Potential Energy Surface of the Dimethylsilylium Cation and Mechanism of the Isomer Interconversion

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The structures of all plausible isomers of the $SiC_2H_7^+$ ion were optimized at the SCF and correlated levels of theory, including the MP2/6-31G** and the B3LYP/6-31G** methods. At all levels of theory the most stable isomer was found to be $(CH_3)_2SiH^+$ (**1**). At the SCF level the next was $C_2H_5SiH_2^+$ (**2**), lying ca. 21 kcal/mol higher, followed by the symmetric SiH_3-bridged $H_3SiCH_2CH_2^+$, which can also be regarded as an addition/elimination complex of SiH_3^+ and C_2H_4 (**5** is ca. 24 kcal/mol higher than **1**). Two other isomers, $CH_3SiH_2CH_2^+$ (**3**) and $CH_3SiH_3CH^+$ (**4**) lie significantly higher. However, at the B3LYP/6-31G** level **3** is no longer a stationary point. No transition state was found for the direct interconversion of **1** and **2**. It is proposed that this experimentally observed interconversion occurs through **5**. The corresponding transition state (**TS1**) has a C_s symmetry and corresponds to the symmetric shift of two hydrogens. At the SCF levels it lies higher than $SiH_3^+ + C_2H_4$, but at correlated levels it becomes several kcal/mol lower, thus allowing isomerization before dissociation. Other transition states connecting **5** with **2** through **4** lie lower than **TS1** at all levels of theory. The symmetric nature of the **TS1** transition state may account for the observed differences in the exchange reactions of $CH_3SiH_2^+$ and $(CH_3)_2SiH^+$ with deuterated ethene.

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Introduction

Silylium (aka silylenium or silicenium) cations are well-known species of considerable stability in the gas phase. Many chemical reactions of these ions have been studied.[1−11] However, silylium ions have still eluded structural characterization by experimental methods, although numerous studies of their reactions, especially by collision-activated rearrangement and dissociation, allowed suggestion of the existence of different isomeric forms of these cations and their interconversion.

Experimental studies of H/D exchange reactions of silylium cations with ethene-d_4 led to puzzling results; i.e., there is only one exchangeable hydrogen in $Si(CH_3)_2H^+$, whereas $Si(CH_3)H_2^+$ exchanges all five, and $Si(C_2H_5)H_2^+$ yields seven H/D exchanges.[9−11] The tentative mechanism of this phenomenon, proposed by Bakhtiar *et al.*,[11] was based on some assumptions concerning the heights of barriers for interconversion, for which reliable estimates still do not exist. Although there have been several theoretical works which predicted the relative energies of the isomeric forms of $SiCH_5^+$,[12−14] $SiC_2H_7^+$,[13,15,16] $SiC_3H_9^+$,[17] and $SiC_5H_{13}^+$ [16] and some recent ab initio studies,[18−23] dealing, however, mainly with the much-discussed problem of the existence of the silylium ions in the condensed phases,[24] the complete potential energy surface of any of these ions has not been analyzed by theoretical methods.

The present work intends to fill this gap by scanning the potential energy surface (PES) of the simplest

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silylium cation, i.e., $SiC_2H_7^+$, for which the process of interest (the addition/elimination of ethene) can be investigated.

Computational Methods

The ion structures were fully optimized at different levels of theory, starting from the self-consistent-field (SCF) level. Three different basis sets were employed within this method: 3-21G,[25] 6-31G*[31] with six d functions on Si ($\alpha = 0.45$) and C ($\alpha = 0.8$), and the last basis set augmented with p functions on H ($\alpha = 1.1$) (6-31G**).

Electron correlation was taken into account by second-order many-body perturbation theory within the Møller−Plesset procedure (MP2)[26] and the hybrid DFT-HF method using a combination of Becke's three-parameter exchange functional (B3)[27] with the Lee−Yang−Parr nonlocal correlation functional (LYP)[28] (B3LYP). These methods were used as they appear in the Gaussian 94 version of the Gaussian suite of programs.[29] The core electrons were not included in the correlation in the MP2 method.

