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Quantum chemical simulation of silicon tetrachloride hydrogenation

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The quantum chemical calculation of the activation parameters of the reduction of a $SiCl_4$ molecule with molecular hydrogen, atomic hydrogen, and atomic chlorine was performed. The energy parameters were determined within the scope of the density functional theory (DFT) with the complete geometry optimization by the unrestricted UB3LYP/6-311+G(d) method. The calculated activation energies allow one to exclude the participation of molecular hydrogen in processes of dehalogenation of chlorosilanes.

Key words: chlorosilanes, hydrogenation, dehalogenation, molecular hydrogen, atomic hydrogen, atomic chlorine, quantum chemical calculations, UB3LYP/6-311+G(d) method, transition state, activation energies.

Considerable attention is given to the study of reactions of silicon tetrachloride hydrogenation due to their importance for the technology of manufacture of semiconducting silicon.

Several methods for carrying out this reaction are described. One of them is plasmochemical hydrogenation in high-pressure (up to $1.3 \cdot 10^4$ Pa) hydrogen plasma. The high yield of $SiHCl_3$ at the pressure higher than $0.91 \cdot 10^4$ Pa is considered[1] to indicate the formation of $SiHCl_3$ involving vibration-excited hydrogen molecules H_2* in the reactions

$$H_2 + e \rightarrow H_2^- \rightarrow H_2^* + e,$$

$$SiCl_4 + H_2^* \rightarrow SiHCl_3 + HCl.$$

The method of catalytic hydrogenation of $SiCl_4$ with aldehydes and ketones by passing a mixture of $SiCl_4$ and CH_2O above γ-Al_2O_3 has earlier[2] been developed. The reaction products contained 86 wt.% SiH_3Cl and SiH_2Cl_2. The yield of SiH_2Cl_2 increased when a smaller amount of formaldehyde was introduced into the solution. Zinc, copper, and aluminum and their silicides were used as catalysts. The mechanism of the process was proposed,[2] whose specific feature is the determining role of hydrogen atoms

$$2\,H_2CO \rightarrow 4\,H^\cdot + 2\,CO,$$

$$SiCl_4 + 2\,H^\cdot \rightarrow :SiCl_2 + 2\,HCl,$$

$$:SiCl_2 + 2\,H^\cdot \rightarrow SiH_2Cl_2.$$

The method of $SiCl_4$ hydrogenation with hydrogen in the presence of titanium hydride of sponge titanium was reported.[3] In the temperature range 250—400 °C the yield of $SiHCl_3$ in a mixture with SiH_2Cl_2, SiH_3Cl, and SiH_4 reached 21 wt.%. The scheme of the process was described by the following reactions:

$$4\,SiCl_4 + TiH_2 + H_2 \rightarrow 4\,SiHCl_3 + TiCl_4, \quad (1)$$

$$2\,SiCl_4 + TiH_2 + H_2 \rightarrow 2\,SiH_2Cl_2 + TiCl_4, \quad (2)$$

$$4\,SiCl_4 + 3\,TiH_2 + 3\,H_2 \rightarrow 4\,SiH_3Cl + 3\,TiCl_4, \quad (3)$$

$$SiCl_4 + TiH_2 + H_2 \rightarrow SiH_4 + TiCl_4. \quad (4)$$

Atomic hydrogen is not evidently involved in reactions (1)—(4).

The mechanism of the reaction between $^\cdot SiH_3$ and $Cl^\cdot$ was studied.[4] This reaction was shown to proceed predominantly *via* the mechanism of direct abstraction with the formation of triplet silylene

$$^\cdot SiH_3 + Cl^\cdot \rightarrow :SiH_2 + HCl.$$

A vibration-excited SiH_3Cl molecule can also be formed by this interaction[4]

$$^\cdot SiH_3 + Cl^\cdot \rightarrow SiH_3Cl^*,$$

which decomposes in one of the following reactions:

