

1-1995

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Abstract

The potential energy surface for the decomposition of CH₃SiH₂⁺ was studied by ab initio electronic structure theory. At the MP2/6-31G(d,p) level of theory, CH₃SiH₂⁺ is the only minimum energy structure on the SiCH₅⁺ potential energy surface. Lower levels of theory reported that +CH₂SiH₃ was also a local minimum, about 40 kcal/mol higher in energy with only a small (ca. 1-2 kcal/mol) barrier for conversion back to CH₃SiH₂⁺. However, at higher levels of theory, the C₂ structure of +CH₂SiH₃ has an imaginary frequency, indicating that it is a saddle point rather than a local minimum on the potential energy surface. The 0 K reaction enthalpies for 1,1-dehydrogenation from silicon, 1,2-dehydrogenation, 1,1-dehydrogenation from carbon, and demethanation were calculated to be 30.2, 69.1, 107.3, and 45.3 kcal/mol, respectively. Activation energies (0 K) were calculated at the MP4/6-311++G(2df,2pd) level of theory with the classical barriers subsequently adjusted for zero-point vibrational energies. The 0 K activation energies for 1,1-dehydrogenation from silicon, 1,2-dehydrogenation, and demethanation are predicted to be 66.6, 72.7, and 73.0 kcal/mol, respectively. All attempts to locate a transition state for the insertion of the carbene-like species, CHSiH₂⁺, into H₂ (reverse of the 1,1-dehydrogenation from carbon) were unsuccessful. This is not surprising since analogous carbene insertions are known to occur without a barrier. Thus, we conclude that this 1,1-H₂ elimination from carbon proceeds monotonically uphill. The closed-shell structures for the products of the above reactions (CH₃Si⁺, CH₂SiH⁺, and CHSiH₂⁺) were calculated at the MP2/6-31G(p,d) level of theory. Finally, triplet products were also examined.

Disciplines

Chemistry

Comments

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Ab Initio Molecular Orbital Investigation of the Unimolecular Decomposition of $\text{CH}_3\text{SiH}_2^+$

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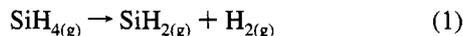
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Received: June 28, 1994; In Final Form: October 19, 1994[Ⓢ]

The potential energy surface for the decomposition of $\text{CH}_3\text{SiH}_2^+$ was studied by *ab initio* electronic structure theory. At the MP2/6-31G(d,p) level of theory, $\text{CH}_3\text{SiH}_2^+$ is the only minimum energy structure on the SiCH_3^+ potential energy surface. Lower levels of theory reported that $^+\text{CH}_2\text{SiH}_3$ was also a local minimum, about 40 kcal/mol higher in energy with only a small (ca. 1–2 kcal/mol) barrier for conversion back to $\text{CH}_3\text{SiH}_2^+$. However, at higher levels of theory, the C_s structure of $^+\text{CH}_2\text{SiH}_3$ has an imaginary frequency, indicating that it is a saddle point rather than a local minimum on the potential energy surface. The 0 K reaction enthalpies for 1,1-dehydrogenation from silicon, 1,2-dehydrogenation, 1,1-dehydrogenation from carbon, and demethanation were calculated to be 30.2, 69.1, 107.3, and 45.3 kcal/mol, respectively. Activation energies (0 K) were calculated at the MP4/6-311++G(2df,2pd) level of theory with the classical barriers subsequently adjusted for zero-point vibrational energies. The 0 K activation energies for 1,1-dehydrogenation from silicon, 1,2-dehydrogenation, and demethanation are predicted to be 66.6, 72.7, and 73.0 kcal/mol, respectively. All attempts to locate a transition state for the insertion of the carbene-like species, CHSiH_2^+ , into H_2 (reverse of the 1,1-dehydrogenation from carbon) were unsuccessful. This is not surprising since analogous carbene insertions are known to occur without a barrier. Thus, we conclude that this 1,1- H_2 elimination from carbon proceeds monotonically uphill. The closed-shell structures for the products of the above reactions (CH_3Si^+ , CH_2SiH^+ , and CHSiH_2^+) were calculated at the MP2/6-31G(p,d) level of theory. Finally, triplet products were also examined.

