Organometallics **1998,** *17,* 2819−2824

Mechanism of Rearrangement and Alkene Addition/Elimination Reactions of $SiC_3H_9^+$

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Received October 15, 1997

Equilibrium geometries of the nine low-energy isomers in the $SiC_3H_9^+$ system and the transition states for their interconversion have been optimized at the SCF and B3LYP levels of theory. It is shown that the experimentally observed interconversion between the lowest energy isomer $(CH_3)_3Si^+$ and the second most stable isomer $(CH_3)(C_2H_5)HSi^+$ goes via the intermediate complex $RH_2Si^+{\cdot}C_2H_4$. This complex is also an intermediate in the ethene elimination. Due to the key role of the transition state in interconversion between the lowest energy isomer and the complex, in the discussed reactions, its classical barrier height is estimated at different levels of theory. The barrier (ΔH_{298}) is found to be in the 4−8 kcal/mol range above the dissociation limit, in contrast to the case of the $SiC_2H_7^+$ cation, where it is below the limit. This explains the significant difference in the reaction efficiency for interconversion of the two lowest energy isomers in the $SiC_2H_7^+$ and $SiC_3H_9^+$ systems. However, for the $SiC_3H_5D_4^+$ system this barrier for isomerization is predicted to be ca. 4 kcal/mol lower than for the undeuterated species. This may explain the observed complete H/D exchange in the reaction between $(CH_3)H_2Si^+$ and C_2D_4. The sequence of transformations of the $SiC_3H_9^+$ cation which rationalize the mechanism of the observed H/CH_3 exchange reaction between SiH_3^+ and propene has also been found. All interconversions between isomers found in this system are provided only by the hydride shifts.

Introduction

The experimental study of ethene addition/elimination reactions of silylium cations poses some questions that cannot be readily answered within the existing body of experimental and theoretical data. One of the most intriguing features of these reactions is a dramatic difference in the exchange reactions with labeled ethene between $(CH_3)_2HSi^+$ and $(CH_3)H_2Si^+$; the former has only one exchangeable hydrogen, whereas the latter exchanges all five.[1−3] The same difference is used to distinguish the $SiC_3H_9^+$ structural isomers, since $(CH_3)_3Si^+$ yields only one H/D exchange with C_2H_4, while $(C_2H_5)(CH_3)HSi^+$ yields seven H/D exchanges.[2]

Our ab initio analysis of the $SiC_2H_7^+$ potential energy surface (PES)[4] allowed us to suppose that the observed difference in the exchange reactions of deuterated ethene with two types of silylium cations, i.e., RH_2Si^+ on one hand and R_2HSi^+ on the other, is connected with the symmetric nature of the $RH_2Si^+{\cdot}C_2H_4$ complex. It was proposed that this complex transforms directly into the most stable isomer $R(CH_3)_2Si^+$ by the simultaneous shift of two hydrogens from the silylium moiety of the complex to the ethene moiety. Multiple interconversions between the isomers completely scramble H with D. This path is not available for the R_2HSi^+ cation, and that is why it exchanges only one hydrogen.

The above mechanism can take place, provided that the activation barrier for this interconversion can be overcome with the supply of energy provided by complexation with ethene. In other words, the height of the barrier for the interconversion due to the symmetric shift of the two hydrogens in $RH_2Si^+{\cdot}C_2H_4$ (**TS1**) should not exceed the dissociation limit. For the case of R = H it has been shown that this is true.[4] However, it is disputable for R = Alk.

It has been proposed[4] that the interconversion between the most stable isomer and the second most stable isomer occurs through the same complex, $RH_2Si^+{\cdot}C_2H_4$. Therefore, the barrier height of **TS1** relative to the dissociation limit is critical for the successful interconversion of these isomers as well as for the exchange reactions. However, a significant difference between the $SiC_2H_7^+$ and $SiC_3H_9^+$ systems was found in the collisional activation study of Bakhtiar, Holznagel, and Jacobson.[2] In contrast to the efficient isomerization of $(C_2H_5)H_2Si^+$ into $(CH_3)_2HSi^+$, only a small amount of $(C_2H_5)(CH_3)HSi^+$ isomerizes into $(CH_3)_3Si^+$. This observation urged the authors to suppose that isomerization in the $SiC_3H_9^+$ system invokes a slightly (5−10 kcal/

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S0276-7333(97)00898-4 CCC: $15.00

mol) higher barrier for conversion to the most stable isomer than in the $SiC_2H_7^+$ system and that the barrier in the former case may approach the energy required for ethene elimination.[2]

Thus, the inefficient isomerization of $(C_2H_5)(CH_3)HSi^+$ into $(CH_3)_3Si^+$ presupposes the existence of a barrier for their interconversion that is above the dissociation limit, while the complete H/D scrambling in the reaction of C_2D_4 with $(CH_3)H_2Si^+$ demands that this barrier should not exceed the energy level of the dissociated molecules.