$$SiH_3Cl^* \rightarrow :SiHCl + H_2,$$

$$SiH_3Cl^* \rightarrow :SiH_2 + HCl,$$

$$SiH_3Cl^* \rightarrow {}^\cdot SiH_2Cl + H^\cdot,$$

$$SiH_3Cl^* \rightarrow {}^\cdot SiH_3 + Cl^\cdot.$$

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The quantum chemical studies of the reaction of silylene with hydrogen by the B3LYP/6-311+G(d) method were also carried out.[5] Silylene is inserted at the H—H bond to form monosilane

$$:SiH_2 + H_2 \rightarrow SiH_4.$$

The quantum chemical studies of the complex formation of carbene analogs, including silylenes, with Lewis acids were carried out.[6] The reactions with the silicon-centered radicals were considered in detail.[7]

In addition, the reactions of $SiCl_4$ and SiH_4 with atomic hydrogen were studied[8]

$$SiH_4 + H^{\bullet} \rightarrow {}^{\bullet}SiH_3 + H_2,$$

$$SiCl_4 + H^{\bullet} \rightarrow {}^{\bullet}SiCl_3 + HCl.$$

The calculations were performed within the scope of the density functional theory (DFT) in the 6-311++G(3df,2pd) basis set.

At present quantum chemical calculations recommended themselves as a reliable method for studying mechanisms of chemical reactions, and they were multiply used to establish the reaction mechanisms in organosilicon chemistry. The mechanisms of reactions of the SiH_n + $^{\bullet}F$ type were discussed on the basis of the results of quantum chemical calculations,[9] and the mechanism of the reaction $^{\bullet}SiH_3$ + $^{\bullet}SiH_3$ was studied.[10,11] The problems appeared during the study of the mechanisms of multichannel reactions of the type radical—radical and examples of such reactions were considered.[12]

The purpose of this study is to perform the quantum chemical calculations of the activation parameters of the reactions of reduction of $SiCl_4$ molecules with hydrogen.

Calculation procedure

The energy parameters of the hydrogenation of $SiCl_4$ were determined within the scope of DFT with the complete geometry optimization by the unrestricted UB3LYP/6-311+G(d) method.[13,14] The obtained values were compared with the experimental values.[15—20]

In the calculations of the transition states, the saddle points were found by the direct optimization[21] and using the QTS2 and QTS3 methods.[22] The presence of only one imaginary frequency served as a criterion for the achievement of the transition state for the corresponding molecular system. Correctness of the found reaction route for a specific transition state was checked by the reduction of the reaction coordinates in terms of the IRC method.[23]

All quantum chemical calculations were performed using the GAUSSIAN-03 program package.[24]

Results and Discussion

The study of $SiCl_4$ hydrogenation is presently rather urgent; however, the commonly accepted mechanism of this process is lacking. The reaction can involve dehydrogenating agents of several types: molecular hydrogen, atomic hydrogen, and atomic chlorine.

To verify the obtained results, we compared the calculated and experimental values of the main geometric parameters and the enthalpies of formation of molecules involved in the reactions studied (Tables 1 and 2). It is seen from the data presented in Table 1 that the geometric parameters of the molecules calculated by the UB3LYP/6-311+G(d) method are rather well consistent with the experimental values (see also Ref. 25). This suggests that the results of the calculations are correct.

A comparison of the calculated and experimental enthalpies of formation of compounds SiH_xCl_y is presented in Table 2. The results obtained suggest that the enthalpies of formation of the organosilicon compounds calculated by the UB3LYP/6-311+G(d) method also agree well with the experimental values.

At the first stage of the study we determined the geometric and activation parameters of chlorosilane hydrogenation with molecular hydrogen. The calculations were performed for the following reactions:

$$SiCl_4 + H_2 \rightarrow SiHCl_3 + HCl, \quad (5)$$

$$SiHCl_3 + H_2 \rightarrow SiH_2Cl_2 + HCl, \quad (6)$$

$$SiH_2Cl_2 + H_2 \rightarrow SiH_3Cl + HCl, \quad (7)$$

$$SiH_3Cl + H_2 \rightarrow SiH_4 + HCl. \quad (8)$$

The geometric structures of the transition states of reactions (5)—(8) are presented in Fig. 1, and their most