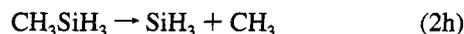
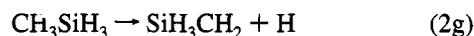
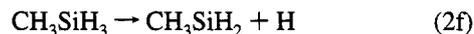
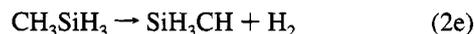
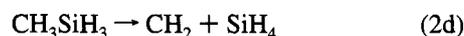
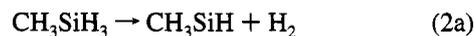
I. Introduction

The determination of accurate potential energy surfaces for small silicon-containing compounds is of interest for a variety of reasons. They have an impact on such processes as chemical vapor deposition (CVD),^{1–8} for example, as initiated by the decomposition of silane, process 1.² *Ab initio* calculations employing fourth-order perturbation theory



and an extended basis set reveal a barrier of 56.9 kcal/mol for process 1, with little or no barrier for the reverse association process.³ Coltrin et al. have developed a model for the CVD process of silane.⁹ The thermal decomposition of methylsilane has also been the focus of recent experimental¹⁰ and theoretical¹¹ studies since it represents the simplest alkylsilane.¹⁰ Experimental studies have shown that CH_3SiH_3 dissociation occurs by three primary pathways: demethanation, 1,2-elimination of dihydrogen, and 1,1-elimination of dihydrogen from the silicon center.^{10b} Fourth-order perturbation theory calculations (with a triple- ζ -plus polarization basis set) on the unimolecular thermal decomposition of methylsilane reveal a large number of energetically accessible pathways, process 2.¹¹ However, the lowest energy processes for dissociation of CH_3SiH_3 are 1,1-eliminations to produce silylenes, processes 2a and 2b. Process 2a is 49.8 kcal/mol endothermic with a barrier of 71.9 kcal/

mol, and process 2b is 52.9 kcal/mol endothermic



with a barrier of 63.3 kcal/mol.¹¹ Process 2a can be compared directly to process 1 for silane, with methyl substitution increasing both the endothermicity and barrier for reaction, *vide supra*.

Since plasma CVD occurs at very high temperatures, at which ions can be important, several models of the gas-phase and surface reactions for silane CVD have been developed which include the involvement of ion–molecule reactions.^{12–14} Reactions of SiH_x^+ ($x = 0–3$) with SiH_4 and CH_3SiH_3 have been studied in the gas phase.^{15–19} Recently, the unimolecular decompositions of the simple silylenium ions ($\text{CH}_3\text{SiH}_2^+$ ^{20,21} and CH_3SiCH^+ ²¹) have been reported. These studies revealed that dehydrogenation is the lowest energy pathway for unimolecular dissociation of $\text{CH}_3\text{SiH}_2^+$ and HCl loss is the lowest energy pathway for CH_3SiCH^+ decomposition, reactions 3 and

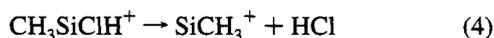
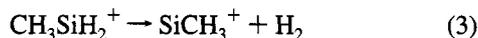
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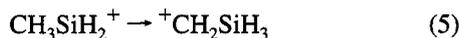
[Ⓢ] Abstract published in *Advance ACS Abstracts*, December 1, 1994.

4, respectively. The kinetic energy release distribution (KERD)²² for dehydrogenation

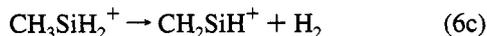
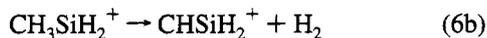
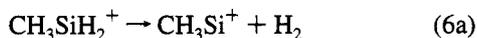


of metastable CH₃SiH₂⁺ suggests two distinct mechanisms with substantially different kinetic energy releases.²⁰ This was interpreted by invoking 1,1-dehydrogenation from the silicon atom (large kinetic energy release) and 1,1-dehydrogenation from the carbon atom (narrow kinetic energy release).²⁰ The mechanism for the dehydrogenation of CH₃SiH₂⁺ was investigated by studying both the metastable decomposition and collision-activated dissociation (CAD) of CH₃SiD₂⁺.^{20,21} Unfortunately, no mechanistic information was obtained due to isotopic scrambling *prior* to decomposition. Organosilylenium ions in the gas phase are known to undergo facile rearrangements.^{23–27}

There have been several previous theoretical studies of SiCH₅⁺. Pople et al., using fourth-order perturbation theory and a double- ζ -plus polarization (DZP) basis set, predicted the CH₃SiH₂⁺ structure to be the most stable isomer.²⁸ Hopkinson and Lien studied the SiCH₅⁺ hypersurface at the Hartree–Fock/DZP level of theory and found that CH₃SiH₂⁺ was the only minimum.²⁹ These authors found that the 1,2-hydrogen migration, reaction 5, is 40 kcal/mol endothermic with little or no barrier in excess of the



overall endothermicity.²⁹ If the barrier for dehydrogenation of CH₃SiH₂⁺ is greater than the 40 kcal/mol required for process 5, then this process can easily account for the observed isotopic scrambling.^{20,21} Tobita and co-workers²⁰ used the semiempirical MNDO method to study the mechanism of dehydrogenation for CH₃SiH₂⁺ and found barriers of 95 kcal/mol for 1,1-dehydrogenation from silicon, 102 kcal/mol for 1,1-dehydrogenation from carbon, and 111 kcal/mol for the 1,2-dehydrogenation process, reaction 6.



