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# Dimethylsilyl and Ethylsilyl Cations: A Detailed Study of the $SiC_2H_7^+$ Potential Energy Surface

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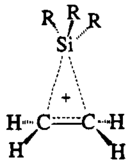
*Ab initio* molecular orbital calculations on stable isomers and on transition structures associated with the $SiC_2H_7^+$ potential energy hypersurface are presented. All critical points below the energies of dissociation into $SiH^+$ + ethane and into $SiH_3^+$ + ethylene have been obtained by gradient optimizations with the split valence-shell basis set 6-31G(d,p), both at the SCF level of theory and with inclusion of electron correlation energy to second-order Møller−Plesset (MP2) perturbation theory. The dimethylsilyl cation, which was found to be at the global minimum on the surface at both levels of theory, was optimized subsequently at MP2/6-311G(d,p). All structures at critical points on the surfaces at both levels of theory were characterized by harmonic frequency calculations, from which zero-point vibrational energies also were obtained. Vibrational frequencies of the dimethylsilyl cation and of the next lowest energy isomer, $H_3CH_2CSiH_2^+$, obtained at MP2/6-31G(d,p), also are reported. Isomers of $SiC_2H_7^+$ which contain fewer Si−H bonds tend to be lower in energy. The inclusion of electron correlation with the same basis set reduces the number of minima on the surface from 5 to 4 and reduces all of the barriers to interconversion between all stable isomers with the exception of that between the two lowest isomers. The latter value increases from 26.6 to 41.9 kcal $mol^{-1}$. This topological feature has permitted the proposal of detailed mechanisms to rationalize hydrogen−deuterium exchange reactions observed elsewhere in the gas phase.

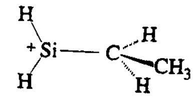
The chemistry of organosilicon compounds has been of considerable interest, both computationally and experimentally, for many years.[1,2] The circumstellar envelope of the carbon star IRC + 10216 has been found to contain molecules such as SiC, $SiC_2$, and $SiC_4$.[3] To date, no organosilicon species which include hydrogen have been detected; however, due to the relative abundance of hydrogen in the universe, it is probable that such species exist. Over the last decade, a vast literature has accumulated on the chemistry of organosilicon compounds. During this time, both theoretical and experimental techniques have improved enormously and both have made large contributions to our understanding of the structure and chemistry of small organosilicon compounds. Recent computational studies have been performed on cations of the formulas $SiC_2H_n^+$ ($n$ = 2, 4[4] and $n$ = 1, 3, 5[5]) in connection with previous gas-phase experimental research involving these ions in the SIFT (selected ion flow tube) apparatus.[6] These computational studies have provided detailed information about thermodynamic stabilities of isomers of a given formula, about barriers to the interconversion of these isomers, and about the geometries of stable ions and of the transition structures to their interconversion.

The $SiC_2H_7^+$ energy surface is of particular interest as it is the smallest cation in which it is possible to study the effects of both α- and β-silyl substituents in saturated carbocations. It also permits comparison of the relative stabilities of isomeric alkyl and silyl cations.[7]

In early high-pressure and tandem mass spectrometric studies on the reaction of $SiH_3^+$ with ethylene, Lampe and co-workers noted a "persistent-sticky complex", $SiC_2H_7^+$, which added a further two ethylene molecules.[8] From this reactivity they concluded that the initial π-adduct, **1a** (R = H), rearranged to the ethylsilyl cation **2** and that addition of further ethylene molecules occurred by insertion into the Si−H bonds of **2**, terminating in the triethylsilyl cation, $Si(C_2H_5)_3^+$.



**1a**



**2**

Much of the subsequent gas-phase work has involved the experimentally more convenient $Si(CH_3)_3$ group. The adduct formed from the addition of $Si(CH_3)_3^+$ to $H_2C{=}CH_2$ loses ethylene in bimolecular displacement reactions,[9] and high-energy collisional activation experi-

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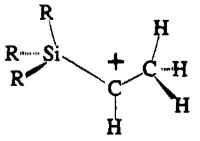
ments on the $(CH_3)_3SiC_2H_4^+$ ion, derived from $(CH_3)_3SiCH_2CH_2OC_6H_5$, have shown the two $CH_2$ groups to be equivalent.[10] Protonation of trimethylvinylsilane, $(CH_3)_3SiCH{=}CH_2$, produces an ion that has behavior identical to that of the adduct formed from $Si(CH_3)_3^+$ plus $H_2C{=}CH_2$, leading to the conclusion that protonation occurs on the carbon adjacent to silicon, formally generating a β-silyl substituted primary carbocation, **1b** (R = $CH_3$).[11] Protonation on the terminal carbon atom of trimethylvinylsilane, which would produce the α-silyl substituted ethyl cation, **3**, does not occur. The proton affinity of trimethylvinylsilane, (199 ± 2) kcal $mol^{-1}$, is much higher than that of ethylene (162.6 kcal $mol^{-1}$) and is similar to those of styrene and of tetramethylethylene, both molecules containing groups which are strongly stabilizing in carbocations.[12]

$R_3SiCH_2CH_2^+$

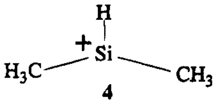
**1b**



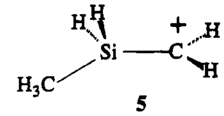
**3**

*Ab initio* molecular orbital calculations on isomers of $SiC_2H_7^+$ have shown the cyclic structure **1a** to be preferred over **1b**, and the β-silyl group has been shown to stabilize the ethyl cation by ~38 kcal $mol^{-1}$.[13] For R = H, MP2/6-31G(d)//HF/3-21G calculations have shown **1a** to be only 5.5 kcal $mol^{-1}$ above **2** and **1b** to be not at a minimum.[14a] Structure **3** is considerably higher in energy than **2** (by 31.0 kcal $mol^{-1}$) and also may not be at a minimum.[14]