To find an explanation for this contradiction, we have to study the $Si(CH_3)_3^+$ potential energy surface (PES). Further, there is one more experimental observation that has importance for the proposed mechanism of the $(CH_3)_3Si^+$ isomer interconversion. It is the H/CH_3 exchange reaction between H_3Si^+ and propene.[1] It yields $(CH_3)H_2Si^+$ and ethene with high efficiency and hence implies small barriers for this reaction. In addition to those problems, which need to be rationalized, the thermochemistry of these cations is of interest in itself, since experimental data are lacking and theoretical studies are limited to only certain isomers of $SiC_3H_9^+$ at lower levels of theory.[5-8]

Computational Methods

The geometries of the cations were fully optimized at different levels of theory, starting from the self-consistent-field (SCF) level. Two different basis sets were used within this method: 3-21G[9] and 6-31G*[10] with one set of six d-like functions on Si ($\alpha = 0.45$) and C ($\alpha = 0.8$).

Of the higher theoretical methods which incorporate the electron correlation, the hybrid DFT/HF method was used. This utilizes Becke's three-parameter exchange functional (B3)[11] with the Lee–Yang–Parr nonlocal correlation functional (LYP)[12] (B3LYP). This method has been shown to give good results in predicting thermochemical values, including the barrier heights of the reactions (see, for example, refs 13–20). The advantage of this method, which becomes more important with the increase of the size of the system studied, is that it is less demanding than the traditional MO methods. The B3LYP method was used with the 6-31G** basis set, in which the polarization p functions are included in the set of the hydrogen basis functions. For the refinement of the relative height of the **TS1** activation barrier the diffuse sp-like (on C and Si) and s-like functions (on H) were used with the 6-31G** as well as with the 6-311G**[21] basis sets.

Due to the importance of the **TS1** barrier height for the interpretation of the reaction mechanism in question, two other correlated MO methods were employed solely for studying this point. These include the second-order Møller–Plesset perturbation theory (MP2)[22] and the coupled-cluster method including all single and double excitations and all connected triple excitations perturbationally (CCSD(T)).[23] In these methods the core-like Si and C orbitals were not included in the correlation. All these methods were used as they are implemented in the Gaussian 94 version of the Gaussian suite of programs.[24]

The zero-point vibrational energy (ZPVE) was used to obtain the theoretical enthalpy at 0 K from the total energy E_e according to the formula $H_0 = E_e + \mathrm{ZPVE}$. The zero-point vibrational energies were introduced only at the B3LYP level, since this method gives vibrational frequencies in close agreement with experimental ones (see, for example, ref 25), so there is no need for scaling. Theoretical enthalpies at 298 K were calculated, taking account of thermal corrections, from $H_{298} = E_e + \Delta H(298)$, where

$$\Delta H(T) = H_{\mathrm{trans}}(T) + H_{\mathrm{rot}}(T) + \Delta H_{\mathrm{vib}}(T) + RT$$

Both corrections were introduced as they are implemented in the Gaussian 94 codes. The reported ΔH_0 and ΔH_{298} values are theoretical enthalpy changes relative to the most stable isomer.

The loosely bound silylium cations have very flat potentials for internal rotations; therefore, they have many rotamers, whose energies, however, usually differ by values not exceeding 0.1 kcal/mol. This problem becomes more important with the increase of the number of methyl groups. While optimizing their geometries, we encountered this problem and tried to locate the lower energy rotamer. However, a complete scan of the rotational potentials was not the goal of this study and we cannot guarantee the absence of lower energy rotamers in some cases.

