?, non-identified products; w, water; and CO_2 , carbon dioxide (H_2O and CO_2 are always present in the matrices because of desorption of these compounds from the internal surface of the vacuum systems and the presence of microleakages in the vacuum setups).

In addition to the bands of the listed products, a number of weak bands was observed in the IR spectra, and the most noticeable of these bands are included in Table 2. The low intensity of these bands impeding their assignment implies their belonging to products of secondary reactions of transformation of primary products or minor directions of the decomposition of AlSiCl_3 .

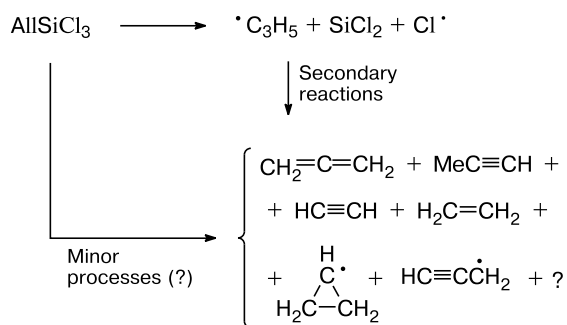
Annealing of the matrices resulted in the weakening of bands of the labile species (C_3H_5 , $c\text{-C}_3\text{H}_5$, and $\text{HC}\equiv\text{CCH}_2$, SiCl_2) because of the decay of their decay in intermolecular reactions upon diffusion in the softened matrices. However, even for matrix annealing at 41 K for 10 min , the band intensities of radical C_3H_5 decreased by not more than twice, indicating a relatively low efficiency of these reactions. For the photolysis of the matrices with the full light of a mercury lamp, in addition to the disappearance of the band belonging to $c\text{-C}_3\text{H}_5$, the bands of radical C_3H_5 appreciably decreased and a series of new weak bands of non-identified products appeared.

Thus, the observed pyrolytic transformations of AlSiCl_3 can be presented by Scheme 1.

The main direction of the thermal decomposition of AlSiCl_3 is the decomposition to SiCl_2 , C_3H_5 , and, as a consequence of the material balance, to atomic Cl . This decomposition can include the primary detachment of SiCl_2



Scheme 1



which is a reaction reverse to one of the characteristic reactions of silylenes: insertion in the $\sigma\text{-C}-\text{Cl}$ bond⁷ followed by $\text{C}-\text{Cl}$ bond cleavage in the formed AlCl , the more so AlCl itself is known as a thermal precursor of C_3H_5 .^{9,11}

To check this assumption, we carried out experiments on the pyrolysis of AlCl in the same temperature range (the matrix IR spectrum of this compound is shown in Fig. 1, d, also see Refs 41 and 42). Like AlSiCl_3 , AlCl began to decompose at $\sim 850\text{ }^\circ\text{C}$. The degree of decomposition increased with temperature, and the formation of the same hydrocarbon products as in experiments on the pyrolysis of AlSiCl_3 was observed (see Fig. 1, c), although

Table 1. Experimental (Ar matrix, 12 K) and calculated (B3LYP/6-31G(2df,p)) vibration frequencies (ν/cm^{-1}) of AllSiCl_3 , their intensities ($I/\text{km mol}^{-1}$), and their assignment to normal modes based on the calculations