Since CH₃SiH₂⁺ is the simplest organosilylenium ion, a detailed understanding of its chemistry may serve as a model to interpret more complex organosilylenium ions. Consequently, we have studied the SiCH₅⁺ system by using high-level theoretical calculations. A number of dissociation channels are described along with activation energies, reaction enthalpies, and optimized geometries.

II. Computational Methods

The molecular structures were initially determined by using the 6-31G(d)³⁰ basis set at the Hartree–Fock (HF) self-consistent-field (SCF) level of theory. These structures were then refined with a slightly larger basis set, 6-31G(d,p), by using second-order many-body perturbation theory³¹ as formulated within the Møller–Plesset³² procedure. This is generally referred to as MP2.³³ The stationary points determined in this manner were verified to be local minima or transition states by computing and then diagonalizing the matrix of energy second

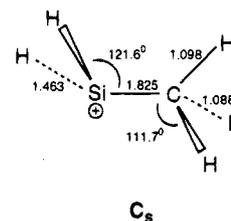


Figure 1. MP2/6-31G(d,p) structure for the parent ion, CH₃SiH₂⁺ (bond lengths in angstroms; angles in degrees).

derivatives (Hessian). This was accomplished by using the analytic derivative codes in GAMESS³⁴ and GAUSSIAN 92.³⁵ The final energetics were determined with the extended 6-311++G(2df,2pd) basis set³⁶ and fourth-order perturbation theory (MP4³³). For triplet states, unrestricted Hartree–Fock (UHF) and their perturbation theory analogues (UMP2, UMP4) were used. The reactants and products connected by each transition state were determined by following each minimum energy path (MEP), using the second-order algorithm developed by Gonzales and Schlegel.³⁷ Since the SCF and MP2 transition structures are quite similar, the MEP's were determined at the simpler SCF level of theory.

III. Results and Discussion

A. SiCH₅⁺. At the SCF/6-31G(d) level of theory, SiCH₅⁺ exists as two isomers, CH₃SiH₂⁺ and ⁺CH₂SiH₃. However, at the MP2/6-31G(d,p) level of theory, the C_s structure of ⁺CH₂SiH₃ has an imaginary frequency, indicating that it is a saddle point rather than a local minimum on the potential energy surface. Distortion of the geometry in the direction indicated by the imaginary mode leads directly to the CH₃SiH₂⁺ structure with *no* intervening barrier. Therefore, at the MP2/6-31G(d,p) level of theory, there is only one minimum on the SiCH₅⁺ potential energy surface. This is consistent with the previous calculations of Hopkinson and Lien.²⁹ However, the ⁺CH₂SiH₃ species is only 40 kcal/mol higher in energy than CH₃SiH₂⁺. Consequently, it is still possible that the carbenium ion species may participate in the decomposition of CH₃SiH₂⁺. For example, if the CH₃SiH₂⁺ ion is activated by 40 kcal/mol or more, then it can sample the transition-state region represented by ⁺CH₂SiH₃ by 1,2-hydrogen migration (i.e., process 5), and this may be followed by decomposition. The calculated geometry for CH₃SiH₂⁺ is given in Figure 1. Note that the Si–C bond length in this species is calculated to be about 0.05 Å shorter than the corresponding distance in the neutral parent, CH₃SiH₃.¹⁰ This observation is consistent with the fact that the Si–C bond energy in the cation is 13–14 kcal/mol greater than that in the neutral parent.^{37a} This difference has been attributed to hyperconjugation between the formally empty Si p orbital and an adjacent CH bond.^{37a} However, note that the planar SiH₂ group is rotated 90° from, rather than being coplanar with, an adjacent CH bond. Consequently, the electron population in the formally empty Si 3p orbital is small (about 0.05 electron), and the interaction is more likely an electrostatic one between the large positive charge on Si and the negative charge on C.