Table 1. Calculated by the UB3LYP/6-311+G(d) method and experimental geometric parameters of chlorosilanes (bond lengths/Å and bond angles/deg)

Compound	Parameter	Value	
		calculation	experiment
$SiCl_4$	Si—Cl	2.043	2.019[15]
	Cl—Si—Cl	109.5	109.5[15]
$SiHCl_3$	Si—Cl	2.052	2.012[16]
	Si—H	1.465	1.466[16]
	Cl—Si—Cl	109.7	110.6[16]
	Cl—Si—H	109.3	109.4[16]
SiH_2Cl_2	Si—Cl	2.064	2.033[17]
	Si—H	1.471	1.480[17]
	Cl—Si—Cl	110.6	109.7[17]
	Cl—Si—H	108.2	—
	H—Si—H	110.5	110.3[17]
SiH_3Cl	Si—Cl	2.081	2.049[18]
	Si—H	1.478	1.485[18]
	H—Si—Cl	108.3	—
	H—Si—H	110.6	110.2[18]
SiH_4	Si—H	1.483	1.481[18]
	H—Si—H	109.5	109.5[19]

Table 2. Calculated by the UB3LYP/6-311+G(d) method and experimental values of the enthalpies of formation of chlorosilanes under standard conditions ($\Delta_f H°_{298}$)

Compound	$-\Delta_f H°_{298}$/kJ mol^{-1}	
	calculation	experiment
$SiCl_4$	587.78	609.72[20]
SiH_3Cl	200.04	200.86[20]
SiH_2Cl_2	334.94	334.71[20]
$SiHCl_3$	472.93	482.11[20]

important characteristics are listed in Table 3. It should be mentioned that at least two transition states, $\mathbf{TS}_1$ and $\mathbf{TS}_2$, are possible for the reactions considered.

In transition state $\mathbf{TS}_1$ (see Fig. 1 and Table 3) the critical vibrations correspond to the imaginary frequency: shortening of the Cl(4)—H(6) and H(7)—Si(1) distances and elongation of the H(6)—H(7) distance. The intensity of this complicated vibration is maximum compared to the intensities of other vibrations, and migrations of the hydrogen atoms during the reaction are also maximum. This is the indicated vibration that can result in the transformation of the initial substances into the reaction products.

In transition state $\mathbf{TS}_2$ (see Fig. 1 and Table 3) the distances Si(1)—H(7) and Cl(3)—H(7) and also Si(1)—H(6) and Cl(3)—H(6) are alternately shortened and elongated. The both transition states are characterized by high activation energies, which indicates the low probability of dehalogenation due to reactions (5)—(8) in the gas phase.

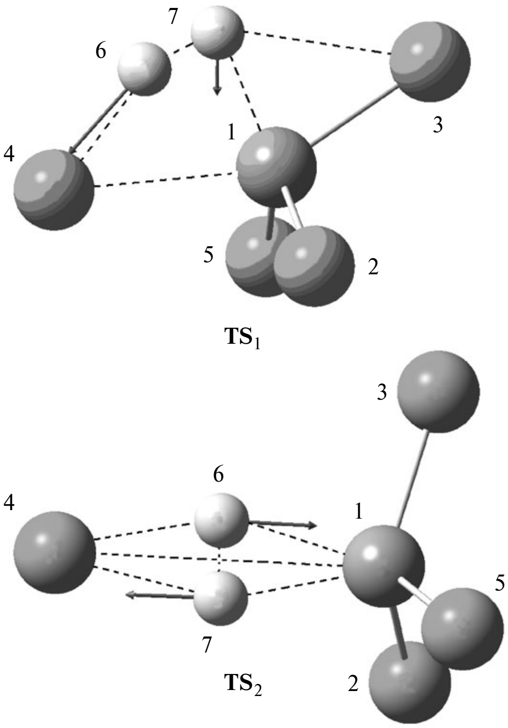

Fig. 1. Geometric structures of transition states $\mathbf{TS}_1$ and $\mathbf{TS}_2$ of the dehalogenation of chlorosilanes SiH_xCl_{4-x} with molecular hydrogen calculated by the UB3LYP/6-311+G(d) method. Here and in Figs 2 and 3, arrows show the vectors of shifts for vibrations with the imaginary frequency, and dotted lines designate the cleaved and formed bonds; digits indicate the numbers of atoms.