Results and Discussion

Two simple rules evidently govern the relative stability of the silylium cation isomers, and they may be deduced from theoretical studies.[4-8,26-31] First, the isomers with a vacant p-orbital (or positive charge) localized at silicon are much more stable than those with a positive charge on carbon. The latter are not actually silylium cations, but rather Si-substituted carbenium cations. Second, the most stable isomer is the one which

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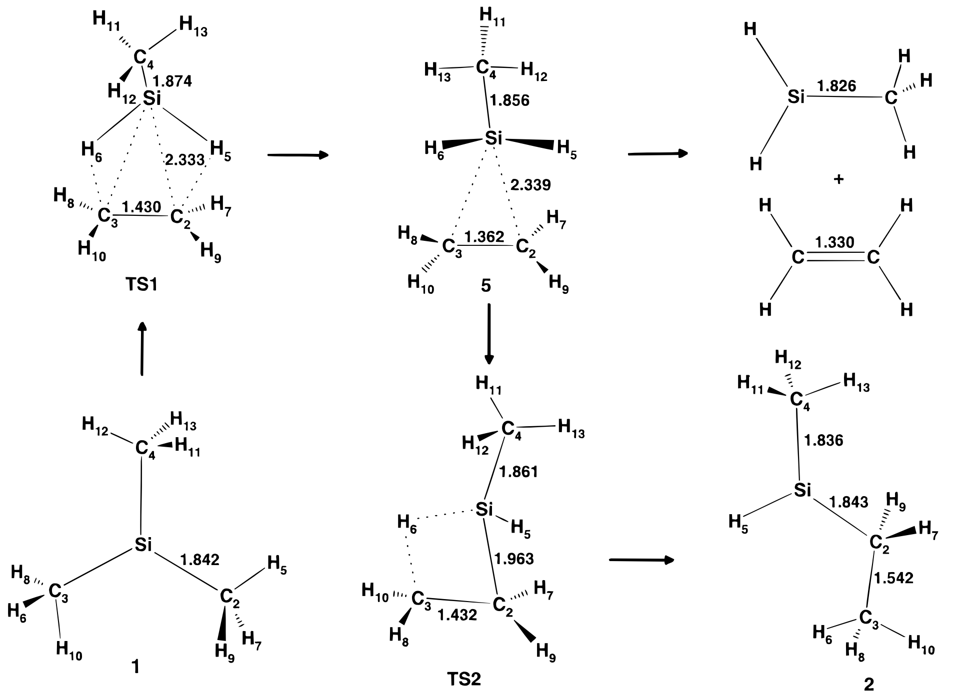
Scheme 1. Geometry and Main Structural Parameters (B3LYP) of the Stationary Points at the $SiC_3H_9^+$ PES



has the maximum possible number of alkyl groups attached to silicon. This order of stability is similar to that of carbenium cations, i.e., tertiary > secondary > primary. According to the above rules, the least stable isomers should be the primary and secondary silyl-substituted carbenium cations. Even their carbon analogues, such as the 1-butyl cation and the isobutyl cation, were found to represent saddle points rather than local minima at the $C_4H_9^+$ PES.[32] Among the silylium cations, the PES of which was studied at correlated levels of theory, the $(SiH_3)H_2C^+$ isomer was not found to represent a local minimum at the MP2 level, and this structure rearranges without a barrier to the more stable silylium cation.[31] Similarly, there was no energy minimum for the $(CH_3)H_2SiH_2C^+$ isomer at the correlated levels of theory.[4] However, the β-silyl-substituted carbenium cation $(H_3Si)(CH_3)HC^+$ did represent a local minimum, even with the correlated methods.[4] This is in keeping with the observation of the destabilizing effect of the α-silyl substitution and the stabilizing effect of the β-silyl substitution relative to the corresponding effects of the alkyl groups.[8] Thus, while in our previous study of the $SiC_2H_7^+$ PES we examined practically all possible isomers of the silylium cation, in the current work we consider only those structures of the carbenium cations which are relevant to the transformations discussed.