Zero-point vibrational energy corrections were introduced only at the B3LYP level, since this method gives vibrational frequencies in close agreement with experimental ones (see, e.g., ref 30). Taking into account the reported good performance of the B3LYP method in predicting the stationary point energies, especially the barrier heights, we may consider the B3LYP+ZPVE results as the best estimates of the current work.

First, the potential energy surface was scanned and the stationary points on it were found at the SCF/3-21G level. Since the silylium cations are rather loosely bound structures, there are many stationary points corresponding to different rotamers with closely spaced energy levels. Since our prime interest is in the rearrangement of the silylium cations, rather than the study of their rotamers with respect to rotations around C−C and Si−C bonds, we started from arbitrary torsional angles for these groups without any symmetry constraints, thus expecting them to come to their lowest-energy conformations. This procedure does not guarantee that the rotamer found in this way is the lowest energy one, however, since the potential functions governing these rotations are very shallow; the energy differences between them do not exceed 0.01 kcal/mol. This does not affect the predicted energy differences for the structural rearrangements of interest, which are several orders of magnitude higher. Vibrational frequencies were calculated for each stationary point found.

Results and Discussion

There are five possible arrangements of atoms for the $SiC_2H_7^+$ ion. The first, which appears to be the global minimum, may be described as $(CH_3)_2SiH^+$ (**1**; Scheme 1). This structure was not considered in ref 16 (to the best of our knowledge, the most elaborate study of the $SiC_2H_7^+$ PES), where the $C_2H_5SiH_2^+$ (**2**) isomer was stated to be the most stable $SiC_2H_7^+$ species. However, according to Apeloig *et al.*[16] the silyl-bridged $H_3SiCH_2CH_2$ is only 5.5 kcal/mol higher in energy (MP2/6-31G*//3-21G). This is structure **5** in our notation (Scheme 1). The last isomer mentioned by Apeloig *et al.*[16] is $CH_3(SiH_3)CH^+$ (**4** in our notation), which "lies much higher in energy than $C_2H_5SiH_2^+$, *i.e.*, by 31.0 kcal/mol, and it is probably not a stationary point on the $SiC_2H_7^+$ PES". One more isomer should be considered. It is $CH_3SiH_2CH_2^+$ (**3a**; Scheme 1).

All of these five isomers were fully optimized at different levels of theory, from SCF/3-21G to B3LYP /6-31G** (Scheme 1). It should be noted that in all previous theoretical studies of the system optimization was carried out only at the SCF level. For structures **1** and **2** (22.5 kcal/mol above **1**; henceforth we shall refer to the ΔH_{298} values predicted at the highest level in this work, B3LYP) there are no dramatic changes in the geometric parameters or in their relative energies (Table 1) on going from SCF to correlated levels of theory. Both isomers have C_s symmetry at all levels of calculation. The predicted geometry and relative energies for these isomers calculated at the SCF/3-21G level differ the most from those estimated by the other methods, but this can be rationalized by taking into account the absence of polarization functions in this basis set.

For isomer **5** (24.0 kcal/mol) all methods with the exception of SCF/3-21G (which predicts the C_1 structure with nonequivalent Si-C distances) give the C_s structure with the SiH_3 group located symmetrically at the plane bisecting the ethene molecule (**5**; Scheme 1). Thus, this structure may be regarded as a complex between the SiH_3^+ cation and the ethene molecule.

The most dramatic changes occur for isomers **3** and **4** on going from the SCF to correlated methods. The SCF calculations give a structure that may be described as $CH_3SiH_2CH_2^+$ (**3a**). There are no significant changes of the geometric parameters on going from the 3-21G to the 6-31G** basis set. However, the MP2/6-31G** equilibrium geometry of this isomer is characterized by the increased Si−C(H_3) bond length and decreased C−Si−C bond angle value (**3b**; Scheme 1). Optimization of this structure at the B3LYP/6-31G** level shows that no stationary point can be found for either the **3a** or the **3b** arrangement of the $CH_3SiH_2CH_2^+$ ion. Instead, the shift of the methyl group toward the C(H_2) atom that manifests itself at the MP2 level **3b** becomes larger at the B3LYP level, resulting in the local minimum found, which coincides with the **2** structure. Thus, the high-level calculation predicts that there is no minimum for the $CH_3SiH_2CH_2^+$ (**3a**) isomer.