B. Thermochemistry. The parent ion (CH₃SiH₂⁺) can dissociate in a number of ways (reactions 6–11). Although the ⁺CH₂SiH₃ species is not a local minimum on the potential energy surface, dehydrogenation may still originate from this species; consequently, two dehydrogenation processes are considered for this ion, reactions 10 and 11. The known thermochemistry

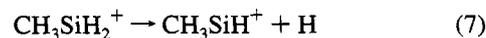


TABLE 1: Literature Heats of Formation (kcal/mol) of Relevant Species at 298 K^a

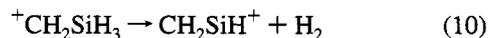
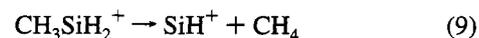
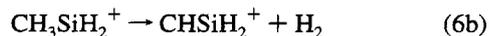
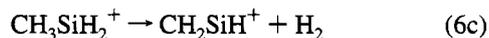
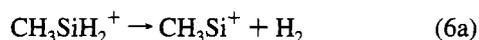
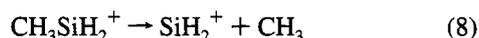
species	ΔH_f° ^b	other values ^c
CH ₃ SiH ₂ ⁺	210(3) ^d	206 ^e
CH ₃ SiH ⁺	242 ^e	248(3) ^{d,f}
CH ₃ Si ⁺	231(2) ^g	
CH ₂ SiH ⁺	273(4) ^{g,h}	
SiH ₂ ⁺	275.5(1.0) ⁱ	278, ^e 277.7(0.7) ^j
SiH ⁺	273.6(1.4) ^g	273.8(1.2) ^j
⁺ CH ₂ SiH ₃	250 ^{k,l}	
CH ₄	-17.8 ^m	
CH ₃	34.8 ^m	
H	52.1 ^m	

^a Ion heats of formation use the thermal electron convention; therefore, ion heats of formation are 1.48 kcal/mol larger than values which do not include the heat of the electron. Numbers in parentheses are the error associated with the value. ^b Values used for thermochemical calculations in the text. ^c Related thermochemical values not used in calculations. ^d Reference 45. ^e Reference 46. ^f This value may represent an upper limit. ^g Reference 47. ^h This structure was inferred to account for a high-energy feature in the data. ⁱ Reference 48. ^j Reference 49. The 0 K values listed in the reference are altered to 298 K according to information given in ref 50. ^k Reference 50. ^l Calculated from the $\Delta H_f^\circ(298\text{ K})$ value for CH₃SiH₂⁺ and that of ⁺CH₂SiH₃ (theoretical calculations have revealed that ⁺CH₂SiH₃ is 40 kcal/mol less stable than CH₃SiH₂⁺, ref 29). ^m Reference 51.

TABLE 2: Summary of Theoretical and Experimental Reaction Enthalpies and Theoretical Activation Energies (kcal/mol)

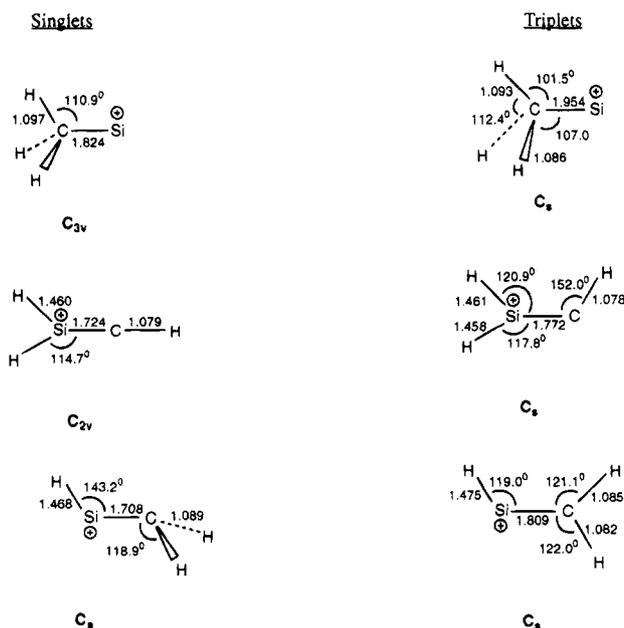
reaction	reaction enthalpy			reaction barrier	
	this work ^a	MNDO ^b	expt ^c	this work	MNDO
7	89.1		84	<i>d</i>	
8	101.5		100	<i>d</i>	
6a	30.2	34.0	21	66.6	95
6c	69.1	69.0	63	72.7	111
6b	107.3	96.0		<i>e</i>	102
9	45.3		46	73.0	<i>f</i>
10	29.1 ^g	13.0 ^h	23 ^g	<i>d</i>	39 ^h

