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Elimination of Ethylene from Metastable Isomeric Silylenium Ions in the Gas Phase: Experiment and Theory

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The slow unimolecular dissociations ($k \approx 10^5$ s^{-1}) of gas-phase silylenium ions, $SiC_nH_{2n+3}^+$ ions ($n = 2-4$) have been studied by mass-analyzed ion kinetic energy spectroscopy. On the microsecond time scale, the $SiC_2H_7^+$ isomers undergo dissociations corresponding to H_2 (72%) and C_2H_4 loss (28%). The product ion translational energy distributions and product ratios are the same for $HSi(CH_3)_2^+$ and $H_2Si(C_2H_5)^+$, indicating that these isomers equilibrate prior to dissociation. For the $SiC_3H_9^+$ isomers, elimination of C_2H_4 is the dominant reaction pathway, comprising 97% of the products for $Si(CH_3)_3^+$ and 89% for $HSi(CH_3)(C_2H_5)^+$. The translational energy distributions for elimination of ethylene from these two ions are different, indicating that equilibration of $Si(CH_3)_3^+$ and $HSi(CH_3)(C_2H_5)^+$ does not occur prior to dissociation. The mechanisms for C_2H_4 loss from the $Si(CH_3)_3^+$ and $HSi(CH_3)(C_2H_5)^+$ ions were characterized by ab initio computational methods, and the results were used for statistical phase space modeling of the experimental translational energy distributions. Excellent agreement between theory and experiment was obtained for ethylene loss from the $SiC_2H_7^+$ isomers and from $HSi(CH_3)(C_2H_5)^+$. The calculated distribution was broader than the experimental distribution for $Si(CH_3)_3^+$. Possible reasons for this result are discussed. The microsecond unimolecular dissociation of $Si(CH_3)_2(C_2H_5)^+$ proceeds exclusively by elimination of C_2H_4, which arises from the ethyl group and not from the two methyl groups.

Introduction

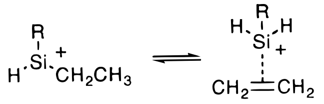
The chemistry of organosilicon ions in the gas phase has been a subject of much interest in recent years.[1,2] Many experimental and theoretical studies have focused on the chemistry of small silylenium ions, $SiC_nH_{2n+3}^+$. These species are known to rearrange with some facility but differ from their carbenium analogues in that isomeric silylenium ions can often be distinguished by reactivity or collisional activation studies. By contrast, carbon scrambling and branching rearrangements in butyl cations occur even at very low temperatures and in the solid state.[3] The collisionally activated dissociation (CAD) mass spectra of gas-phase carbenium ions formed from isomeric precursors are frequently indistinguishable.[4]

In an early study of silylenium ion chemistry, Allen and Lampe found evidence for formation of persistent collision complexes in the reaction of SiH_3^+ with C_2H_4 and proposed that the complex is a nascent β-silylcarbenium ion that rearranges by a reversible β-hydrogen transfer to form $H_2Si(C_2H_5)^+$ (eq 1).[5] In subsequent studies, Lampe and co-workers observed

$$H_3Si^+ + C_2H_4 \rightleftharpoons [H_3SiCH_2CH_2^+] \rightleftharpoons H_2Si^+CH_2CH_3 \quad (1)$$

extensive H/D exchange occurring during a single collision of SiH_3^+ with C_2D_4, even at a 2.6 eV collision energy.[6] They also observed addition of up to three C_2H_4 molecules to SiH_3^+, resulting in the formation of $Si(C_2H_5)_3^+$.[7] Stabilization of carbenium ions by β-silicon groups is a well-known effect in solution and has been attributed to hyperconjugation.[8] Studies of nascent α-silylcarbenium ions reveal that they rearrange rapidly by 1,2-group shifts, apparently without barrier, to give the lower energy silylenium ion isomers.[9−15]