In keeping with the above rules, the most stable isomer of $SiC_3H_9^+$ should be $(CH_3)_3Si^+$ (as in the case of the carbon analogue $C_4H_9^+$). Indeed, isomer **1** (Scheme 1) was found to represent the global minimum. It has a C_{3h} symmetry with a planar arrangement of the heavy-atom skeleton and with one of the C−H bonds of each methyl group lying in the plane formed by the heavy atoms. This arrangement is similar to that of the lowest energy rotamer of the *tert*-butyl cation.[32] In both cases the rotation of the methyl groups is determined by the compromise between the orientation of C−H bonds, which favors hyperconjugation between the formally vacant p-orbitals on Si (or C) and CH on one hand, and the positions of hydrogens which minimize their repulsion on the other hand. The hyperconjugating C−H bonds are longer than those lying in the plane; however, their difference is not as great as in the case of the *tert*-butyl cation. The other silicon analogue of the *tert*-butyl cation, i.e., $(CH_3)_2(SiH_3)C^+$ (**7**; Scheme 2) is significantly higher in energy (Table 1).

The next most stable form should be the secondary silylium isomer, i.e., $(C_2H_5)(CH_3)HSi^+$ (**2**; Scheme 1). It lies 20.4 kcal/mol above **1** (the ΔH_{298} B3LYP values relative to **1** will be cited henceforth) and can be regarded as the silicon analogue of the 2-butyl cation. The minimum energy conformation possesses a C_s symmetry.

For the primary silylium cations there are two possible isomers which correspond to two forms of the propyl group attached to silicon, i.e., *n*-propyl (**3**; Scheme 3) and isopropyl (**4**; Scheme 2).

In the energy gap between **2** and all other forms there are two isomers which can be characterized as alkene−silyl cation complexes: the complex of $(CH_3)H_2Si^+$ with ethene (**5** in Scheme 1, 28.5 kcal/mol) and the complex of H_3Si^+ and propene (**6** in Schemes 2 and 3, 30.4 kcal/mol). Actually, only **5** may be regarded as a pure complex with a slightly increased ethene C=C bond length of 1.362 Å (B3LYP/6-31G** value in Scheme 1; compare with the ethene equilibrium distance 1.330 Å), with significantly lengthened Si−C bonds (2.339 Å) and negative Mulliken charges on the carbons (−0.26). In **6** silicon is predominantly bound to C_2 (Scheme 2), and the charge on C_1 becomes positive (0.06). Thus, **6** may be regarded also as a secondary Si−carbenium ion,

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Scheme 2. Geometry and Main Structural Parameters (B3LYP) of the Stationary Points at the $SiC_3H_9^+$ PES

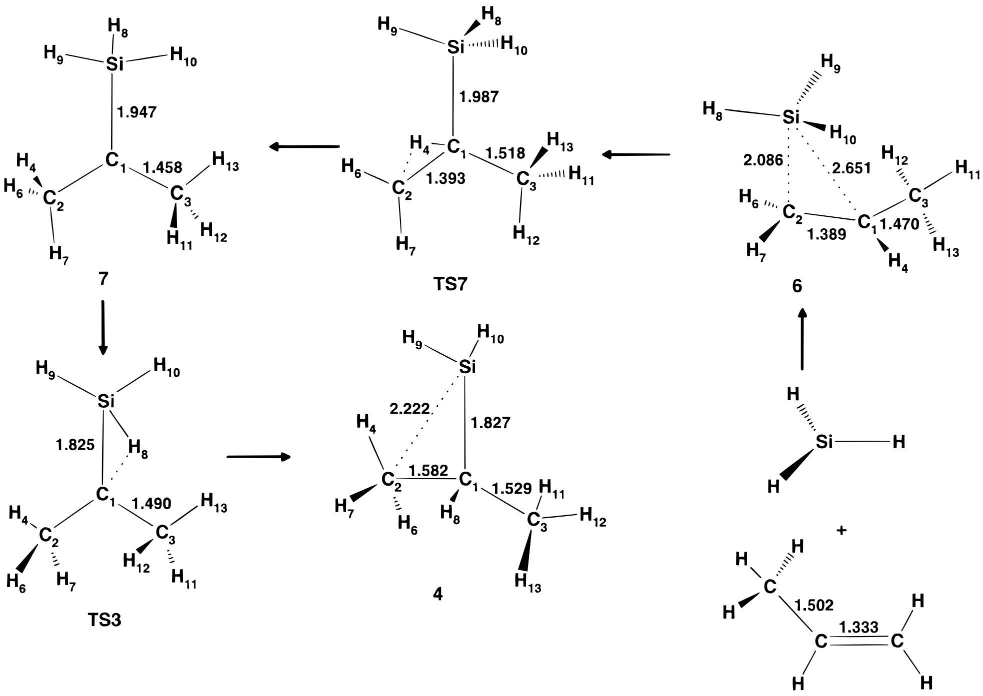

Table 1. Total Energy, Δ*H* (0 and 298 K), for the Most Stable Isomer (Hartrees) and Their Relative Values (kcal/mol) for Other Isomers and Transition States on the $SiC_3H_9^+$ Potential Energy Surface