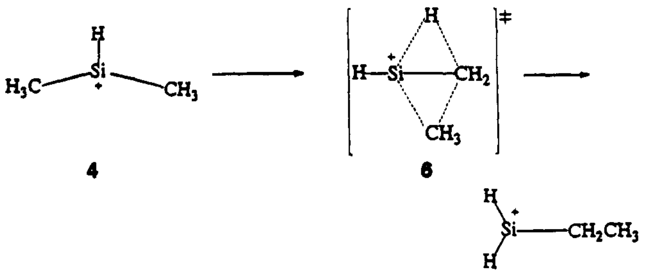
As in carbocation chemistry, secondary silyl cations are usually more stable than primary ions, and therefore, ion **4** would be expected to be at the global minimum on the $SiC_2H_7^+$ potential energy surface. Gas-phase $^{13}C$ labeling studies have shown $Si(CH_3)_3^+$ to isomerize to $Si(C_2H_5)(CH_3)H^+$ prior to the loss of ethylene, and a similar reaction is believed to occur between $Si(CH_3)_2H^+$, ion **4**, and $Si(C_2H_5)H_2^+$, ion **2**.[15b,c] This rearrangement requires either the intermediacy of the primary carbocation **5**, formed by a 1,2-hydride shift from $CH_3$ (in **4**) to $Si^+$, or the simultaneous (dyotropic) migration of H and $CH_3$ through transition structure **6**.



**4**



**5**



**2**

There has been no reported *ab initio* molecular orbital study of **4** or of the transition structures for the interconversion of ions **1**–**5**. Here we report an *ab initio* study of the $SiC_2H_7^+$ potential energy surface using structure optimization both at SCF and at MP2 levels of theory.

## Computational Methods

*Ab initio* molecular orbital calculations were performed using the GAUSSIAN suite of programs.[16] All structures were optimized at both the SCF/6-31G(d,p)[17] and MP2(full)/6-31G(d,p)[17,18] levels of theory using gradient techniques.[19] The structure which was found to exist at the global minimum on the MP2 surface was optimized subsequently at the MP2(full)/6-311G(d,p)[17e,20] level of theory. Transition structures were obtained either with the eigenvector-following (EF)[21] method or the CALCALL[16] algorithm. All critical points were characterized by harmonic frequency calculations both at SCF/6-31G(d,p) and at MP2(full)/6-31G(d,p), and the intrinsic reaction coordinate (IRC) method was used to establish which two minima were associated with each transition structure.[22] For all critical points on the MP2 surface other than that at the global minimum, single-point calculations at the MP2(full)/6-311G(d,p) level of theory were performed. Bond lengths and bond angles which involve heavy (non-hydrogen) atoms, as well as those which involve migrating hydrogen atoms, are reported.

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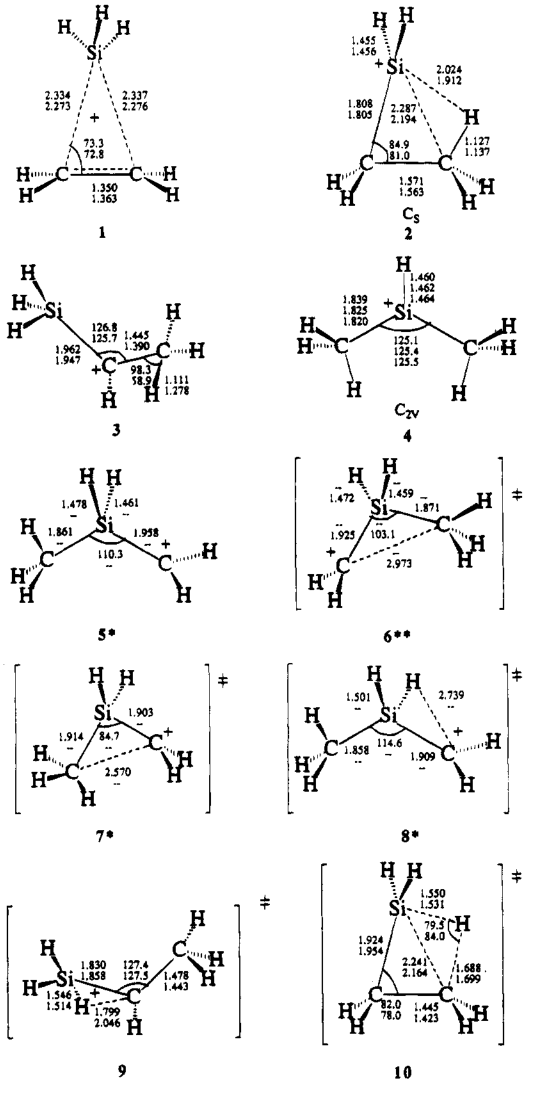
**Table 1. Total Energies (hartrees) for $SiC_2H_7^+$ Isomers and Transition Structures**[a]

| ion | RHF/6-31G(d,p) | ZPE[b] | MP2(full)/6-31G(d,p) | ZPE[c] | MP2(full)/6-311G(d,p) |
|---|---|---|---|---|---|
| **1** | −368.439 43 (+23.2) | 47.0 | −368.828 09 (+26.5) | 49.1 | −369.020 07 (+26.5) |
| **2** | −368.445 01 (+20.6) | 47.9 | −368.840 00 (+17.8) | 49.3 | −369.034 23 (+17.8) |
| **3** | −368.415 30 (+36.5) | 45.2 | −368.793 76 (+45.1) | 46.2 | −368.986 77 (+44.5)[e] |
| **4** | −368.477 46 (0) | 47.7 | −368.869 50 (0) | 48.6 | −369.061 52[d] (0) |
| **5** | −368.402 36 (+45.0) | 45.6 | | | |
| **6** | | | −368.768 74 (+61.1) | 46.5 | −368.960 30 (+61.4) |
| **7** | −368.399 43 (+47.2) | 45.9 | | | |
| **8** | −368.401 94 (+45.1) | 45.4 | | | |
| **9** | −368.404 47 (+43.5) | 45.4 | −368.784 55 (+50.3) | 45.6 | −368.977 79 (+49.5) |
| **10** | −368.415 59 (+37.8) | 46.7 | −368.809 31 (+36.7) | 47.5 | −369.003 55 (+35.3)[e] |
| $SiH^+ + C_2H_6$ | −368.372 83 (+61.8) | 43.8 | −368.751 37 (+69.7) | 44.2 | −368.947 05[d] (+67.4) |
| $SiH_3^+ + C_2H_4$ | −368.376 41 (+62.9) | 47.2 | −368.758 20 (+69.5) | 48.3 | −368.949 96[d] (+69.7) |