^a Calculated at the MP4/6-311++G(2df,2pd) level of theory at 0 K. See text for details. ^b Reference 20. ^c Calculated from the experimental values in Table 1 at 298 K. ^d Assumed barrierless. ^e There appeared to be no barrier to the reverse association process. ^f Not calculated in ref 20. ^g This reaction enthalpy is for decomposition from ⁺CH₂SiH₃ which is 40 kcal/mol higher in energy than CH₃SiH₂⁺. Consequently, 40 kcal/mol should be added to this value for the total energy requirement for comparison to CH₃SiH₂⁺. ^h Similar to *g* except ⁺CH₂SiH₃ is calculated to be 56 kcal/mol less stable than CH₃SiH₂⁺.



for the related silicon ions is summarized in Table 1 with reaction enthalpies summarized in Table 2. The radical losses (reactions 7 and 8) are high-energy processes and are assumed to have no intervening barrier. In addition, the dehydrogenation process, reaction 11, is also an energetically prohibitive process since it produces a carbene¹¹ and will not be considered further.

The MP2/6-31G(d,p) closed-shell structures for the products of reactions 6a–6c are given in Figure 2. Note that the C–Si

PRODUCTS**Figure 2.** MP2/6-31G(d,p) closed-shell structures for the singlet and UMP 2/6-31G(d,p) for the triplet products in processes 6a–6c (bond lengths in angstroms; angles in degrees).

bond lengths in H₂CSiH⁺ and H₂SiCH⁺ are rather short, indicating some contribution from π -bonding. The enthalpies for reactions 6a–6c, 9, and 10, calculated at the MP4/6-311++G(2df,2pd) level, are summarized in Table 2. The 0 K enthalpies for these reactions are in excellent agreement with experimental values (Table 2). There are no experimental values available for process 6b; however, the excellent agreement between theory and experiment suggests that the calculated enthalpy for process 6b is equally reliable. MNDO calculations are also summarized in Table 2,²⁰ and are in generally good agreement with our values. Clearly, the thermodynamically most favored process is 1,1-dehydrogenation to yield CH₃Si⁺, reaction 6a.

C. Reaction Barriers. In addition to reaction enthalpy, the barrier to a reaction must also be known for the role of that process to be evaluated. We now consider the barriers for processes 6a–6c, 9, and 10. [As noted above, the radical losses (reactions 7 and 8) are high-energy processes and are assumed to have no intervening barrier.] The saddle-point structures are given in Figure 3. The classical barrier heights corresponding to processes 6a, 6c, and 9 are 69.0, 74.5, and 75.4 kcal/mol, respectively. Adjusting these values for zero-point vibrational energies yields 0 K activation energies of 66.6, 72.7, and 73.0 kcal/mol, respectively. Note that these results suggest that the reverse of process 6c occurs with only a slight barrier (ca. 3.6 kcal/mol), yet a transition state is found at a respectable level of theory (MP2/6-31G(d,p)). All attempts to locate a transition state for the insertion of the carbene-like species CHSiH₂⁺ into H₂ (the reverse of the 1,1-H₂ elimination, process 6b) were unsuccessful. This is not surprising since analogous carbene insertions are known to proceed without a barrier.³⁸ Thus, we conclude that this 1,1-H₂ elimination (process 6b) proceeds monotonically uphill.

Process 10 involves a 1,2-dehydrogenation from ⁺CH₂SiH₃. However, this species is itself predicted to be a transition state on the MP2/6-31G(d,p) potential energy surface. So a 1,2-H₂ elimination from this species would require traversing a second-order saddle point, presumably much higher in energy. One approach for determining the degree to which this region of space (⁺CH₂SiH₃ and the associated 1,2-H₂ elimination barrier

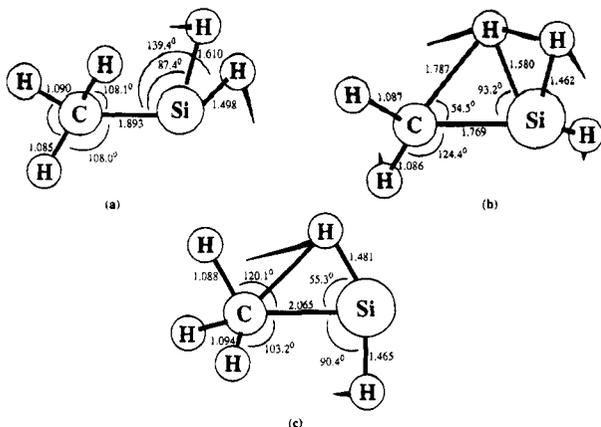


Figure 3. MP2/6-31G(d,p) saddle-point structures corresponding to processes 6a, 6c, and 9 designated as a, b, and c, respectively (bond lengths in angstroms; angles in degrees). The amplitudes of the normal mode displacements are indicated by headless arrows.