ν_{exp}	$\nu_{\text{calcd}} (I)$		Assignment	ν_{exp}	$\nu_{\text{calcd}} (I)$		Assignment
	<i>gauche</i> -conformer	<i>cis</i> -conformer			<i>gauche</i> -conformer	<i>cis</i> -conformer	
—	3233 (10)	3235 (14)	$\nu_{\text{ac}}(=\text{CH}_2)$	988 m	—	—	—
3093 w	3157 (5)	3130 (17)	$\nu(=\text{CH})$	987 sh	—	—	—
3016 w	3146 (6)	3157 (2)	$\nu_{\text{c}}(=\text{CH}_2)$	923 w	—	—	—
2989 w	3081 (2)	3034 (2)	$\nu_{\text{ac}}(\text{CH}_2)$	919 m	941 (13)	936 (11)	$\nu(\text{C}-\text{C}) + \rho(=\text{CH}_2)$
—	3025 (5)	3004 (7)	$\nu_{\text{c}}(\text{CH}_2)$	916 sh	—	—	—
1841 w	—	—	—	915 s	952 (31)	956 (35)	$\omega(=\text{CH}_2)$
1836 sh	—	—	—	909 m	—	—	—
1834 sh	—	—	—	778 sh	—	—	—
1832 w	—	—	—	775 sh	—	—	—
1637 m	1708 (9)	1718 (19)	$\nu(\text{C}=\text{C})$	773 s	793 (41)	812 (28)	$\rho(\text{CH}_2)$
1423 sh	—	—	—	772 sh	—	—	—
1422 sh	—	—	—	767 sh	—	—	—
1420 m	1459 (5)	1462 (5)	$\delta_{\text{c}}(=\text{CH}_2)$	765 sh	—	—	—
1419 sh	—	—	—	763 s	759 (32)	711 (59)	$\nu(\text{Si}-\text{C})$
1397 w	—	—	—	760 sh	—	—	—
1388 m	1427 (6)	1421 (5)	$\delta_{\text{c}}(\text{CH}_2)$	623 s	—	—	—
1304 w	—	—	—	619 s	624 (82)	517 (0)	$\nu(\text{Si}-\text{C}) + \delta(=\text{CH})$
1300 w	1332 (1)	1347 (2)	$\delta(=\text{CH})$	590 vs	—	—	—
1212 sh	—	—	—	589 sh	580 (172)	586 (170)	$\nu(\text{Si}-\text{Cl})$
1210 w	—	—	—	583 vs	—	—	—
1207 sh	—	1274 (7)	$\omega(\text{CH}_2)$	582 sh	569 (134)	577 (168)	$\nu(\text{Si}-\text{Cl})$
1190 m	—	—	—	580 sh	—	—	—
1182 w, br	1213 (3)	1170 (12)	$\tau(\text{CH}_2)$	—	441 (25)	411 (10)	$\nu(\text{Si}-\text{Cl})$
1173 m	—	—	—	—	395 (0)	534 (32)	$\delta(\text{C}=\text{C}-\text{C})$
1168 m	1201 (6)	—	$\omega(\text{CH}_2)$	—	297 (1)	240 (7)	—
1166 sh	—	—	—	—	220 (7)	213 (5)	—
1044 sh	—	—	—	—	207 (5)	208 (2)	—
1030 m	1060 (21)	1059 (0)	$\nu(\text{C}-\text{C}) + \rho(=\text{CH}_2)$	—	171 (2)	164 (1)	—
1024 sh	—	—	—	—	149 (0)	153 (1)	—
998 sh	—	—	—	—	120 (0)	57 (0)	—
995 sh	—	—	—	—	65 (0)	101 (0)	—
992 sh	—	—	—	—	48 (0)	67 (0)	—
989 sh	1031 (6)	1034 (9)	$\tau(=\text{CH}_2) + \delta(=\text{CH})$	—	—	—	—

Note: br is broad, s is strong, vs is very strong, w is weak, m is medium, and sh is shoulder; for the most part of bands, matrix splitting is observed resulting in the appearance of shoulders at the major absorption bands; matrix splitting is partially eliminated by matrix annealing.

the relative amount of allene was a little higher and those of acetylene and ethylene were noticeably lower than for the pyrolysis of AllSiCl_3 at the same temperatures. Of the most intense non-assigned bands presented in Table 2, only the band at 674 cm^{-1} was observed in the spectra, whereas the bands at 976 , 974 , and 788 cm^{-1} were absent, indicating their belonging to the minor products specific for the decomposition of AllSiCl_3 . Even at $1000 \text{ }^\circ\text{C}$ (see Fig. 1, c) the intensity of the strongest bands of non-

decomposed AllCl exceeded the intensity of the strongest band of allyl radical at 801 cm^{-1} (see Fig. 1, c); *i.e.*, a considerable portion of AllCl underwent no decomposition, whereas no formation of AllCl was observed for the pyrolysis of AllSiCl_3 . Therefore, the pyrolysis of AllSiCl_3 proceeds *via* a different route.