	SCF		B3LYP			
stationary points	3-21G	6-31G*	ΔE_e	ΔH_0[a]	ΔH_{298}	*b*
1	−405.376287	−407.527815	−408.997943	−408.888514	−408.879668	0
2	23.6	18.3	20.8	20.8	20.4	0
3	45.9	36.0	37.5	37.9	36.6	0
4	46.8	37.7	38.7	38.8	37.7	0
5	40.6	28.2	29.9	29.0	28.5	0
6	45.5	30.0	33.0	31.2	30.4	0
7	57.0	39.6	45.9	42.4	41.9	0
8	69.8	52.8	56.7	54.8	54.0	0
9	67.6	48.9	50.3	49.6	48.5	0
TS1	102.7	94.4	71.2	69.2	68.3	1189
TS2	57.7	42.4	38.9	37.8	36.6	690
TS3	73.9	53.7	53.3	50.2	49.1	625
TS4	74.6	56.4	61.9	58.1	57.1	156
TS5	83.8	58.3	59.4	57.0	55.6	374
TS6	82.4	61.6	63.1	59.7	58.6	455
TS7	78.2	57.4	61.7	57.9	57.0	796
$C_2H_4 + (CH_3)H_2Si^+$	72.3	61.3	68.4	64.1	64.4	0
$C_3H_6 + H_3Si^+$	96.6	80.0	90.5	85.9	86.0	0

[a] $E_0 = E_e + ZPVE$. [b] Imaginary frequencies. B3LYP values.

although its energy is significantly lower than that of the other Si−carbenium isomer studied here (**8**) and even the shortest Si−C bond in **6** (2.086 Å) is longer than in the "pure" Si−carbenium ion **8**. Two conformations of the heavy-atom skeleton of isomer **8** were found at the SCF level. One of the forms is the cis-like isomer, while the other has a gauche conformation (**8**; Scheme 3). However, the former does not exist at the B3LYP level; attempts to optimize it at B3LYP/6-31G** lead to hydride transfer from C_1 to C_2, which results in the lower energy isomer **6**. Note that **5** is only 8 kcal/mol above **2** and the activation barrier for its rearrangement into **2** is also only 8 kcal/mol.

All isomers of the $SiC_3H_9^+$ cation may be divided into two classes: one originating from the complex of the $(CH_3)H_2Si+$ cation with ethene (Scheme 1) and the other from that of H_3Si^+ with propene (Schemes 2 and 3). As in the previously examined case of the $SiC_2H_7^+$ system, complex **5** transforms into the lowest energy isomer **1** through the transition state **TS1** by the symmetric shift of the two hydrogens of the silylium moiety (Scheme 1). This process breaks the C−C bond of the ethene moiety and forms two Si−C bonds, leading to isomer **1**, in which all three methyl groups are equivalent. This mechanism explains the exchange of all five hydrogens in the reaction of $(CH_3)H_2Si^+$ with C_2D_4. According to this mechanism the complex $(CH_3)H_2Si^+{\cdot}C_2D_4$ (**5**) directly converts into $(CH_3)(CD_2H)_2Si^+$ (**1**) through **TS1**. The reverse reaction may lead to $(CD_2H)HDSi^+ + C_2H_3D$. Multiple transformations of **5** into **1**

Scheme 3. Geometry and Main Structural Parameters (B3LYP) of the Stationary Points at the $SiC_3H_9^+$ PES