At the next stage of calculations we checked the assumption that the dehalogenation occurs under the action

Table 3. Characteristics of transition states $\mathbf{TS}_1$ and $\mathbf{TS}_2$ of the dehalogenation of chlorosilanes SiH_xCl_{4-x} with molecular hydrogen (bond lengths, imaginary frequencies (ν_i), dipole moments (μ), and activation energies of the forward and backward reactions ($E_a^{(+)}$ and $E_a^{(-)}$, respectively)) (see Fig. 1)

Parameter	$SiCl_4$		$SiHCl_3$		SiH_2Cl_2		SiH_3Cl	
	$\mathbf{TS}_1$	$\mathbf{TS}_2$	$\mathbf{TS}_1$	$\mathbf{TS}_2$	$\mathbf{TS}_1$	$\mathbf{TS}_2$	$\mathbf{TS}_1$	$\mathbf{TS}_2$
Si(1)—Cl(2)/Å	2.037	2.036	1.460*	2.042	1.465*	2.043	1.486*	1.473*
Si(1)—Cl(3)/Å	2.094	2.039	2.090	1.469*	1.481*	1.473*	1.491*	1.475*
Si(1)—Cl(4)/Å	2.503	3.635	2.516	3.669	2.587	3.681	2.587	3.695
Si(1)—Cl(5)/Å	2.048	2.036	2.038	2.039	2.059	1.473*	1.469*	1.473*
Si(1)—H(6)/Å	1.892	1.847	1.876	1.844	1.899	1.826	1.873	1.806
Si(1)—H(7)/Å	1.697	1.845	1.695	1.847	1.723	1.826	1746	1.814
Cl(4)—H(6)/Å	1.688	1.888	1.699	1.920	1.708	1.954	1.792	1.984
Cl(4)—H(7)/Å	2.525	1.885	2.544	1.923	2.562	1.954	2.620	1.978
H(6)—H(7)/Å	0.907	0.859	0.906	0.849	0.903	0.847	0.872	0.845
Cl(3)—H(7)/Å	2.507	3.369	2.556	2.751	2.129	2.792	2.106	2.797
ν_i/cm^{-1}	1023.49*i*	2177.43*i*	983.13*i*	2132.11*i*	1046.75*i*	2062.49*i*	971.27*i*	1992.71*i*
μ/D	1.3	4.7	1.3	5.7	3.5	6.6	4.0	7.4
$E_a^{(+)}$/kcal mol^{-1}	46.00	56.48	45.70	57.30	43.81	81.46	60.86	41.45
$E_a^{(-)}$/kcal mol^{-1}	34.79	45.27	36.55	44.24	45.44	42.64	43.00	43.32

* The Si—H bond length.

of such radical species as hydrogen and chlorine atoms. For this purpose, we calculated the transition states and activation parameters of the reactions

$$\mathrm{SiCl_4 + H^{\bullet} \rightarrow {}^{\bullet}SiCl_3 + HCl}, \tag{9}$$

$$\mathrm{HSiCl_3 + H^{\bullet} \rightarrow {}^{\bullet}HSiCl_2 + HCl}, \tag{10}$$

$$\mathrm{H_2SiCl_2 + H^{\bullet} \rightarrow {}^{\bullet}H_2SiCl + HCl}, \tag{11}$$

$$\mathrm{H_3SiCl + H^{\bullet} \rightarrow {}^{\bullet}H_3Si + HCl}. \tag{12}$$

The geometric structures of the transition states of reactions (9)—(12) are shown in Fig. 2, *a*, and their most important properties are presented in Table 4. According to the results obtained (see Tables 3 and 4), the reaction of chlorine atom abstraction by the hydrogen atom is more probable than the reaction of molecular hydrogen with chlorosilane. In the transition state the critical vibration corresponds to the imaginary frequency: the change in the H(6)—Cl(2) (the maximum shift of the atoms) and Cl(2)—Si(1) distances. Similar results were obtained earlier.[8] In addition, the same reaction was studied.[26] The calculations were performed by the UMP4 (SDTQ) and UQCISDCT methods using the 6-311G(d,p) basis set. The obtained values of activation energy are 24.34 and 22.62 kcal mol^{-1}, respectively.