[a] Relative energies in kcal mol$^{-1}$ using scaled zero-point energies from SCF level calculations, except where zero-point energy has been obtained from MP2 level calculations, are listed in parentheses. [b] Zero-point energy from RHF/6-31G(d,p) in kcal mol$^{-1}$, scaled by a factor of 0.89,[28] except where specified otherwise. [c] Zero-point energy from MP2(full)/6-31G(d,p) in kcal mol$^{-1}$, scaled by a factor of 0.93.[29] [d] Optimized at MP2(full)/6-311G(d,p). [e] At MP2(fc)/6-311G(2df,2p) total energies (hartrees) are −368.886 46 for **3** and −368.877 62 for **10**.



*Structures 5, 7, and 8 do not exist at the MP2 level of theory.
**Structure 6 does not exist at the SCF level of theory.

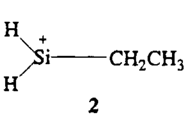
**Figure 1.** Optimized structural parameters. Bond lengths are in angstroms, and bond angles are in degrees. Upper values are at SCF/6-31G(d,p), and lower values are at MP2-(full)/6-31G(d,p). Structures **5**, **7**, and **8** do not exist at the MP2 level of theory. Structure **6** does not exist at the SCF level of theory.

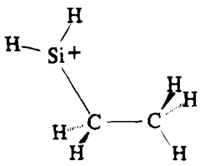
## Results and Discussion

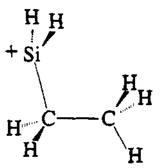
**Details of the $SiC_2H_7^+$ Potential Energy Surface.** Structural details for the ions **1**−**10** are given in Figure 1. On the SCF potential energy surface, ions **1**−**5** all are at minima, although the barriers to the rearrangements of the two highest energy isomers, **3** and **5**, are low (see Figure 2). We were, however, unable to locate a stable geometric analogue for structure **5** when electron correlation was included in the calculation.

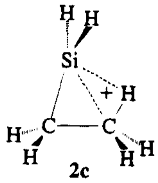
Structure **4**, the dimethylsilyl cation, has been found to be at the global minimum on both the SCF and the MP2 surfaces. This result is consistent with the trend observed for other $SiC_2H_n^+$ surfaces (Table 1) in which isomers which contain as many hydrogen atoms bonded to carbon (rather than to silicon) as possible tend to be more stable than are other isomers.[4,5]

It should be noted that there are three different conformational isomers associated with the skeletal structure depicted by ion **2** on the SCF surface.


**2**


**2a**


**2b**


**2c**

Each of these rotamers exists at a local minimum at SCF/6-31G(d,p) and, in order of increasing energy, they are ranked **2a** < **2b** < **2c**. However, **2a**, **2b**, and **2c** are only 2.1 kcal mol$^{-1}$ apart in energy at this level of theory and there are negligible barriers to their interconversion. At MP2/6-31G(d,p), **2b** collapses into **2c** without a barrier, and the latter is 2.6 kcal mol$^{-1}$ more stable than **2a**. It should be noted as well that the Si−C−C bond angle in **2c** at MP2 is 81.0°; that of **2a** is 116.5°; thus, the reversal of stabilities of **2a** and **2c** between the SCF and MP2 levels of theory can be justified on the grounds that post-SCF level calculations tend to favor more nonclassical structures than do SCF-level optimizations. While **2c** cannot be considered a cyclic structure, there is, nevertheless, more interaction between the silicon atom and the carbon to which it is not

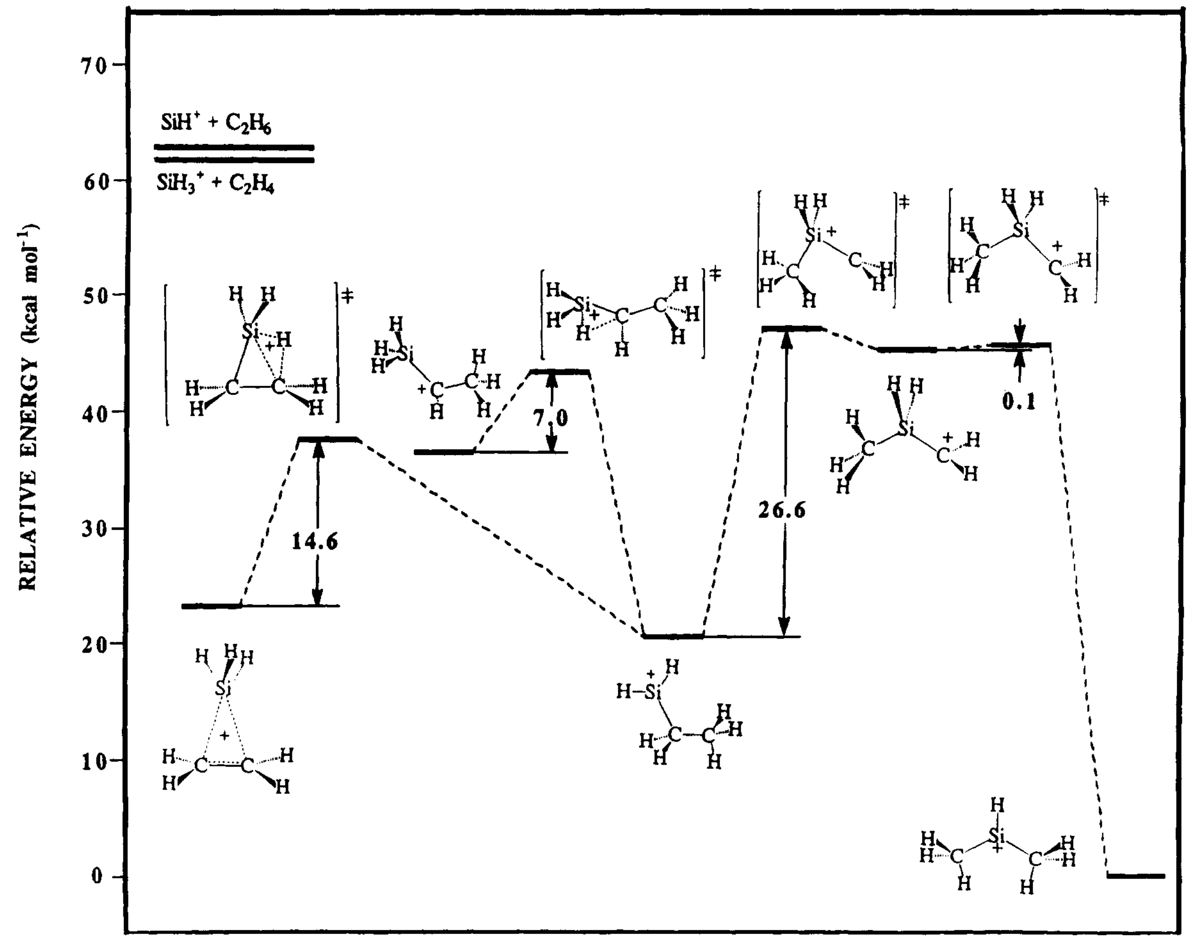
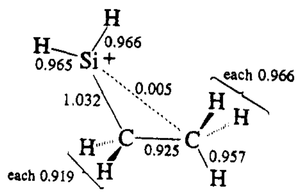
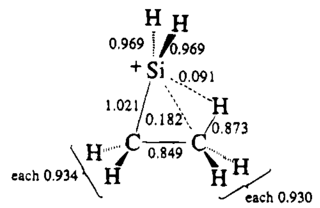