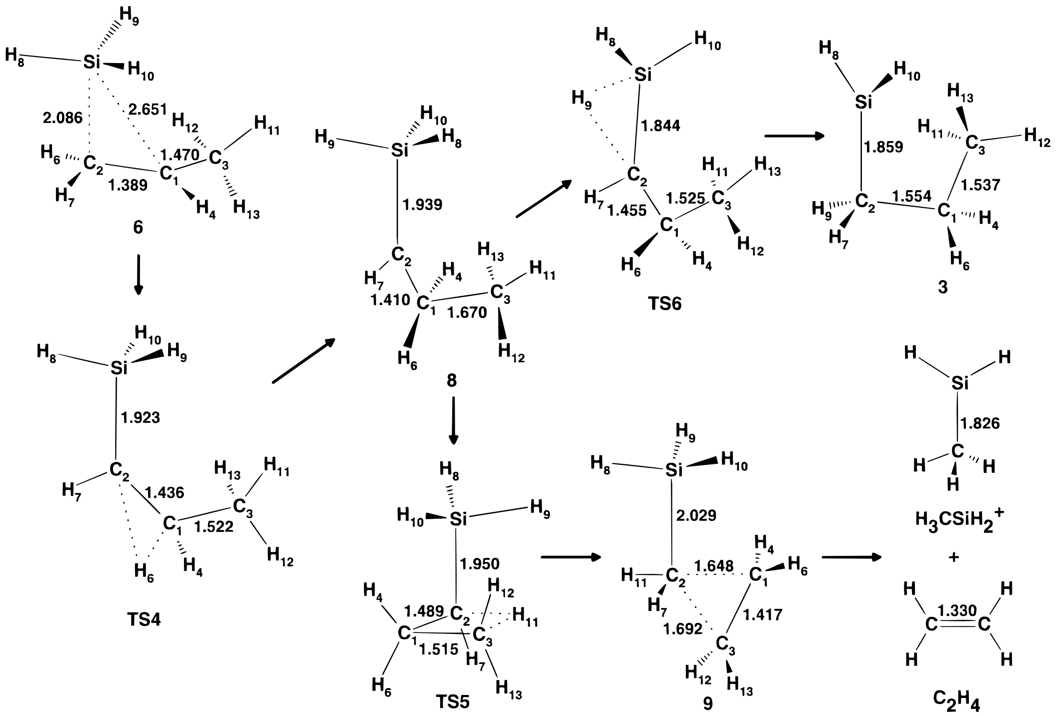

Table 2. TS1 Total Energy (Hartree) and the Barrier Height (kcal/mol) Relative to ΔH_{298} of the Dissociated Fragments $C_2H_4(C_2D_4)$ + $(CH_3)H_2Si^+$ for Undeuterated ($\Delta H_{298}{}^H$) and Deuterated ($\Delta H_{298}{}^D$) Species

method/basis set	E_e	$\Delta H_{298}{}^H$	$\Delta H_{298}{}^D$
B3LYP/6-31G**	-408.884 359	3.8	0.0
B3LYP/6-31++G**	-408.886 756	6.7	2.9
B3LYP/6-311++G**	-408.931 613	7.8	4.1
MP2(FC)/6-311+G**	-408.014 234	4.0	0.5
CCSD(T)/6-311++G**//B3LYP/6-311++G**	-408.090 519	7.3	3.6

and back can completely perform the H/D exchange in $(CH_3)H_2Si^+$ provided that the activation barrier for this interconversion lies below the dissociation limit.

Thus, the height of the **TS1** barrier relative to the dissociation limit (ΔH_{298}(**TS1**)) is the critical parameter for the discussion of the two groups of experimental data: (i) the complete H/D scrambling in the $(CH_3)H_2Si^+$ + C_2D_4 reaction and (ii) the inefficient isomerization of $(C_2H_5)(CH_3)HSi^+$ into $(CH_3)_3Si^+$. For (i) the **TS1** barrier height should be below the sum of energies of $(CH_3)H_2Si^+$ + C_2D_4 and for (ii) the barrier should be above the dissociation limit. ΔE_0(**TS1**) at the B3LYP/6-31G** level is 2.8 kcal/mol; ΔH_0(**TS1**) and ΔH_{298}(**TS1**) are even higher, i.e., 5.1 and 3.9 kcal/mol, respectively (Table 1). If we take into account that the latter value in the $SiC_2H_7^+$ system is 7.6 kcal/mol below the dissociation limit,[4] the overall increase of the barrier height by 12.5 kcal/mol in going from $SiC_2H_7^+$ to $SiC_3H_9^+$ is in fair accord with the experimental estimate of 5−10 kcal/mol[2]. Thus, according to the B3LYP/6-31G** predictions the classical barrier height for the interconversion between **5** and **1** exceeds the complexation energy by only a few kilocalories per mole and this barrier may be overcome in the reaction of C_2D_4 with $(CH_3)H_2Si^+$. Moreover, accounting for the differences in the zero-point vibrational energy (ZPVE) and thermal corrections between the $H_3Si^+{\cdot}C_2H_4$ and $H_3Si^+{\cdot}C_2D_4$ systems indicates that the ΔH_{298}(**TS1**) values for the latter system lie slightly (−0.02 kcal/mol) below the dissociation limit (Table 2).