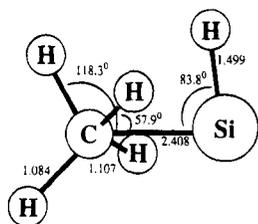


Figure 4. MP2/6-31G(d,p) local minimum (ion-dipole complex) on IRC for reaction 9 (See text). Bond lengths in angstroms, angles in degrees.

region) is sampled as a function of the available energy would be to carefully map out the potential energy surface in this region and then perform semiclassical trajectory calculations.^{39,40} MNDO calculations predict barriers for processes 6a, 6b, 6c, and 10 of 95, 111, 102, and 39 kcal/mol, respectively.^{20,41} These barrier heights are significantly higher than the barrier heights calculated at our much more reliable level of theory, *vide supra*.

The net reaction enthalpies predicted for the processes of interest (Table 2) are quite variable; however, the activation energies are surprisingly much closer to each other (Table 2). Nonetheless, process 6a (the most favorable thermodynamically) is predicted to have the lowest overall energy demand by about 6 kcal/mol. The barrier for process 10 is unknown; however, the overall endothermicity for the stepwise process



is 69.1 kcal/mol. This is already about 2.5 kcal/mol greater than the barrier for process 8, and 1,2- H_2 elimination barriers are generally quite high.¹⁰

The lowest barrier for decomposition of $\text{CH}_3\text{SiH}_2^+$ (66.6 kcal/mol, process 6a) is significantly larger than that for the 1,2-hydrogen shift, process 5, which only requires 40 kcal/mol. In addition, process 5 occurs with *no* barrier to the reverse process (it is not a local minimum on the potential energy surface). Consequently, $\text{CH}_3\text{SiH}_2^+$ ions, which have gained the minimum internal energy for fragmentation, could rapidly interconvert with ${}^+\text{CH}_2\text{SiH}_3$. Hence, $\text{CH}_3\text{SiD}_2^+$ would undergo isotopic scrambling prior to decomposition as observed experimentally.^{20,21} Analysis of the minimum energy path for process 9 reveals an unusual feature on the potential energy surface. Rather than falling apart to the indicated products, this reaction leads to the stable ion-dipole complex shown in Figure 4. At the highest level of theory used here, this complex is 17.7 kcal/mol lower in energy than the separated products (15.6 kcal/mol when zero-

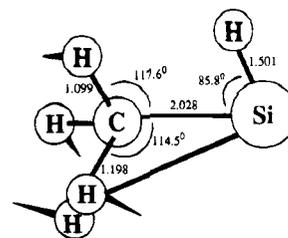


Figure 5. MP2/6-31G(d,p) geometry and imaginary normal mode for transition state for dihydrogen (Si-C) exchange; bond lengths in angstroms, angles in degrees. The amplitudes of the normal mode displacements are indicated by headless arrows.

point vibrational energies are included). Raghavachari has found similar complexes in related all-silicon surfaces.¹⁹ Equally interesting is the existence of another transition structure (Figure 5) which corresponds to exchange of two hydrogens between Si and C in this complex. At the MP4/6-311++G(2df,2pd) level of theory, the barrier height (activation energy) corresponding to this process is 66.5(63.6) kcal/mol. Thus, it is possible that this transition structure may also contribute to the observed H-D scrambling.^{20,21} However, isotopic scrambling for $\text{CH}_3\text{SiD}_2^+$ was induced by collisional activation *without* subsequent fragmentation.²¹ This suggests that there is a mechanism for isotopic scrambling which has an energy requirement much less than that required for decomposition. Isotopic scrambling by process 5 is consistent with this observation.