**Figure 2.** Potential energy surface as optimized at SCF/6-31G(d,p).



2a



2c

**Table 2. Harmonic Vibrational Frequencies (cm$^{-1}$) and Intensities (km/mol) for Structures 2 and 4 on the SiC$_2$H$_7$$^+$ Surface from MP2(full)/6-31G(d,p) Calculations[c]**

| 4 ($C_{2v}$)[a] | | | 2 ($C_s$)[b] | | |
|---|---|---|---|---|---|
| freq | intensity | sym | freq | intensity | sym |
| 3265.3 | 13.7 | $a_1$ | 3319.7 | 22.4 | a″ |
| 3264.6 | 5.9 | $b_2$ | 3303.5 | 7.2 | a″ |
| 3195.7 | 28.0 | $b_1$ | 3230.2 | 13.0 | a′ |
| 3194.2 | 0.0 | $a_2$ | 3206.3 | 10.0 | a′ |
| 3112.9 | 3.7 | $a_1$ | 2708.4 | 77.1 | a′ |
| 3111.0 | 66.2 | $b_2$ | 2479.0 | 17.0 | a″ |
| 2429.7 | 34.4 | $a_1$ | 2430.2 | 8.8 | a′ |
| 1474.4 | 24.3 | $b_1$ | 1612.3 | 14.3 | a′ |
| 1470.7 | 15.7 | $a_1$ | 1511.8 | 5.5 | a′ |
| 1462.7 | 0.0 | $a_2$ | 1472.9 | 10.9 | a′ |
| 1457.9 | 3.6 | $b_2$ | 1455.7 | 7.6 | a″ |
| 1361.5 | 5.6 | $a_1$ | 1211.6 | 13.0 | a′ |
| 1354.1 | 92.9 | $b_2$ | 1196.2 | 7.2 | a″ |
| 985.4 | 158.8 | $b_2$ | 1031.6 | 10.6 | a′ |
| 924.4 | 73.6 | $a_1$ | 991.8 | 76.8 | a′ |
| 880.0 | 88.2 | $b_1$ | 956.5 | 12.5 | a″ |
| 838.4 | 29.5 | $b_2$ | 955.1 | 29.2 | a′ |
| 672.8 | 1.0 | $a_1$ | 861.9 | 25.4 | a″ |
| 659.7 | 1.7 | $b_2$ | 741.0 | 7.8 | a′ |
| 641.0 | 0.0 | $a_2$ | 713.3 | 56.4 | a′ |
| 481.2 | 12.0 | $b_1$ | 556.6 | 6.6 | a″ |
| 226.3 | 4.3 | $a_1$ | 501.4 | 4.4 | a″ |
| 50.0 | 0.4 | $b_1$ | 372.8 | 66.1 | a′ |
| 34.7 | 0.0 | $a_2$ | 241.4 | 0.7 | a″ |

[a] ZPE = 48.6 kcal mol$^{-1}$. [b] ZPE = 49.3 kcal mol$^{-1}$. [c] Frequencies have not been scaled, but ZPE has been scaled by a factor of 0.93.

(formally) bonded than is the case in **2a** (as is shown in the Mayer bond order[24] analyses of these two conformers). Furthermore, there is a noteworthy interaction between the Si atom and the eclipsing H atom of the neighboring methyl group (Mayer bond order = 0.091), an interaction which does not exist in **2a**. In addition, there are substantial differences in the bond orders associated with the C−C and C−H bonds of the two conformers. For example, the C−C bond order in **2a** is 0.925; that of **2c** is 0.849. As well, the C−H bond orders in the methyl group of **2c** have distinctly different values; those associated with the out-of-plane hydrogen atoms are small (0.930) relative to their counterparts in **2a** (0.966) but are large compared to the in-plane methyl C−H bond of **2c** (0.873). Thus, it is evident that all bonds associated with the β-carbon of **2c** are weak relative to their analogues in **2a**. This depletion of electron density associated with these bonds is accompanied by the existence of significant through-space interactions between Si and the β-C and between Si and H of the adjacent methyl group. Due to the differences in the relative energies of these rotamers at SCF and at MP2, we include only the most stable conformer at

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[24] Mayer, I. *Int. J. Quant. Chem.* **1986**, *29*, 477.