The experimental value of activation energy for this reaction is[26] 9.54±5.17 kcal mol^{-1}. It should be mentioned that the value obtained by us and equal to 9.60 kcal mol^{-1} agrees well with the experimental value. It is most likely that the use of the UB3LYP/6-311+G(d) method is more justified for calculations of these reactions than the use of the UMP4 and UQCISD(T) methods. The geometric parameters of the transition state obtained by us are rather close to the published[26] parameters (the Si(1)—Cl(2) bond lengths coincide (2.290 Å), although the Si(1)—Cl(3), Si(1)—Cl(4), Si(1)—Cl(5), and Cl(2)—H(6) bonds are longer in our case).

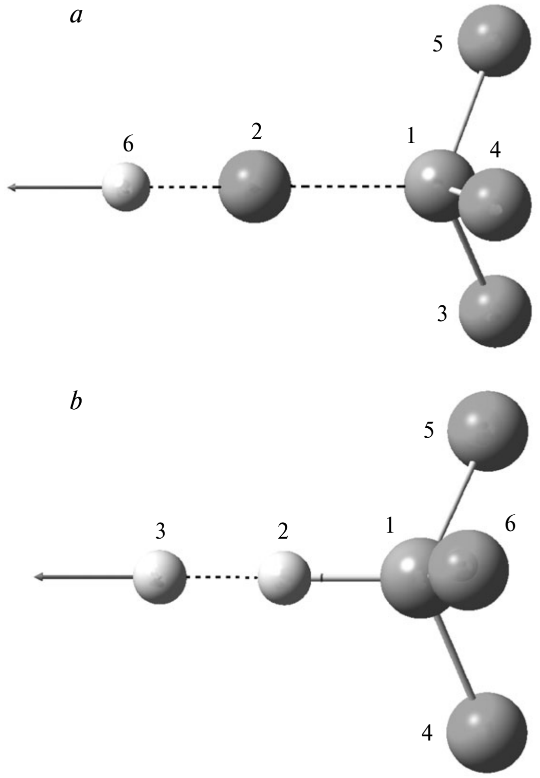

Fig. 2. Geometric structures of the transition states of reactions (9)—(12) (*a*) and the attack of the hydrogen atom of chlorosilane by a hydrogen atom (*b*) calculated by the UB3LYP/6-311+G(d) method.

As can be seen from the data presented in Table 4, the activation energy of the forward reaction of $\mathrm{SiCl_4}$ with $\mathrm{H^{\bullet}}$

Table 4. Characteristics of the transition states of the dehalogenation of chlorosilanes $\mathrm{SiH_xCl_{4-x}}$ with atomic hydrogen (**TS**$_3$) and atomic chlorine (**TS**$_4$) (bond lengths, angles, imaginary frequencies (ν_i), dipole moments (μ), and activation energies of the forward and backward reactions ($E_a^{(+)}$ and $E_a^{(-)}$, respectively))