Dehydrogenation is the predominant fragmentation for the metastable decomposition of $\text{CH}_3\text{SiH}_2^+$; however, it occurs by two distinct mechanisms; one with a small kinetic energy release distribution (KERD) and one with a large KERD.²⁰ The large KERD is indicative of a process with a large barrier to the reverse association process, whereas a small KERD suggests a process with a small barrier to the reverse association process.^{42,43} The process with a large KERD was assigned to reaction 6a, which has a calculated barrier of 36.4 kcal/mol (our results, Table 2) to the reverse association process.²⁰ The process with a small KERD was previously assigned to reaction 6b.²⁰ Although the reverse of process 6b apparently occurs with *no* barrier, it seems unreasonable that it is responsible for the small KERD because of its high (prohibitive) energy requirement (Table 2). Process 6c, however, could be responsible for the small KERD. The barrier for process 6c is only 6.1 kcal/mol higher than that for process 6a; thus, it is energetically accessible. In addition, there is a small barrier (ca. 3.6 kcal/mol) for the reverse association process. Consequently, it appears that $\text{CH}_3\text{SiH}_2^+$ has two competing dehydrogenation processes for metastable ion decomposition; 1,1-elimination from silicon (process 6a) and 1,2-elimination (process 6c). It is also possible that dehydrogenation by process 10 also contributes to the small KERD process; however, the barrier is unknown.

Next, consider the selectivity of SORI-CAD^{21,44} for elucidating the lowest energy pathway for ion dissociation. This method (sustained off-resonance irradiation for collision-activated dissociation) results in slow activation of ions by multiple low-energy collisions, allowing near-threshold dissociation. The two competing decompositions that can be observed by mass spectrometry are dehydrogenation and demethanation. Demethanation (reaction 9) has a predicted activation barrier of 73.0 vs 66.6 kcal/mol for dehydrogenation (process 6a). Both of these processes have high barriers with only a 6.4 kcal/mol difference. Despite this small difference, SORI-CAD was able to decompose $\text{CH}_3\text{SiH}_2^+$ *exclusively* by dehydrogenation!²¹ In addition, this induced dehydrogenation should occur *exclusively* by process 6a. If process 6c was also involved in the SORI-CAD

decomposition, then demethanation (process 9) should also be observed (processes 6c and 9 have barriers that differ by less than 1 kcal/mol, Table 2).

The 1,1-elimination processes, reactions 6a and 9, can be compared with the corresponding 1,1-eliminations from neutral methylsilane, processes 2a and 2b. The 1,1-dehydrogenation from silicon for $\text{CH}_3\text{SiH}_2^+$ (process 6a) has about a 5.5 kcal/mol lower activation energy and is about 19.6 kcal/mol less endothermic than the corresponding process with CH_3SiH_3 (reaction 2a).¹⁰ The endothermicity for demethanation from $\text{CH}_3\text{SiH}_2^+$ (process 9) is about 7.6 kcal/mol less with a 9.5 kcal/mol higher barrier than that for the neutral CH_3SiH_3 , process 2b.¹⁰ Hence, dehydrogenation is favored for $\text{CH}_3\text{SiH}_2^+$ (lower barrier), whereas demethanation is favored for CH_3SiH_3 (lower barrier).

Finally, the two radical loss channels, reactions 7 and 8, have experimental endothermicities of 84 and 100 kcal/mol, respectively (Table 2), and the calculated enthalpies are in excellent agreement with these values. Although the barriers for reactions 6a, 6c, and 9 are substantial, they are still more than 11 kcal/mol less than the energy required for process 7. Consequently, radical losses should not be important for plasma decomposition of $\text{CH}_3\text{SiH}_2^+$. Since the barrier for process 6b (1,1- H_2 elimination from the carbon end) is much higher than the endothermicity for the radical losses, reactions 7 and 8, and also much higher than the barriers for processes 6a, 6c, and 9, process 6b should not play an important role in $\text{CH}_3\text{SiH}_2^+$ decomposition, even under high-energy conditions.

D. Triplet Products. Since HCSiH_2^+ is a cationic analogue of a carbene and carbenes frequently have triplet ground states, the structure of the lowest triplet state of this species was optimized by using the unrestricted second-order perturbation (UMP2) method. For completeness, the triplet states of $\text{H}_2\text{-CSiH}^+$ and H_3CSi^+ were optimized at the same level of theory. Since silylenes typically have singlet ground states, one expects the triplets to become successively higher than the corresponding singlets as H's are transferred from Si to C.