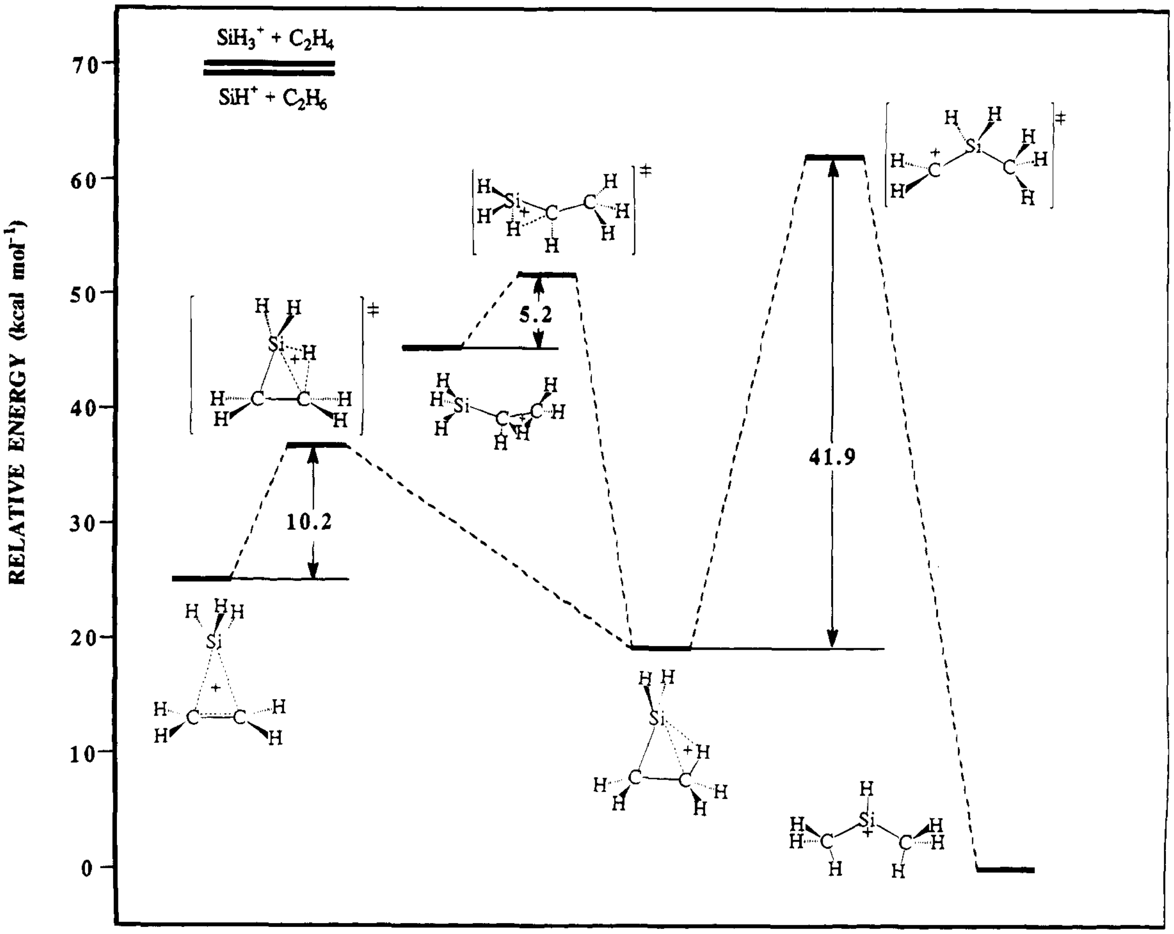

**Figure 3.** Potential energy surface as optimized at MP2/6-31G(d,p).

each level of theory in the energy level diagrams shown in Figures 2 and 3. Geometric parameters for only conformer **2c** are given in Figure 1.

One also may note the differences in bond orders associated with the α-carbons of the two conformers. The two equivalent C−H bonds of **2a** (Mayer bond order = 0.919) are weaker than their counterparts in **2c** (0.934). These results suggest that charge delocalization in **2a**, from $CH_2$ to $Si^+$, occurs to a greater extent than in **2c**.

When electron correlation is included, the surface reduces to four minima, with ion **2** being 19.2 kcal $mol^{-1}$ above **4**, with ion **1** being 25.2 kcal $mol^{-1}$ above **4**, and with ion **3** being 45.1 kcal $mol^{-1}$ above **4**. As suggested by the early gas-phase results of Lampe and co-workers,[8] the barrier for conversion of **1** into **2** is quite low, 14.6 kcal $mol^{-1}$ at SCF/6-31G(d,p) and 10.2 kcal $mol^{-1}$ at MP2(full)/6-31G(d,p). This trend toward a lower isomerization barrier, as well as a trend toward a greater thermodynamic stability of **2** vis-à-vis **1** on inclusion of electron correlation (see Figures 2 and 3), suggest that **2** should be considerably more abundant than **1** in the gas phase.

The largest barrier is for the interconversion of the two lowest energy species, ions **2** and **4**, and at MP2/6-31G(d,p), this value (41.9 kcal $mol^{-1}$) is quite substantial, as suggested by Fourier transform mass spectrometry.[15c] These two ions have different gas-phase reactions with methanol and with ethene-$d_4$; such experiments have been used to show that these ions isomerize slowly unless activated by collision.[15c]

The interconversion of ions **2** and **4** is involved in the most dramatic topological difference between the SCF and MP2 surfaces. At the former level of theory, this interconversion is a two-stage process involving the intermediacy of ion **5**, as well as two transition structures (**7** and **8**). The higher barrier which must be surmounted, that for the conversion of **2** into **5** (through **7**), is 26.6 kcal $mol^{-1}$ above **2**. At the MP2 level, **5** collapses into **4** without a barrier, and the critical points associated with structures **7**, **5**, and **8** coalesce into a single transition structure (**6**). This significant topological change is accompanied by a large increase in the barrier to interconversion of **2** and **4**, to 41.9 kcal $mol^{-1}$. This substantial barrier indicates the formation of a transition structure which is rather diffuse in geometry, as may be inferred by the existence of Si−C bond lengths (1.871 and 1.925 Å) which are longer than that obtained experimentally for silaethane (1.867 Å).[25] Therefore, the energy lowering caused by the inclusion of electron correlation is greater in the case of minima **2** and **4** than is the case for transition structure **6** at MP2.