Groenewold et al. were perhaps the first to observe the elimination of C_2H_4 from $Si(CH_3)_3^+$ in a study of unimolecular dissociations of trimethyl “enium” ions, $M(CH_3)_3^+$, of the group 14 elements.[16] The mechanism of this dissociation and the rearrangements leading to it have been the focus of several studies by Jacobson and co-workers, who have examined the unimolecular dissociations and bimolecular reactivity of the isomeric forms of $SiC_2H_7^+$ and $SiC_3H_9^+$ and higher homologues.[17,18] They find that for isomeric $SiC_2H_7^+$ or $SiC_3H_9^+$ silylenium ions, the CAD mass spectra are too similar to be useful for the purposes of structural diagnostics, although the energy dependence of fragmentation differs somewhat between isomeric forms. However, reactivity studies using methanol and labeled ethylene show different reactivity for the putative isomers, providing a method to track the isomerizations. Reactivity studies with C_2D_4 show that hydrogens directly bound to Si and those on ethyl groups are readily exchangeable, but those on methyl groups are much slower to exchange. This has been interpreted in terms of rapid interconversion between classical ethylsilylenium ions and a nonclassical structure in which a silylenium ion bridges the π bond of an ethylene molecule (eq 2). The energy barrier for interconversion of $RSi(CH_3)_2^+$ to either $R(H)Si(C_2H_5)^+$ or the π-bridged structure was proposed to be sufficiently large to inhibit the exchange of the methyl hydrogens. The interconversion of $RSi(CH_3)_2^+$ to $R(H)Si(C_2H_5)^+$ was proposed to involve a concerted 1,2-hydrogen/1,2-methyl transfer, a dyotropic rearrangement (eq 3).[18]



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Bakhtiar et al. have shown that $Si(CH_3)_3^+$ and $HSi(CH_3)(C_2H_5)^+$ can be induced to interconvert by multiple low-energy

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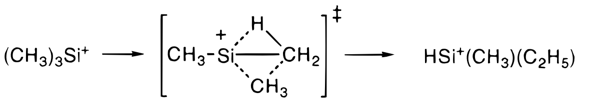

(3)

collisions but that fragmentation to $H_2Si(CH_3)^+$ and C_2H_4 competes with the isomerization, suggesting that the isomerization barrier is similar in energy to the fragmentation barrier.[18] In contrast, using the same multiple low-energy collision method, they found that $H_2Si(C_2H_5)^+$ and $HSi(CH_3)_2^+$ can be induced to interconvert without competing fragmentation.[19]

Theoretical studies have been carried out for the $SiC_2H_7^+$ potential energy surface at both SCF and correlated levels of theory.[14,20] These studies show that the global minimum is the dimethylsilylenium ion. The results for the primary α-silylcarbenium ion $H_2Si(CH_3)(CH_2^+)$ are very sensitive to the level of calculation. The species is found to occupy a shallow minimum at the SCF level but is a saddle point at MP2 and lies considerably higher in energy relative to $Si(CH_3)_3^+$.[14,15] At the MP2 level, the α-silylcarbenium ion appears to be a transition state linking the $H_2Si(C_2H_5)^+$ and $HSi(CH_3)_2^+$ species.[14] Thus far, no transition state has been located for a dyotropic rearrangement between $H_2Si(C_2H_5)^+$ and $HSi(CH_3)_2^+$ (eq 3).[20] The rearrangement between $H_2Si(C_2H_5)^+$ and the nonclassical structure (eq 2) has been suggested to involve either sequential 1,2-hydrogen shifts[20] or a single β-hydrogen shift.[14] To our knowledge, calculations have not been reported for the $SiC_3H_9^+$ system.

In this paper, we report the product ion kinetic energy release distributions (KERDs) for unimolecular dissociations of isomeric $SiC_2H_7^+$ and $SiC_3H_9^+$ species generated from several neutral precursors, focusing on those ions with lifetimes on the order of 10^{-5} s or "metastable" ions.[21] Detailed ab initio calculations were carried out at a correlated level of theory for the $SiC_3H_9^+$ surface, and these results were used to model the KERDs for the unimolecular dissociations. We find evidence for facile rearrangements between the dimethyl and ethyl isomers in the $SiC_2H_7^+$ system at the dissociation threshold and for efficient competition of fragmentation with rearrangement between the trimethyl and ethylmethyl isomers in the $SiC_3H_9^+$ system. We also report the results from analysis of the metastable dissociations of $Si(CH_3)_2(C_2H_5)^+$ and show that ethylene loss occurs essentially exclusively from the ethyl moiety.