However, it is known from the literature[13−20] that the B3LYP method usually underestimates the barrier heights, so it is possible that the closeness of the **TS1** barrier height and the dissociation level is an artifact of the B3LYP method. Therefore, we carried out the calculation of the ΔH_{298}(**TS1**) value for both deuterated and undeuterated systems by other quantum-chemical methods. The studied systems are large enough for the employment of the high level correlated method for their optimization. Such approaches as coupled-cluster theory methods are very accurate and reliable for the prediction of thermochemical properties.[33] However, we used the single-point CCSD(T) calculations at the B3LYP/6-311++G** optimized geometry. This method gives ΔH_{298}(**TS1**) values 3.5 kcal/mol above those of B3LYP/6-31G** (Table 2). The MP2 values are close to those of B3LYP/6-31G**. Barrier heights in the B3LYP calculations with basis sets which include the diffuse s and p functions are slightly higher, but the scatter of results still does not exceeed 4 kcal/mol with the highest $\Delta H_{298}{}^D$ value only 4.1 kcal/mol above the dissociation limit (Table 2). This is within the accuracy of the theoretical methods employed in the prediction of the barrier heights, and we still expect that this barrier can be overcome with the excess complexation energy in the C_2D_4 + $(CH_3)H_2Si^+$ reaction.

In the above paragraph we discussed the isomerization path from $(C_2H_5)(CH_3)HSi^+$ (**2**) to $(CH_3)_3Si^+$ (**1**), without mentioning the second part of the sequence

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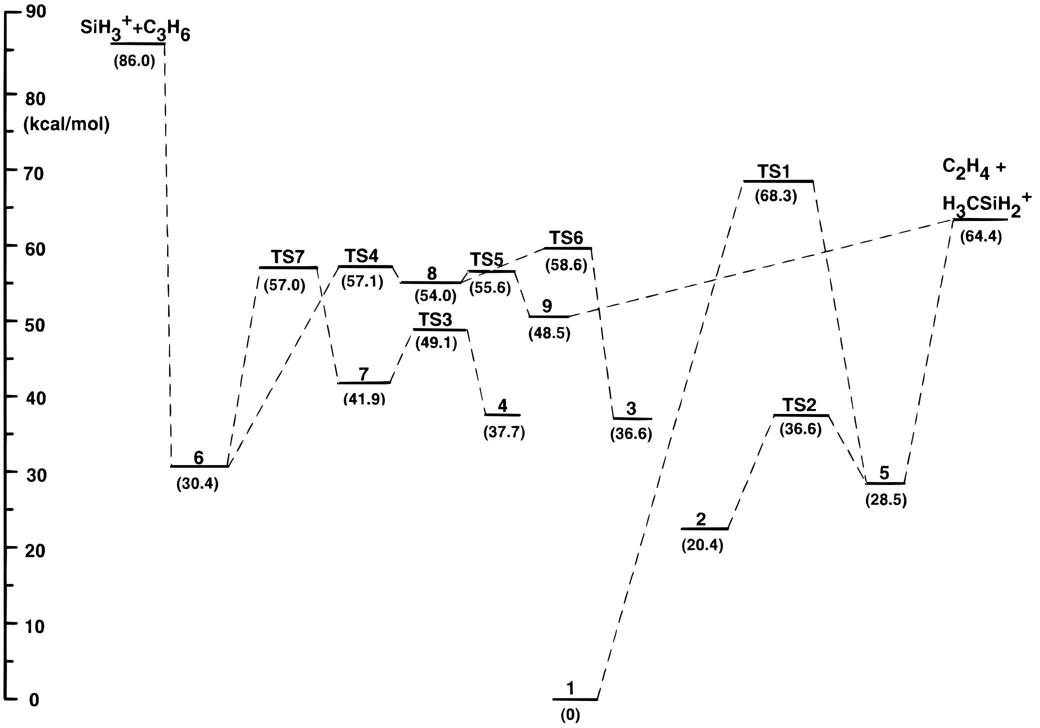
Chart 1. Representation of the Energy Profiles for the $SiC_3H_9^+$ Isomer Interconversion