The UMP2/6-31G(d,p) triplet structures are shown in Figure 2. All three triplet C-Si bond lengths are 0.05–0.1 Å longer than those in the corresponding singlets. At the highest level of theory, UMP4/6-311++G(2df,2pd), triplet HCSiH_2^+ is 7.7 kcal/mol (7.9 kcal/mol when vibrational zero-point energies are included) lower in energy than its singlet counterpart. This is just a bit smaller than the singlet-triplet splitting in CH_2 .⁵² For H_2CSiH^+ at the same level of theory, the singlet is predicted to be lower by 12.3 kcal/mol, while singlet H_3CSi^+ is lower than the triplet by a much larger 53.5 kcal/mol. Thus, it is unlikely that the triplet surface plays a significant role in the observed chemistry.

IV. Conclusions

The decomposition pathway for $\text{CH}_3\text{SiH}_2^+$ with the lowest energy barrier is 1,1-elimination of H_2 from silicon (reaction 6a), with a predicted barrier of 66.6 kcal/mol. The 1,2-elimination of H_2 (process 6c) and demethanation (process 9) have predicted barriers slightly higher (72.7 and 73.0 kcal/mol, respectively). All attempts to locate a transition state for the insertion of the carbene-like species, CHSiH_2^+ , into H_2 (reverse of the 1,1-dehydrogenation from carbon, reaction 6b) were unsuccessful. This is not surprising since analogous carbene insertions are known to occur without a barrier. Thus, we conclude that this 1,1- H_2 elimination from carbon proceeds monotonically uphill (endothermic by 107.3 kcal/mol). The high endothermicity for process 6b suggests that it will not play a significant role in the decomposition of $\text{CH}_3\text{SiH}_2^+$. The

endothermicities for the radical eliminations, processes 7 and 8, are 84 and 100 kcal/mol, respectively. These values are greater than the activation energies for processes 6a, 6c, and 9. Consequently, the radical processes also should only play a minor role in the decomposition chemistry of $\text{CH}_3\text{SiH}_2^+$. Although $^+\text{CH}_2\text{SiH}_3$ is only 40 kcal/mol higher in energy than $\text{CH}_3\text{SiH}_2^+$, the former is not a minimum on the potential energy surface for SiCH_5^+ . However, since the lowest energy barrier for $\text{CH}_3\text{SiH}_2^+$ decomposition is 66.6 kcal/mol, decomposition by 1,1-dehydrogenation from $^+\text{CH}_2\text{SiH}_3$, process 10, must be considered, at least in a dynamic sense. The overall endothermicity for 1,1-dehydrogenation from $^+\text{CH}_2\text{SiH}_3$ is 69.1 kcal/mol when starting with $\text{CH}_3\text{SiH}_2^+$. Since the barrier for 1,2-dehydrogenation, process 9, is only 3.6 kcal/mol above this 69.1 kcal/mol endothermicity, 1,1-dehydrogenation from $^+\text{CH}_2\text{SiH}_3$, process 10, would only be important if the latter had only a small barrier in excess of the underlying endothermicity. This is unlikely to be the case.

Kinetic energy release distributions for dehydrogenation of metastable $\text{CH}_3\text{SiH}_2^+$ have revealed that there are two distinct pathways, one with a low barrier to the reverse association process and another with a high barrier to the reverse association process.²⁰ The activation barriers for 1,1-dehydrogenation (process 8) and 1,2-dehydrogenation (process 9) are 66.6 and 72.7 kcal/mol, respectively. This small difference in these relatively large barriers suggests that both processes should be occurring for the dehydrogenation of metastable $\text{CH}_3\text{SiH}_2^+$. Further, the barrier for the reverse association for process 6a is 36.4 kcal/mol, which should, therefore, yield a large release of energy to product translation. Conversely, the barrier for the reverse association for process 6c is only 3.6 kcal/mol. So, a small release of energy to product translation should be observed. Hence, our results suggest that the dehydrogenation of metastable $\text{CH}_3\text{SiH}_2^+$ should involve both processes 6a and 6c.

SORI-CAD⁴⁴ has revealed that dehydrogenation has the lowest energy barrier pathway for decomposition of $\text{CH}_3\text{SiH}_2^+$.²¹ The barrier for demethanation (process 9) is only 6.4 kcal/mol above that for dehydrogenation by process 6a. Both processes, however, have high barriers. Consequently, the SORI-CAD technique is very selective for determining the lowest energy pathway for ion decomposition.

Acknowledgment. This project was supported by grants (to M.S.G.) from the National Science Foundation (CHE-9317317) and the Air Force Office of Scientific Research (92-0105). The calculations were performed on an IBM RS 6000 computer obtained by grants from the National Science Foundation and from funds generously provided by Iowa State University. Several helpful discussions with Dr. Kiet Nguyen are gratefully acknowledged.

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