Experimental Section

These experiments were performed using a reverse-geometry double-focusing mass spectrometer (V. G. Analytical, ZAB-1F). The $Si(CH_3)_3^+$ ions were generated by dissociative electron ionization (50 and 70 eV) of chlorotrimethylsilane and vinyltrimethylsilane and $Si(CD_3)_3^+$ was generated by ionization of tetramethylsilane-d_{12}. The $HSi(CH_3)(C_2H_5)^+$ and $Si(CH_3)_2(C_2H_5)^+$ ions were generated by dissociative electron ionization of ethyldimethylsilane. The $HSi(CH_3)_2^+$ ion was generated from chlorodimethylsilane, vinyltrimethylsilane, or dimethylethoxysilane, and $H_2Si(C_2H_5)^+$ was obtained from ionization of diethylsilane. The ions were extracted from the source and accelerated into the magnetic sector for mass selection. Ionic products of dissociations that occurred in the field-free region between the magnetic and electrostatic sectors were energy-analyzed at the electrostatic analyzer. This technique is known as mass-analyzed ion kinetic energy spectroscopy (MIKES). Metastable ion dissociation branching ratios were determined by scanning over all fragment ions and integrating the peak areas. The KERDs were obtained by a transformation of coordinates using a previously described method.[22] All of the compounds used in this study, except tetramethylsilane-d_{12}, were obtained commercially; chlorotrimethylsilane, vinyltrimethylsilane, and chlorodimethylsilane were obtained from Sigma-Aldrich and ethyldimethylsilane and dimethylethoxysilane from Gelest Inc. (PA). The tetramethylsilane-d_{12} was synthesized by reaction of CD_3MgCl and $SiCl_4$, which were obtained from Sigma-Aldrich.

TABLE 1: Experimental Product Ratios for Unimolecular Dissociations of Metastable $SiC_nH_{2n+3}^+$

precursor ion	neutral product	product distribution, %
$HSi(CH_3)_2^+$	H_2	72 ± 6
	C_2H_4	28 ± 6
$H_2Si(C_2H_5)^+$	C_2H_4	72 ± 1
	H_2	28 ± 1
$Si(CH_3)_3^+$	C_2H_4	97 ± 3
	H_2	3 ± 3
$HSi(CH_3)(C_2H_5)^+$	C_2H_4	89 ± 4
	H_2	8 ± 2
	H	3 ± 2
$Si(CH_3)(C_2H_5)^+$	C_2H_4	100

Ab initio calculations were performed using the Gaussian92 software package,[23] running on a DEC alpha server (model 400). Geometry optimizations were performed using the 6-31G(d,p) basis set at the Hartree−Fock (HF) level of theory. The geometries were reoptimized accounting for electron correlation by using second-order Moller−Plesset (MP2) perturbation theory.[24,25] Single-point calculations were performed for certain species at the MP4/6-31G(d,p)//MP2/6-31G(d,p) level. Frequency calculations were performed in order to determine zero-point energies and to verify stationary points. The frequencies calculated at the HF level were corrected by a factor of 0.893, and frequencies calculated at MP2 were corrected by 0.93.[26−28] Intrinsic reaction coordinate calculations were performed to determine the minima connected by each transition state.[29,30] Statistical phase space theory[31−34] was used to model the experimental KERDs. A brief description of the model is given in the Appendix, and further details along with parameters used for the calculations are available as Supporting Information.

Results and Discussion

The silylenium ions formed in the ion source of the mass spectrometer by dissociative electron ionization at 50 or 70 eV of neutral organosilanes have a range of internal energies. The portion of the ion population studied here consists of those ions with sufficient internal energy to overcome barriers to dissociation but which dissociate relatively slowly, on roughly a 10^{-5} s time scale (the flight time to the field-free region between the magnetic and electrastatic sectors). These metastable ions are characterized by internal energies that are close to the energetic thresholds for dissociation, and in this energy regime, rearrangements and elimination of stable neutral molecules dominate the dissociation process. The product distributions for the unimolecular dissociations of the metastable $SiC_nH_{2n+3}^+$ ions studied are given in Table 1 and correspond to loss of H_2 or C_2H_4. For the $SiC_2H_7^+$ isomers, H_2 loss dominates and both isomers yield the same product ratio. Loss of C_2H_4 dominates for the $SiC_3H_9^+$ ions, and the two isomers dissociate with different product ratios. The $HSi(CH_3)(C_2H_5)^+$ ion also exhibits a third reaction pathway corresponding to loss of an H atom. Loss of H_2 or H was not reported in previous collisionally activated dissociation studies of these ions.[16−18] The H_2 loss pathways are the subject of ongoing investigations in our laboratory and will not be discussed further here. For the metastable $SiC_4H_{11}^+$ ion, dissociation occurs exclusively by loss of C_2H_4.