In the theoretical analysis of AllSiCl_3 decomposition, we considered three possible routes of transformations of this compound (Scheme 2).

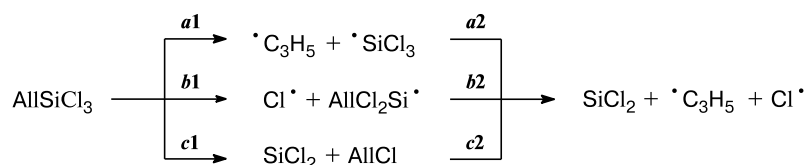
Scheme 2

Table 2. IR bands of the pyrolysis products of AllSiCl₃

ν/cm^{-1}	Product	ν/cm^{-1}	Product
3776 w	H ₂ O	1331 vw	HC≡CH
3756 w	H ₂ O	1317 vw	C ₃ H ₅
3711 w	H ₂ O	1284 vw	C ₃ H ₅
3323 w	HC≡CMe	1247 vw	HC≡CMe
3308 vw	HC≡CCH ₂	1183 vw	C ₃ H ₅
3303 vw	HC≡CH	984 w	C ₃ H ₅
3289 w	HC≡CH	976 vw	Was not assigned*
3109 vw, br	C ₃ H ₅	974 sh	Was not assigned*
3053 vw	C ₃ H ₅	973 sh	C ₃ H ₅
3040 vw	c-C ₃ H ₅	948 vw	H ₂ C=CH ₂
3027 vw	C ₃ H ₅	844 sh	H ₂ C=C=CH ₂
3020 vw	C ₃ H ₅	837 w	H ₂ C=C=CH ₂
2888 w	H ³⁵ Cl	801 s	C ₃ H ₅
2886 sh	H ³⁷ Cl	788 w, br	Was not assigned*
2345 w	CO ₂	737 m	HC≡CH
2339 w	CO ₂	734 sh	HC≡CH
2137 vw	HC≡CMe	731 sh	HC≡CH
1998 vw	H ₂ C=C=CH ₂	687 vw	HC≡CCH ₂
1956 m	H ₂ C=C=CH ₂	674 w, br	Was not assigned
1680 vw	H ₂ C=C=CH ₂	664 w	CO ₂
1624 w	H ₂ O	662 w	CO ₂
1608 w	H ₂ O	630 sh	HC≡CMe
1603 vw	C ₃ H ₅	512 s	²⁸ Si ³⁵ Cl ₂
1589 vw	H ₂ O	510 m	²⁸ Si ³⁵ Cl ³⁷ Cl
1477 w	C ₃ H ₅	507 vw	²⁹ Si ³⁵ Cl ₂
1463 vw	C ₃ H ₅	506 vw	²⁸ Si ³⁷ Cl ₂
1440 vw	H ₂ C=CH ₂	501 s	²⁸ Si ³⁵ Cl ₂
1389 w	C ₃ H ₅	498 s	²⁸ Si ³⁵ Cl ³⁷ Cl
1386 sh	C ₃ H ₅	496 m	²⁸ Si ³⁷ Cl ₂ + ²⁹ Si ³⁵ Cl ₂
1335 vw	HC≡CH	493 w	²⁹ Si ³⁵ Cl ³⁷ Cl
1242 vw	C ₃ H ₅	491 w	³⁰ Si ³⁵ Cl ₂
		488 vw	³⁰ Si ³⁵ Cl ³⁷ Cl

* The band belongs to a non-established minor product of AllSiCl₃ decomposition (was not observed for the thermal decomposition of AllCl).