depicted in Scheme 1, i.e., the path from **5** to **2**. This transformation goes through **TS2**, which corresponds to the shift of one hydrogen of the silylium moiety of the complex **5** to the ethene moiety of the complex. The barrier for this transformation (**TS2**) is low (Chart 1) compared to the barrier height of the **5** to **1** transformation (**TS1**) and thus the entire sequence of transformations from **1** to **2** is determined by the height of the highest barrier (**TS1**). It is worth noting that in our previous work on $SiC_2H_7^+$ [4] we did not find a transition state analogous to **TS2** (it was found later) and proposed the path leading from **5** to **2** through isomer **4**. This path was also found at the SCF level, but it became cut at the B3LYP level, since we failed to find the stationary point corresponding to **TS3** within this approximation.

The other sequence of transformations (Schemes 2 and 3) has the H_3Si^+−propene complex **6** as a key structure. Note (as was discussed above) that this structure may be treated as a silyl carbocation as well. In **6** the SiH_3 group is in the bridging position toward the C=C bond of the propene molecule, similar to the position of the $SiH_2(CH_3)$ group toward ethene in complex **5**. However, in contrast to **5,** where two Si−C distances are equal (2.339 Å at the B3LYP/6-31G** optimized geometry), in complex **6** these two distances are equal to 2.086 and 2.651 Å (**6**; Scheme 2). The shift of the hydrogen from the central carbon of the propene moiety to the terminal one through **TS7** leads to isomer **7**, in which the silicon atom becomes coordinated to the central carbon of the propene moiety (SiC = 1.947 Å). Formally **7** is a Si-substituted *tert*-butyl cation and thus its relative energy (41.9 kcal/mol) is sufficiently higher than that of the genuine silylium cations. This isomer can comparatively easily (with an activation barrier of ca. 7 kcal/mol) rearrange to the *iso*propylsilylium cation (**4**). This rearrangement takes place by the shift of one of the hydrogens of the SiH_3 group to the central carbon with the vacant p-orbital (**7** → **TS3** → **4**; Scheme 2). However, the *iso*propylsilylium cation (**4**) has a nonclassical structure with the SiH_2 group in the bridging position ($Si-C_1 = 1.827$ Å and $Si-C_2 = 2.222$ Å).

There is another sequence of transformations of complex **6** (Scheme 3). It starts with hydride transfer (H_6) from C_2 to C_1 through transition state **TS4**. This transfer results in isomer **8**, which is a secondary carbenium ion and therefore it lies ca. 12 kcal/mol higher than the tertiary cation **7**. However, the barrier heights for the transformation of **6** to **7** and **6** to **8** are practically of the same value.

The carbenium ion **8** also has two possibilities for further rearrangement. The first path leads to the significantly more stable *n*-propylsilylium cation (**3**; Scheme 3). More interesting is the second path for the transformation of **8**. It goes through the very low barrier of **TS5** to an isomer which can be characterized as a complex between ethene and $(SiH_3)H_2C^+$ (**9**). This complex may dissociate to the methylsilylium cation (since its carbenium isomer does not correspond to a minimum at the PES[31]) and ethene.

This sequence of transformations of the $SiC_3H_9^+$ isomers reveals the mechanism of the reaction $H_3Si^+ + C_3H_6 \rightarrow CH_3H_2Si^+ + C_2H_4$ observed earlier by Reuter and Jacobson.[1] Although it was called formally a H/CH_3 exchange reaction, our proposed mechanism shows that the reactions may proceed only by hydride shifts, providing the comparatively low barrier for this process. Note that the predicted exothermicity of the reaction (21.6 kcal/mol) agrees fairly well with that estimated from the thermochemical data by Reuter and Jacobson[1] (23.3 kcal/mol).

Acknowledgment. I.S.I. thanks the Russian Foundation for Basic Research for supporting this work (Grant No. 96-03-33254).

OM970898+