The geometry of transition structure **6** is instructive in the context of the proposed dyotropic isomerization process between **2** and **4**.[15c] The suggested transition structure involves a hydrogen atom and a methyl group, both of which are depicted as bridging the remaining Si−C bond. However, it is evident from Figure 1 that **6** is considerably different in geometry. In our computed

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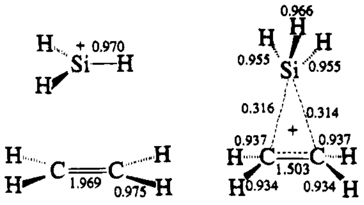
(25) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

transition structure, the methyl group has completed its migration from C to Si, whereas the H atom, which must move in the opposite direction, still is firmly bonded to silicon. We have verified by the use of an IRC analysis that **6** interconverts **2** and **4**, and a subsequent attempt at obtaining a transition structure with a geometry more reminiscent of that proposed previously[15c] has been unsuccessful. Clearly then the dyotropic isomerization between **2** and **4** proceeds in an asynchronous fashion.

Ion **1**, created formally from the addition of $SiH_3^+$ to ethylene, contains long Si–C distances, and the C–C bond distance is slightly longer than an experimental double bond length of ethylene (1.339 Å)[25] at both levels of theory. The weak Si–C interactions also are apparent from the Mayer bond orders (shown below). The long Si–C distances can be attributed to the donation of a $\pi$-electron pair from ethylene to the empty p-orbital of the electron deficient Si of the $SiH_3^+$ group. However, unlike in the case of the formation of ground state $SiC_2H_4^+$ ($^2B_2$) from the addition of $Si^+$ ($^2P$) to ethylene, there is no back-donation of electrons from $SiH_3^+$ to the $\pi^*$ LUMO of ethylene in the formation of **1**. As a result, a three-center, two-electron bonding arrangement is created in **1**; thus, less than full Si–C bonds are created, and the resulting Si–C distances are much greater than what would be considered "normal" for an Si–C bond. The inclusion of electron correlation in the optimization of **1** has the effect of shortening the C–Si distances and of lengthening the C–C separation. These geometric changes are consistent with the tendency of post-SCF wave functions to give better descriptions of nonclassical structures than SCF-level wave functions. Clearly, there exist interactions between the Si atom and the carbons in **1**, but as is shown by the Mayer bond order[24] analysis this ion should be considered more correctly to be a $\pi$-complex than a genuine three-membered ring.



**Separated reactants** **Pi-complex**

Despite the long C–Si distance associated with this $\pi$-complex, the binding energy of **1** is 43.2 kcal mol$^{-1}$ when compared to the separated $SiH_3^+$ + ethylene. This binding energy is considerably greater than that of the trimethylated cation **1a** (R = $CH_3$) (23 kcal mol$^{-1}$ at "corrected" HF/6-31G(d)//HF/3-21G).[14a] This difference in binding energies is attributed to the greater intrinsic stability of the trimethylsilyl cation arising from the delocalization of charge onto the methyl groups.

Ion **3**, an α-silyl substituted ethyl cation as optimized at SCF/6-31G(d,p), lies 36.5 kcal mol$^{-1}$ above **4**. However, the structure of **3** undergoes substantial modification on reoptimization at MP2(full)/6-31G(d,p). At this level, the optimized structure contains one hydrogen atom which bridges the two carbon atoms. In this way, ion **3** undergoes structural changes similar to those of the ethyl cation[26] on proceeding from SCF to post-SCF levels of theory. The structure of **3**, as well, is reminiscent of that of a high-energy isomer of $SiC_2H_5^+$, as has been reported elsewhere.[5]

Ion **3** is a further illustration of the well-established trend in which post-SCF level optimizations tend to favor nonclassical structures, such as cyclic ions. However, as can be seen in Figures 2 and 3, the barrier for the conversion of **3** to **2** is 7.0 kcal mol$^{-1}$ at SCF/6-31G(d,p), and this is reduced to 5.2 kcal mol$^{-1}$ at MP2/6-31G(d,p). Despite the large difference in the position of the bridging H atom in structure **3** as optimized at the SCF and MP2 levels, the overall barrier to rearrangement of **3** is only slightly reduced by the inclusion of electron correlation (from 7.0 kcal mol$^{-1}$). Inclusion of additional polarization functions has been found to be necessary for a satisfactory description of some particularly electron-deficient hydrogen-bridged cations,[27] and we therefore examined structures **3** and **10** at a considerably higher level of theory, MP2 (frozen core)/6-311G(2df,2p). The results of this extension were consistent with our findings at MP2(full)/6-31G(d,p). Ion **3** is still at a local minimum, **10** is a transition structure, and both structures are almost identical to those obtained at MP2/6-31G(d,p). The barrier for the conversion of **3** and **2** is reduced slightly, to 4.9 kcal mol$^{-1}$. Further extension of the basis set and recovery of more correlation energy may lead to further small reductions in the barrier. However, it seems probable that **3** will be at a local minimum at all levels of theory but the barrier to its rearrangement is sufficiently low to prevent it from being an observable species in room-temperature gas-phase chemistry.