As follows from the set of the major final products (SiCl₂, C₃H₅, and Cl), the thermal decomposition of AllSiCl₃ comes to the cleavage of the Si—C and Si—Cl bonds. The simultaneous cleavage of two bonds is energetically rather expensive and, hence, the decomposition should undoubtedly consist of at least two steps. In the case of the decomposition *via* route **a** (see Scheme 2), the initial cleavage of the Si—C bond occurring in AllSiCl₃ (reaction **a1**) is followed by the Si—Cl bond cleavage (reaction **a2**) in trichlorosilyl radical (SiCl₃) formed in the first step. Route **b** consists of the initial cleavage of the Si—Cl bond (reaction **b1**) and subsequent Si—C bond cleavage (reaction **b2**) in allyldichlorosilyl radical (AllSiCl₂). Route **c** is also included into the consideration for comparison as a route that certainly does not occur. Route **c** starts from the detachment of SiCl₂ from the AllSiCl₂ molecule (reaction **c1**) and completes with the C—Cl bond cleavage in the AllCl molecule (reaction **c2**).

According to the calculations of six listed reactions, only reaction **c1** proceeds with the formation of the transition state(s) (TS(s)). The absence of TSs in the reactions of simple bond cleavage, such as reactions **a1**, **b1**, and **c2**, is a fairly known fact related to the absence of barriers in recombination of radicals (*i.e.*, in reactions inverse to the presented ones) and the principle of microscopic reversibility. The absence of TSs in reactions **a2** and **b2** is consistent with the data of calculations for similar systems.⁴³

The calculated structures of molecules involved in the transformations presented in Scheme 2 and transition states for reaction **c1** (TS1—TS3) are shown in Fig. 2. The structures of more stable *gauche*-conformers (*g*-AllSiCl₃ and *g*-AllCl) are presented for AllSiCl₃ and AllCl. According to the calculations, the energies of less stable *cis*-conformers of these molecules are higher by 2.0 and 0.4 kcal mol⁻¹, respectively. Note that the calculated difference in enthalpies under normal conditions for *cis*- and *gauche*-conformers of AllCl is 0.35 kcal mol⁻¹, which almost coincides with the value of 0.42±0.6 kcal mol⁻¹, which was experimentally obtained in solutions in liquid Xe in a temperature range of 176—216 K.⁴¹ Such a small difference in energies of the conformers is insubstantial for the analyzed processes, and the transformations involving only *g*-AllSiCl₃ and *g*-AllCl will be considered further, the more so all found TSs of reaction **c1** are related to these conformers.

Many conformers can exist in the case of radical AllSiCl₂. By analogy to AllSiCl₃ and AllCl, it is reasonable to assume that the conformers of AllSiCl₂ formed by the rotation of the CH₂SiCl₂ group relative to the simple C—C bond do not strongly differ in energy. To check the influence of the turning angle of the SiCl₂ group relative to the Si—C bond, we calculated conformers AllSiCl₂-1, AllSiCl₂-2, and AllSiCl₂-3 (see Fig. 2). As expected, their energies differ insignificantly (less than by 1 kcal mol⁻¹) and, therefore, only conformer AllSiCl₂-1 was considered in an analysis of the thermochemical characteristics.

The total energies, enthalpies, and free energies at different temperatures for the structures shown in Fig. 2 are given in Tables 3 and 4. The changes in the energy, enthalpy, and free energy at different temperatures for the reactions shown in Scheme 2 are presented in Tables 5 and 6.