Parameter	$\mathrm{SiCl_4}$		$\mathrm{SiHCl_3}$		$\mathrm{SiH_2Cl_2}$		$\mathrm{SiH_3Cl}$	
	TS$_3$	**TS**$_4$	**TS**$_3$	**TS**$_4$	**TS**$_3$	**TS**$_4$	**TS**$_3$	**TS**$_4$
Si(1)—Cl(2)/Å	2.290	2.064	2.326	1.480*	2.359	1.472*	2.381	1.478*
Si(1)—Cl(3)/Å	2.054	2.888	1.475*	2.919	1.478*	2.336	1.480*	3.102
Si(1)—Cl(4)/Å	2.054	2.059	2.060	2.068	1.478*	2.091	1.480*	1.484*
Si(1)—Cl(5)/Å	2.054	2.060	2.060	2.061	2.069	1.465*	1.480*	1.479*
Cl(2)—H(6)/Å	1.587	3.545	1.566	3.591	1.552	2.435	1.551	3.700
Cl(3)—Cl(6)/Å	—	2.194	—	2.191	—	2.616	—	2.192
Cl(6)—Cl(3)—Si(1)/deg	—	87.3	—	88.1	—	58.6	—	86.9
Cl(6)—Cl(3)—Si(1)—Cl(2)/deg	—	54.1	—	84.4	—	156.5	—	94.2
ν_i/cm^{-1}	661.06*i*	417.281*i*	600.718*i*	377.971*i*	567.556*i*	190.413*i*	562.752*i*	399.976*i*
μ/D	0.6	0.6	1.2	1.1	1.5	1.4	1.2	2.4
$E_a^{(+)}$/kcal mol^{-1}	9.60	37.47	10.45	38.27	10.72	23.64	10.31	38.59
$E_a^{(-)}$/kcal mol^{-1}	9.65	4.75	9.71	3.92	8.18	25.20	8.10	3.72

* The Si—H bond length.

is lower than that of the backward reaction. The transition to chlorosilanes in which some chlorine atoms are replaced by hydrogen atoms results in an increase in the activation energies of the forward reactions. The major product is radical $^{\cdot}SiCl_3$, which is further stabilized through dimerization, disproportionation, or in the form of $HSiCl_3$. This conclusion is well consistent with the fact that this is trichlorosilane which is one of the major reaction products of thermolysis.[27]

Dehalogenation can occur due to the attack of the chlorine atom of chlorosilane by atomic chlorine to form molecular chlorine and the silicon-centered radical

$$SiCl_4 + Cl^{\cdot} \rightarrow {}^{\cdot}SiCl_3 + Cl_2, \quad (13)$$

$$HSiCl_3 + Cl^{\cdot} \rightarrow {}^{\cdot}HSiCl_2 + Cl_2, \quad (14)$$

$$H_2SiCl_2 + Cl^{\cdot} \rightarrow {}^{\cdot}H_2SiCl + Cl_2, \quad (15)$$

$$H_3SiCl + Cl^{\cdot} \rightarrow {}^{\cdot}H_3Si + Cl_2. \quad (16)$$

The geometric structures of the corresponding transition states for the reactions in the gas phase are shown in Fig. 3, and their most important properties are presented in Table 4. According to the results obtained (see Tables 3 and 4), the reaction of abstraction of the chlorine atom of chlorosilane by the attacking chlorine atom is more probable than the reaction of molecular hydrogen and chlorosilane. In the transition state the critical vibrations of the following type correspond to the imaginary frequency: the Cl(3) and Cl(5), Cl(3) and Si(1) atoms are brought together, and the Cl(6) atom remotes from the Cl(3) atom. According to the data[28] for reaction (13), $\Delta_r H_{298}$ = 52.90 kcal mol^{-1}. We obtained the value of 47.95 kcal mol^{-1}, which suggests a good correspondence of the calculated and experimental data and asserts that the calculated activation energies for this reaction can be considered realistic.

Note that the structures of the transition states for reactions (13)—(16) somewhat differ, but these differences are small. The activation energies obtained by us for the forward reaction at all x exceed the corresponding activation energies of chlorine atom abstraction by the hydrogen atom (see Table 4). In addition, the activation energies of the backward reactions are low. Therefore, we may assert that the reaction of chlorine atom abstraction by atomic chlorine from chlorosilanes does not introduce a considerable contribution to the occurrence of the process at high temperatures.

Atomic hydrogen can attack not only the chlorine atom but also the hydrogen atom. The model of transition states for this reaction route is shown in Fig. 2, *b*, and their properties are listed in Table 5. Although the activation energies of hydrogen atom abstraction from the Si—H bond are very low, the reactions

$$SiH_xCl_{4-x} + H^{\cdot} \rightarrow {}^{\cdot}SiH_{x-1}Cl_{4-x} + H_2$$

do not noticeably contribute to dehalogenation; however, they decrease, most likely, the efficiency of the overall process.