Comparison of the SCF-optimized geometries and the MP2-optimized geometries for transition structure **10** (for the interconversion of **1** and **2**) and for transition structure **9** (for the isomerization of **3** → **2**) shows increases in Si–C bond lengths and decreases in C–C bond lengths on inclusion of electron correlation. As well, the Si–C–C angle in **10** is observed to decrease markedly (from 82.0 to 78.0°) on inclusion of electron correlation. These structural differences are consistent with a shift in the geometry of the transition structures toward the higher energy isomer in each case on proceeding from SCF-level optimizations to MP2-level optimizations. These geometric changes can be justified easily on considering the fact that the differences in the energies of **1** and **2**, and of **3** and **2**, in turn, are greater at the MP2 level (where **2** is the more stable isomer of each pair). The Hammond postulate[28] predicts that the transition structure should be closer in geometry to the higher energy isomer; thus, shifts in the transition structure geometries of **10** and of **9** toward **1** and **3**, respectively, are not unexpected.

**Mechanistic Consequences.** The observed characteristics of the $SiC_2H_7^+$ potential energy hypersurface have significant implications for the interpretation of results obtained from gas-phase experimental work. The existence of a large barrier to the interconversion of **2** and **4** suggests strongly that both isomers exist as stable species in the gas phase at normal temperatures. This result confirms the hypothesis made from the results of experimental observations that isomerization of these

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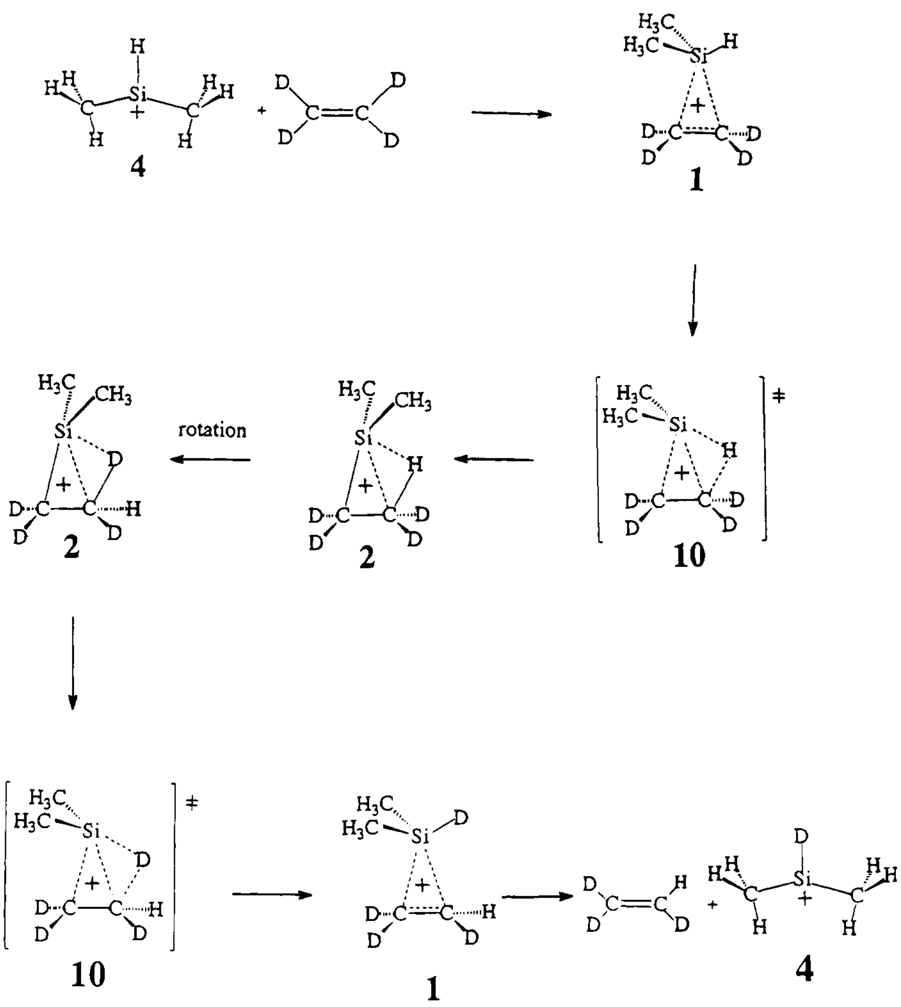
(26) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.

(27) Glukhovtsev, M. N.; Schleyer, P. v. R.; Hommes, N. J. R. v. E.; Carneiro, J. W. de M.; Koch, W. *J. Comput. Chem.* **1993**, *14*, 285.

(28) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

**Scheme 1**



two species "should have a considerable barrier".[15b] Experiments also have been performed on these two $SiC_2H_7^+$ isomers using FTMS in an attempt to distinguish between them on the basis of their reactions with ethylene-$d_4$ and with $^{13}C_2H_4$, studies from which one H/D exchange for species **4** (to form $H_3CSiDCH_3^+$) and seven H/D exchanges for structure **2** were reported.[15c]

The results of our computational study of the $SiC_2H_7^+$ potential energy hypersurface yield greater mechanistic insight into these reactions than are obtained from experimental studies alone. Scheme 1 illustrates a plausible mechanism for the single H/D exchange observed in the reaction of **4** with ethylene-$d_4$, in a scheme analogous to that proposed previously.[15a,b] The reaction may proceed via electrophilic attack of the positively-charged Si on ethylene-$d_4$, to form a structure analogous to **1**, but with two methyl groups replacing hydrogen atoms on silicon. This step may be followed by a 1,2-H shift, from Si to C, to form a dimethyl analogue to ion **2**. Free rotation about the C−C single bond may allow the formation of a rotamer in which a deuterium atom, rather than a hydrogen atom, eclipses the silicon of the $Si(CH_3)_2^+$ moiety, upon which a 1,2-D migration and subsequent elimination of $D_2C{=}CDH$, in reverse order to the process described above, regenerates the dimethylsilyl cation but with a deuterium atom bonded to silicon.