Unfortunately, the calculated and experimentally obtained^{47,48} values of ΔH° (see Table 5) can be compared only for two reactions (**a2** and **c2**). As can be seen, the G4(MP2) calculations reproduce well the experimental data. The agreement is also observed between ΔH and ΔG calculated at the G4(MP2) level for different temperatures for reaction **a2** and the corresponding values obtained earlier by the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVDZ method.⁴⁹

The typical values of energies (*D*) of the Si—C and Si—Cl bonds are about 90 and 110 kcal mol⁻¹, respectively (see Ref. 48); *i.e.*, the Si—Cl bonds are appreciably stron-

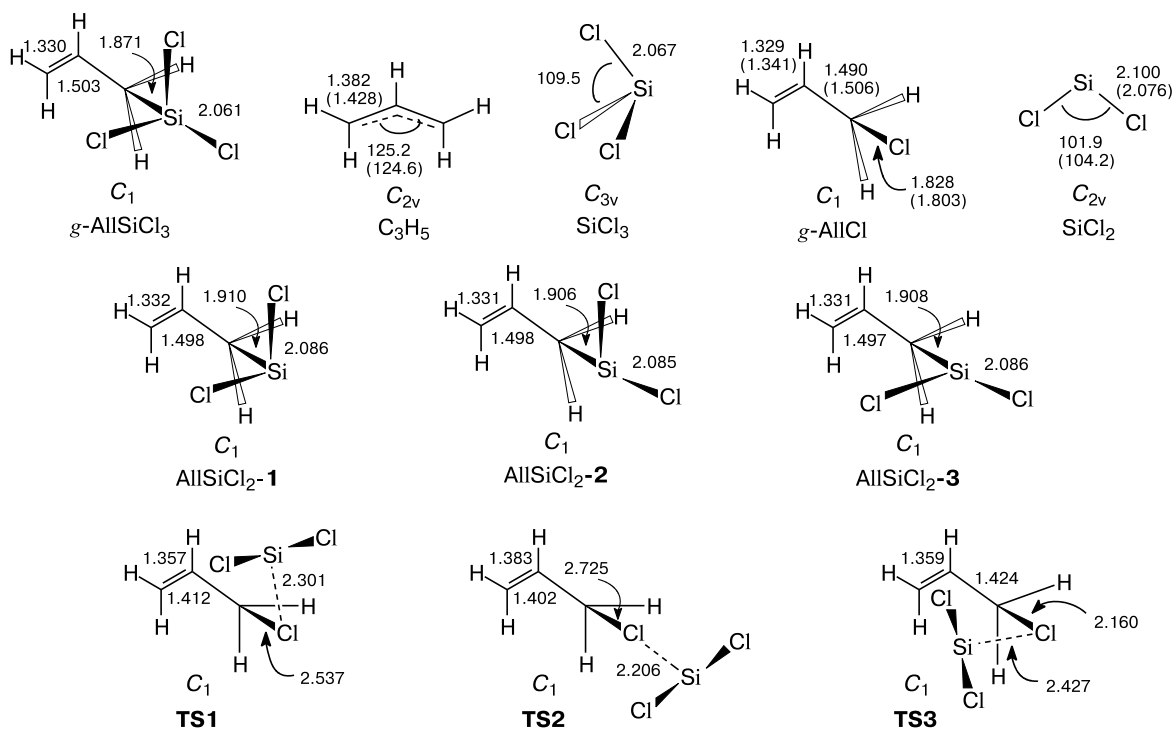


Fig. 2. Structures of molecules involved in the transformations (see Scheme 2) according to the B3LYP/6-31G(2df,p) calculations. Bond lengths are given in Å, and angles are given in deg. The experimental values for AllCl,⁴⁴ C₃H₅,⁴⁵ and SiCl₂⁴⁶ are given in parentheses.

ger than the Si—C bonds. The presence of alkyl groups at the Si atom results in some increase in the strength of other bonds at this atom, such as Si—H, Si—C, Si—Si, and Si—Cl.⁴⁸ The more alkyl groups are added to the Si atom, the higher is the strengthening of these bonds. As shown by a comparison of the bond energies in SiH₃Cl and SiMe₃Cl,⁴⁸ their difference can reach ~10 kcal mol⁻¹.