In contrast to **3**, isomer **4** (40.9 kcal/mol), although it changes its structure with an increase of the theory level, has at the B3LYP/6-31G** level a configuration which is similar to those of SCF (**4a**; Scheme 1). Only at the MP2/6-31G** level is its structure characterized by the hydrogen atom being in the bridging position between two carbons (**4b**; Scheme 1). It should be noted that, as in the case of isomer **3**, the MP2/6-31G** method "prefers" a hydrogen to be in the bridging position (compare **3b** and **4b** in Scheme 1).

Structure **4** may be regarded as an intermediate between **2** and **5**; both these isomers may be produced from **4** by hydrogen shifts. Indeed, two transition states

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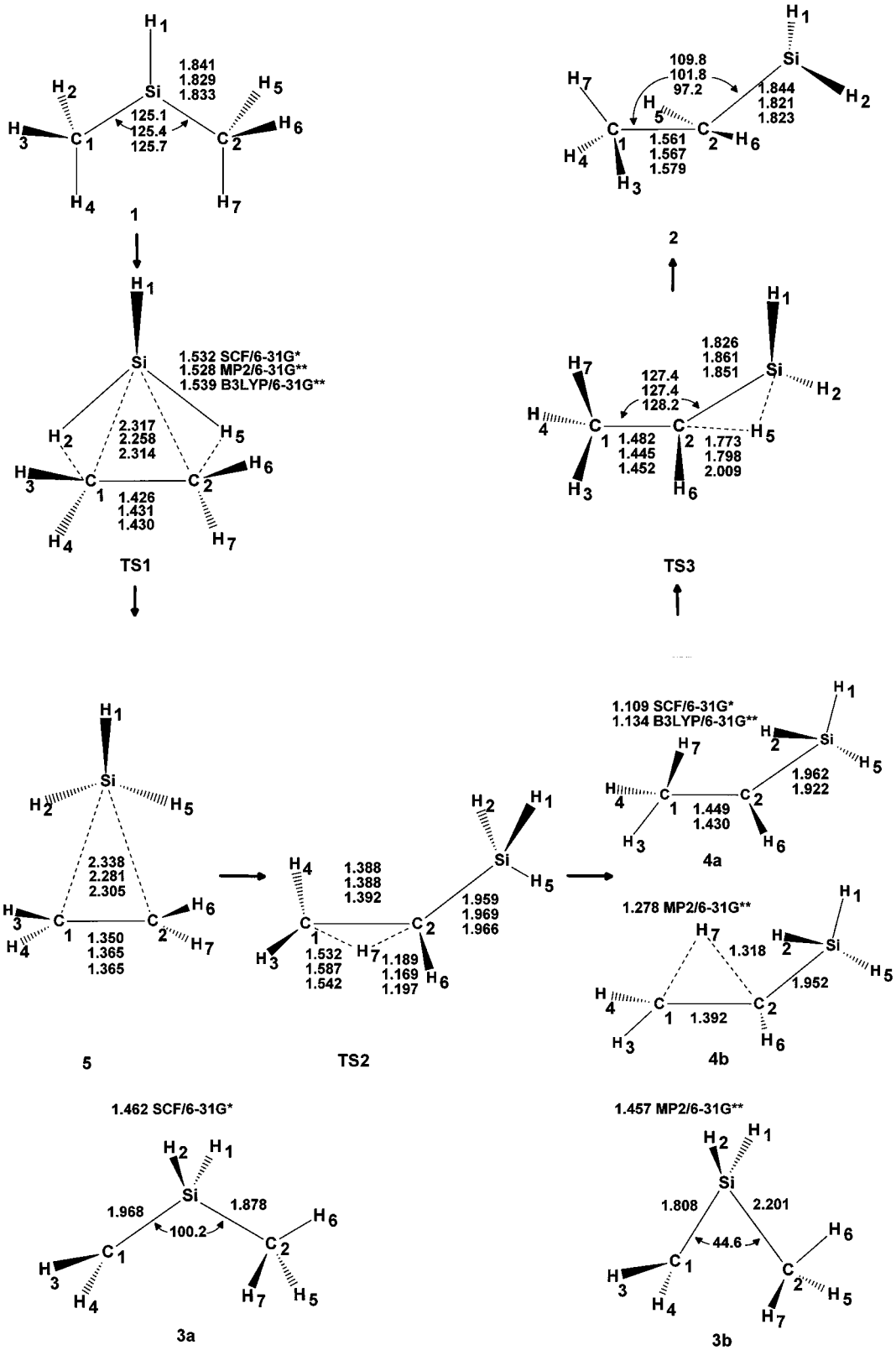
Scheme 1. Main Structural Parameters of Stationary Points at the $SiC_2H_7^+$ PES