The question about the appearance of radical species remains unanswered. It is most likely that the mechanism including the thermal or surface (interaction with the surface of the reaction vessel or catalyst) activation of either molecular hydrogen or chlorosilane followed by their decomposition is the most probable.

Another possibility is the transition of the molecules to the triplet state, for example, due to the interaction of chlorosilanes or molecular hydrogen with the high-energy radiation or a heavy metal atom. The problem about the possible role of triplet states in these reactions was not discussed, although the presence of "heavy" atoms, including silicon and chlorine atoms, in the reaction mix-

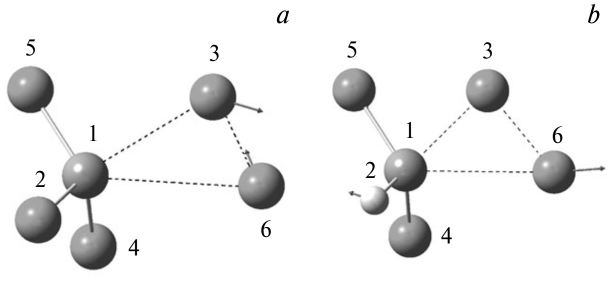

Fig. 3. Geometric structures of the transition states of reactions (13) (*a*) and (14) (*b*) calculated by the UB3LYP/6-311+G(d) method.

Table 5. Characteristics of the transition states of the dehydrogenation of chlorosilanes SiH_xCl_{4-x} with atomic hydrogen (bond lengths, angles, imaginary frequencies (ν_i), dipole moments (μ), and activation energies of the forward and backward reactions ($E_a^{(+)}$ and $E_a^{(-)}$, respectively)) (see Fig. 2, *b*)

Parameter	$SiHCl_3$	SiH_2Cl_2	SiH_3Cl	SiH_4
Si(1)—H(2)/Å	1.520	1.531	1.541	1.547
H(2)—H(3)/Å	1.383	1.366	1.348	1.340
Si(1)—Cl(4)/Å	2.054	1.474*	1.479*	1.484*
Si(1)—Cl(5)/Å	2.054	2.064	2.078	1.484*
Si(1)—Cl(6)/Å	2.054	2.064	1.479*	1.484*
Cl(4)—Cl(5)**/Å	3.361	2.891	2.909	2.432
Cl(4)—Cl(5)—Si(1)**/deg	35.1	28.9	28.8	34.9
Cl(4)—Cl(5)—Si(1)—Cl(6)** /deg	120.8	118.8	120.9	121.4
ν_i/cm^{-1}	607.53*i*	613.74*i*	632.10*i*	615.06
μ/D	0.8	1.4	1.7	0.6
$E_a^{(+)}$/kcal mol^{-1}	0.77	0.80	0.89	1.45
$E_a^{(-)}$/kcal mol^{-1}	11.90	11.73	11.20	15.70

* The Si—H bond length.

** The atom with number 4 in SiH_2Cl_2 and SiH_3Cl, the atoms with numbers 4 and 6 in SiH_3Cl, and the atoms with numbers 4, 5, and 6 in SiH_4 are hydrogen atoms.

tures results in the situation where the forbidden singlet—triplet transition becomes partially allowed due to the spin-orbital coupling.[29] In addition, the involvement of triplet states and radicals in chlorosilane dehalogenation cannot be excluded because of the possible participation in the dehalogenation of silylenes, for which the possibility of transition to the triplet state was assumed earlier.[30]

Thus, the results of our quantum chemical calculations of the dehalogenation of chlorosilanes with molecular hydrogen, atomic hydrogen, and atomic chlorine show that the UB3LYP/6-311+G(d) method can adequately describe these reactions. The obtained structural data, activation energies, and thermodynamic values are well consistent with the experimental data. The calculated activation energies make it possible to exclude the participation of molecular hydrogen in processes of chlorosilane dehalogenation. It is most probable that atomic hydrogen is responsible for the dehalogenation reaction.

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