The effect of presence of Cl atoms and the dependence on their number are less pronounced: the $D(\text{Si—Cl})$ values in SiH₃Cl and SiCl₄ are 109 and 110 kcal mol⁻¹, respectively,⁴⁸ *i.e.*, almost coincide. Unfortunately, as far as we know, literature data on the influence of the allyl group on the strength of the bonds at the Si atom and on the $D(\text{Si—C})$ value for AllSiCl₃ are lacking. Nevertheless, it can be as-

Table 3. Total energies including ZPE (E_0) and enthalpies (H) at different temperatures and $p = 1$ atm for the compounds involved in the transformations (see Scheme 2) according to the G4(MP2) calculations

Compound	$-E_0/\text{au}$	$-H/\text{au}$ at T/K						
		298.15	600	900	1100	1300	1500	1700
g-AllSiCl ₃ ^a	1785.663971	1785.653559	1785.634201	1785.610361	1785.592949	1785.574693	1785.555804	1785.536435
C ₃ H ₅	117.049137	117.044338	117.034593	117.021310	117.011178	117.000306	116.988863	116.976981
SiCl ₃	1668.493239	1668.487047	1668.478213	1668.468978	1668.462744	1668.456480	1668.450197	1668.443902
AllSiCl ₂ -1 ^a	1325.786993	1325.777947	1325.761054	1325.739891	1325.724313	1325.707911	1325.690888	1325.673394
Cl	459.703691	459.701330	459.698940	459.696565	459.694982	459.693398	459.691815	459.690232
g-AllCl ^a	576.862832	576.857049	576.845666	576.830220	576.818470	576.805898	576.792703	576.779033
SiCl ₂	1208.683756	1208.678941	1208.672666	1208.6666167	1208.661789	1208.657395	1208.652990	1208.648579
TS1	1785.507271	1785.496363	1785.477200	1785.454000	1785.437131	1785.419465	1785.401192	1785.382452
TS3	1785.533392	1785.522926	1785.504064	1785.481005	1785.464186	1785.446552	1785.428301	1785.409577
TS2	1785.530444	1785.519419	1785.500184	1785.476943	1785.460057	1785.442380	1785.424100	1785.405355

^a The values of E_0 , $H(298.15 \text{ K})$, and $G(298.15 \text{ K})$ for *cis*-AllSiCl₃: -1785.660752 , -1785.650256 , and -1785.697395 au; for *cis*-AllCl: -576.862221 , -576.856500 , and -576.890137 au; for AllSiCl₂-2: -1325.785828 , -1325.776739 , and -1325.821179 au; and for AllSiCl₂-3: -1325.785421 , -1325.776321 , and -1325.820807 au.

Table 4. Total free Gibbs energies (G) calculated at the G4(MP2) level at different temperatures and $p = 1$ atm for the compounds involved in the transformations (see Scheme 2)

Com- pound	$-G/\text{au}$ at T/K						
	298.15	600	900	1100	1300	1500	1700
g-AllSiCl ₃	1785.700605	1785.755272	1785.820830	1785.869388	1785.921206	1785.975893	1785.033137
C ₃ H ₅	117.073638	117.106720	117.145546	117.174189	117.204751	117.237036	117.270880
SiCl ₃	1668.523563	1668.563907	1668.608744	1668.640449	1668.673297	1668.707113	1668.741771
AllSiCl ₂ -1	1325.822200	1325.873109	1325.933585	1325.978226	1326.02579	1326.075934	1326.128387
Cl	459.719368	459.738562	459.758886	459.772899	459.787202	459.801750	459.816509
g-AllCl	576.890882	576.929140	576.974091	577.007263	577.042658	577.080042	577.119223
SiCl ₂	1208.711042	1208.745947	1208.783989	1208.810625	1208.838063	1208.866181	1208.894888
TS1	1785.545220	1785.601687	1785.668826	1785.718298	1785.770925	1785.826328	1785.884205
TS3	1785.570255	1785.625051	1785.690405	1785.738665	1785.790074	1785.844253	1785.900905
TS2	1785.569598	1785.627444	1785.695981	1785.746390	1785.799958	1785.856302	1785.915122