were found for these reactions, i.e. the **TS2** structure, which is a transition state for the hydrogen shift pathway in the ethene moiety of the ethene−silyl cation complex **5**, and the **TS3** structure connecting **4** and **2** by the shift of the silyl group hydrogen toward the central carbon (Scheme 1). The barriers for these reactions are only a few kilocalories per mole above **4** at all levels of theory, including correlated ones (2.3 kcal/mol for TS2 and 0.8 kcal/mol for TS3 at the B3LYP level); therefore, the energy of isomer **4** practically defines the barrier for the **2**−**5** interconversion.

Numerous attempts were made to find the transition state for the direct **1**−**2** conversion. This pathway, i.e. the dyotropic 1,2-hydrogen/1,2-methyl migration, was proposed by Bakhtiar et al.[11] to rationalize the differences in the deuterium exchange reactions of $SiC_2H_7^+$ and $SiCH_5$. However, no transition state was located for this process.

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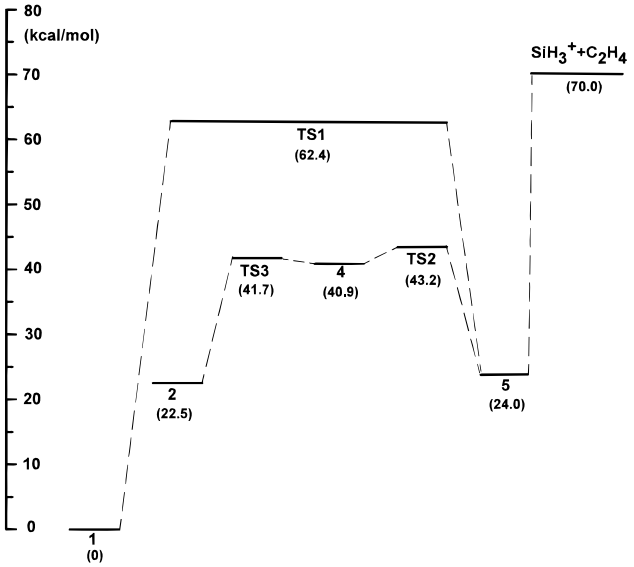
Table 1. Total Energy of the Global Minimum (hartree) and Relative Energies (kcal/mol) of the Stationary Points at the $SiC_2H_7^+$ PES

stationary points	SCF 3-21G	SCF 6-31G*	SCF 6-31G**	MP2	B3LYP ΔE_e	B3LYP ΔE_0[a]	B3LYP ΔH_{298}	*b*
1	−366.519 391	−368.464 657 1	−368.477 463	−368.847 148	−369.648 710			
1	0	0	0	0	0	0	0	0
2	24.7	20.1	20.9	21.0	22.7	22.7	22.5	0
3	54.2	47.1	47.6	18.2				
4	50.9	38.5	39.0	47.0	44.4	41.1	40.9	0
5	35.0	23.3	23.9	25.5	25.4	24.3	24.0	0
TS1	97.6	87.8	86.7	67.8	65.5	63.2	62.4	1180 i
TS2	61.8	43.5	43.0	49.4	47.3	43.9	43.2	650 i
TS3	60.8	45.6	45.8	52.8	45.5	42.3	41.7	394 i
$C_2H_4 + SiH_3$	75.3	65.8	65.6	72.9	74.2	69.6	70.0	0

[a] $E_0 = E_e + ZPVE$. [b] Imaginary frequencies: B3LYP values (cm^{-1}).