Scheme 2 provides a more detailed rationalization of the mechanism for seven H/D exchanges in the reaction of **2** with ethylene-$d_4$. This process is more complicated than that discussed in Scheme 1 because it involves internal H/D scrambling between Si and C of a given "intermediate" $SiC_2H_nD_{7-n}$ species. It must be noted, as well, that, as our proposed pathway involves the intermediacy of species **1** as well as a series of 1,2-$H^-$ shifts and 1,2-$D^-$ shifts, it differs in this respect from that proposed previously, in which the existence of a species with the structure of **1** in gas-phase experimental studies was not considered.[15c]

**Vibrational Frequencies.** As the two lowest energy isomers on the $SiC_2H_7^+$ surface are separated by a high-energy barrier, it is probable that both ions **2** and **4** will be observable in the gas phase at room temperature. Here we report the harmonic vibrational frequencies as obtained at MP2(full)/6-31G(d,p) on each of these two isomers, as well as the intensities, the symmetry assignments, and the scaled (by 0.93)[29] zero-point vibrational energies, in the hope that this information may be of use to experimental chemists who wish to study these ions spectroscopically.

## Conclusions

Structural isomers associated with critical points on the $SiC_2H_7^+$ potential energy hypersurface have been investigated by *ab initio* MO theory. Our results

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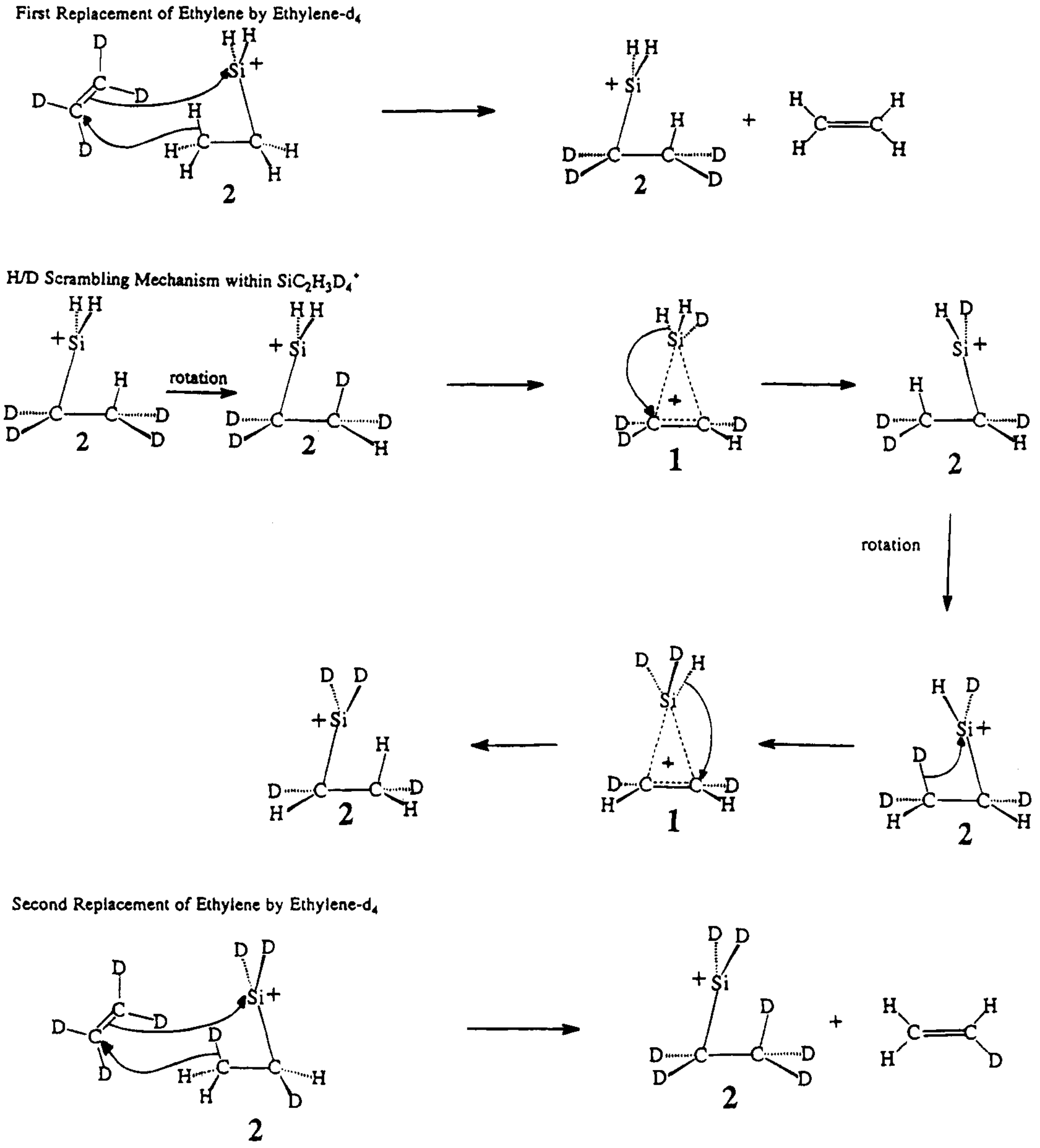
(29) Rodriquez, C. F. Ph.D. Dissertation, **1994**.

**Scheme 2**



First Replacement of Ethylene by Ethylene-$d_4$

H/D Scrambling Mechanism within $SiC_2H_3D_4^+$

Second Replacement of Ethylene by Ethylene-$d_4$

reinforce the observations made for other organosilicon cationic surfaces that isomers on a given surface with fewer H atoms bonded to Si (as opposed to being bonded to C) tend to have the lowest electronic energies. The existence of a large energy barrier to the isomerization of structures **2** and **4**, calculated to be 42 kcal mol$^{-1}$ and estimated experimentally to be ~35 kcal mol$^{-1}$.[15d] supports the postulate of Jacobson and coworkers[15c] and provides strong evidence for the presence of both isomers in the gas phase. By contrast, the existence of a small, but not insignificant, barrier (10 kcal mol$^{-1}$, the same as the value estimated experimentally[15d]) to the interconversion of **1** and **2** may have important experimental ramifications in another sense. As Jacobson's group did not consider the possibility of the existence of species **1** in its gas-phase experiments but, as illustrated in Schemes 1 and 2, the mechanisms of H/D exchanges may proceed through such an isomer, it is conceivable that what was observed may, in fact, have been a mixture of **1** and **2**. Further experimental verification, however, is required before any conclusions can be made about the mechanism.

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