Table 5. Relative energies including ZPE (ΔE_0) and enthalpies (ΔH) obtained at the G4(MP2) level at different temperatures and $p = 1$ atm for the reactions presented in Scheme 2

Reaction	ΔE_0 /kcal mol ⁻¹	$\Delta H/\text{kcal mol}^{-1}$ at T/K						
		298.15	600	900	1100	1300	1500	1700
a1	76.3	76.7	76.2	75.3	74.7	74.0	73.3	72.5
b1	108.7	109.4	109.3	109.1	109.0	108.8	108.6	108.4
TS1	98.3	98.6	98.5	98.1	97.8	97.4	97.0	96.6
TS2	83.8	84.2	84.1	83.7	83.4	83.0	82.6	82.3
TS3	81.9	82.0	81.7	81.2	80.8	80.4	80.0	79.6
c1	73.7	73.8	72.7	71.5	70.7	69.9	69.1	68.3
a2	66.4	67.0 (66±3)*	66.9	66.7	66.5	66.3	66.1	65.9
b2	33.2	34.3	33.8	32.9	32.2	31.5	30.8	30.0
c2	69.0	69.9 (69)*	70.4	70.5	70.5	70.4	70.3	70.2
g-AllSiCl ₃ → → C ₃ H ₅ + SiCl ₂ + Cl	142.7	143.7	143.1	142.0	141.2	140.3	139.4	138.5

* The values of ΔH° obtained on the basis of the available experimental data^{47,48} on ΔH_f° are given in parentheses.

Table 6. Free Gibbs energies (ΔG) calculated at the G4(MP2) level at different temperatures and $p = 1$ atm for the reactions presented in Scheme 2

Reaction	$\Delta G/\text{kcal mol}^{-1}$ at T/K						
	298.15	600	900	1100	1300	1500	1700
a1	64.9	53.1	41.8	34.4	27.1	19.9	12.9
b1	99.8	90.1	80.5	74.2	67.9	61.6	55.4
TS1	97.5	96.4	95.4	94.8	94.3	93.9	93.5
TS2	82.2	80.2	78.3	77.2	76.1	75.0	74.1
TS3	81.8	81.7	81.8	82.0	82.3	82.6	83.0
c1	61.9	50.3	39.4	32.3	25.4	18.6	11.9
a2	58.5	49.8	41.3	35.7	30.1	24.6	19.1
b2	23.5	12.8	2.5	-4.1	-10.7	-17.1	-23.5
c2	61.4	52.6	43.7	37.8	31.8	25.9	20.0
g-AllSiCl ₃ → → C ₃ H ₅ + SiCl ₂ + Cl	123.3	102.9	83.1	70.1	57.2	44.5	31.9

sumed that the effects of the All and Me groups are similar, and by analogy with the data on $D(C-C)$ in hydrocarbons and chlorinated hydrocarbons,⁴⁷ the bond between the Si atom and allyl group should be much weaker (in the case of hydrocarbons, by ~ 30 kcal mol⁻¹)⁴⁷ than the typical Si-C bond. In fact, the value of $D(Si-C)$ in AllSiCl₃ (77 kcal mol⁻¹) obtained by us in the calculations is ~ 13 kcal mol⁻¹ lower than the typical value and the $D(Si-Cl)$ value (109 kcal mol⁻¹) coincides with the typical one.

A change in the enthalpy for all the six reactions and the activation enthalpy for reaction **c1** depend weakly on the temperature (see Table 5) and insignificantly decreases with temperature. The least endothermic reaction is the detachment of SiCl₂ from AllSiCl₂ (reaction **b2**), the ΔH° value of this reaction is 34 kcal mol⁻¹; *i.e.*, the Si-C bond in radical AllSiCl₂ is substantially weakened.