Scheme 2. Representation of the Energy Profiles for the $SiC_2H_7^+$ Isomer Interconversion Description



Only one transition structure for the rearrangement of the most stable isomer **1** was found. This transition state connects **1** with the complex **5** (**TS1**; Scheme 1). The **TS1** structure is characterized by the symmetric (with respect to the symmetry plane bisecting the ethene molecule and the SiH_3 cation) shift of two hydrogens of the silyl group of complex **5** toward the ethene carbons. In contrast to the case of **TS2** and **TS3**, where there are no dramatic changes in their heights on going from SCF to correlated methods, the height of the **TS1** barrier decreases significantly when the correlation is switched on (see Scheme 2); at the SCF level it lies above the level of dissociated molecules, whereas at the correlated levels **TS1** is several kilocalories per mole below $C_2H_4 + SiH_3^+$ (about 4 kcal/mol at B3LYP+ZPVE).

Thus, the complexation energy of $C_2H_4 + SiH_3^+$ is sufficient to drive the interconversion between isomers which is observed experimentally for the silylium cations.[10,11] Moreover, the symmetric nature of **TS1** may account for the differences in the reactions of the silylium cations with deuterated ethene.

Analyzing the experimental data on these reactions,[9−11] we notice that R_2SiH^+ yields only one exchangeable hydrogen in reactions with C_2D_4, while all hydrogens are exchangeable for the $RSiH_2^+$ ions (R = CH_3 and C_2H_5). There is also no ^{13}C exchange for $(CH_3)_2SiH^+$ in reactions with ethene-$^{13}C_2$. The results of this work can explain these experimental findings. The model described in this work corresponds to the case of R = H in the system $RSiH_2^+ + C_2D_4$, while experimental data are for R = CH_3. However, the interconversions between isomers of this system may be considered on the basis of the scheme proposed in this work, i.e. the conversion of the complex $RSiH_2^+ \cdot C_2H_4$ to the most stable structure $RSi(CH_3)_2^+$ by the simultaneous transfer of the two silylium hydrogens to the CH_2 groups of the ethene moiety. In the case of R = CH_3 the latter is the symmetric ion $Si(CH_3)_3^+$, and this provides the complete scrambling of all hydrogens.

The encounter complex $(CH_3)SiH_2^+ \cdot C_2D_4$ which has a structure similar to that of structure **5**, transforms to the global minimum similar to **1**, $CH_3Si(CD_2H)_2^+$, by the migration of the two hydrogens attached to silicon. This reaction proceeds through the transition state (similar to **TS1**) which has a barrier height below the complexation energy. Conversion back to complex **5** may produce $(CD_2H)SiHD^+ + H_2C{=}CHD$, for instance. Multiple interconversions may scramble all H and D and result in completely deuterated methylsilylium cation. However, since these speculations are based on the model with R = H, one assumption should be true; i.e., the system with R = CH_3 must follow the same pattern of interconversion as one with R = H. Preliminary results of our study of the $SiC_3H_9^+$ PES show that the substitution of H by CH_3 does not affect the pattern of the isomer interconversion.

In contrast to the $(CH_3)SiH_2^+ + D_2C{=}CD_2$ system, only one hydrogen may be transferred from the silylium cation to the ethene moiety in the $(CH_3)_2SiH + D_2C{=}CD_2$ system. This process gives the most stable isomer, $(CH_3)_2SiCD_2CD_2\ H^+$. The reverse transformation may produce only $(CH_3)_2SiD^+ + HDC{=}CD_2$, while scrambling of the methyl hydrogens with D cannot be achieved by the low-barrier hydrogen migrations.

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Supporting Information Available: Tables of the geometric parameters of the different isomers and transition states, calculated at different levels of theory, and a table of the B3LYP/6-31G** frequencies of the different isomers (4 pages). Ordering information is given on any current masthead page.

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