Of the primary reactions (**a1**, **b1**, **c1**), the decomposition of AllSiCl₃ to AllCl and SiCl₂ (reaction **c1**) is the least endothermic at all temperatures. However, this reaction to occur needs to surmount the activation barrier (**TS3**) with the activation enthalpy exceeding the enthalpy of AllSiCl₃ decomposition to C₃H₅ and SiCl₃ (reaction **a1**). Reaction **b1** is the most endothermic process at all temperatures. Thus, starting from the thermochemical data only, it can be expected that the main primary process of AllSiCl₃ decomposition at the temperatures 1120–1270 K is the cleavage of the Si-C bond, whereas the detachment of SiCl₂ to form AllCl is the next in accessibility.

The values of changes in the free Gibbs energies should be compared for a more reliable establishment of the preferential process. In all cases, except for the formation of **TS1–TS3**, the values of ΔG decrease noticeably with temperature, which is determined by the contribution of the entropy factor. It should be mentioned that for **TS1** and **TS2** the ΔG values also somewhat decrease, whereas ΔG of the formation of **TS3** slightly increases (see Table 6). Although reactions **a1**, **a2**, **b1**, **b2**, and **c2** are decomposition reactions with the formation of two species, a decrease in ΔG with temperature for these reactions differs noticeably (from 39 kcal mol⁻¹ for reaction **a2** to 52 kcal mol⁻¹ for reaction **a1**). Nevertheless, the data on both ΔG and ΔH indicate that it is the decomposition of AllSiCl₃ to C₃H₅ and SiCl₃ (reaction **a1**) which is the main direction of the primary transformations of this compound. The reaction of AllSiCl₃ decomposition to AllSiCl₂ and Cl (reaction **b1**) is thermodynamically significantly less favorable at elevated temperatures, whereas reaction **c1**, which is thermodynamically more favorable and kinetically accessible at room temperature compared to reaction **b1**, becomes kinetically least accessible beginning from 900 K.

Radical SiCl₃ formed in step **a1** is very unstable with respect to the decomposition to SiCl₂ and Cl (reaction **a2**), and the ΔG value for its decomposition is comparable with the value for primary reaction **a1**. This explains the formation of SiCl₂ upon the pyrolysis of AllSiCl₃ in the absence

of detectable amounts of SiCl₃, although, taking into account that the most intense band of SiCl₃ at 582 cm⁻¹ exists⁵⁰ in the same range as the intense band of Si-Cl vibrations of non-decomposed AllSiCl₃, we cannot completely exclude its presence in the matrix in minor amounts. The obtained data also indicate that if reaction **b1** would occur under the considered conditions, we could not detect the formation of radical AllSiCl₂, since its existence at $T > 1100$ K is thermodynamically unfavorable.

Thus, the decomposition of AllSiCl₃ represents a typical decomposition of a precursor molecule to two radicals: C₃H₅ and SiCl₃. However, since the Si-Cl bond in radical SiCl₃ is weak and its energy is somewhat lower than the energy of the Si-C bond in the initial AllSiCl₃, this radical undergoes the further decomposition, resulting in the formation of three intermediates from AllSiCl₃, *viz.*, C₃H₅, SiCl₂, and Cl, which belong to different classes of labile compounds. This determines that the whole process is very untypical of the processes of generation of labile intermediates. It is most likely that a similar stepped decomposition is inherent in other allylsilanes. For example, the formation of C₃H₅ was observed for the pyrolysis of AllSiMe₃, whereas no SiMe₃ radical was detected.⁵¹ Undoubtedly, a deeper fragmentation of the trimethylsilyl radical occurred in this case, which is indicated, in particular, by the band of CH₃ in the detected matrix IR spectra of the pyrolysis products.⁵¹

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