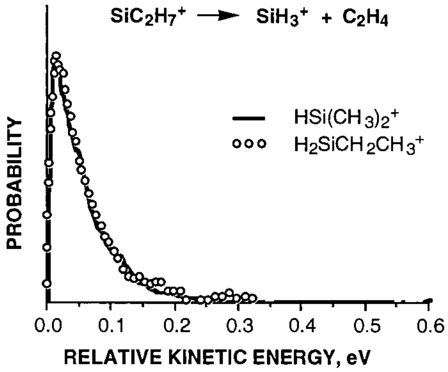

Figure 1. Experimental kinetic energy release distributions for C_2H_4 loss from the $SiC_2H_7^+$ isomers, $HSi(CH_3)_2^+$ and $H_2Si(C_2H_5)^+$.

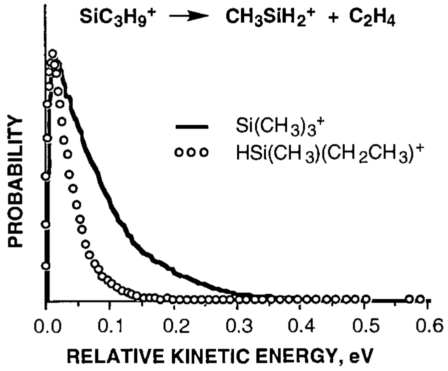

Figure 2. Experimental KERDs for C_2H_4 loss from the $SiC_3H_9^+$ isomers, $Si(CH_3)_3^+$ and $HSi(CH_3)(C_2H_5)^+$.

The product ion kinetic energy release distributions (KERDs) for C_2H_4 loss from the $SiC_2H_7^+$ isomers (eqs 4 and 5) and the $SiC_3H_9^+$ isomers (eqs 6 and 7) are shown in Figures 1 and 2, respectively. All of the distributions peak near zero and drop

$$HSi^+(CH_3)_2 \rightarrow H_3Si^+ + C_2H_4 \tag{4}$$

$$H_2Si^+C_2H_5 \rightarrow H_3Si^+ + C_2H_4 \tag{5}$$

$$(CH_3)_3Si^+ \rightarrow H_2Si^+CH_3 + C_2H_4 \tag{6}$$

$$HSi^+(CH_3)(C_2H_5) \rightarrow H_2Si^+CH_3 + C_2H_4 \tag{7}$$

off smoothly with increasing energy. This is characteristic of a process that does not have a reverse activation barrier.[35] That is, the barrier to dissociation in these processes is equivalent to the energy of the separated species relative to the precursor ion such that the potential energy increases smoothly to the asymptotic energy of the separated products.

It can be seen in Figure 1 that the KERDs for loss of ethylene from $HSi(CH_3)_2^+$ and $H_2Si(C_2H_5)^+$ are the same within experimental error. The similarity of the KERDs for these reactions is consistent with rapid interconversion prior to dissociation. In contrast, the KERDs for the reactions of the $SiC_3H_9^+$ isomers differ, with the dissociation of $HSi(CH_3)(C_2H_5)^+$ releasing less energy than that for $Si(CH_3)_3^+$ (Figure 2). This difference indicates that the rate of isomerization is slow compared to the rate of dissociation, even for ions near threshold. These results are consistent with the results of Bakhtiar et al. who observed that collision-induced dissociation competes with isomerization for these $SiC_3H_9^+$ isomers, even very close to threshold.[19] The experimental average kinetic energy released, $\langle E_t \rangle_{exp}$, for the reactions in eqs 4−7 are given in Table 2. Whereas the average releases for the $SiC_2H_7^+$ isomers are equal within experimental error, the $\langle E_t \rangle_{exp}$ for the $Si(CH_3)_3^+$ reaction is much larger than that for the $HSi(CH_3)(C_2H_5)^+$ reaction.

TABLE 2: Average Kinetic Energy Released, $\langle E_t \rangle_{exp}$, in Dissociation of Metastable $SiC_nH_{2n+3}^+$

reaction	$\langle E_t \rangle_{exp}$, meV
$HSi^+(CH_3)_2 \rightarrow H_3Si^+ + C_2H_4$	56 ± 6
$H_2Si^+C_2H_5 \rightarrow H_3Si^+ + C_2H_4$	54 ± 1
$(CH_3)_3Si^+ \rightarrow H_2Si^+CH_3 + C_2H_4$	82 ± 7
$HSi^+(CH_3)(C_2H_5) \rightarrow H_2Si^+CH_3 + C_2H_4$	34 ± 1
$Si(CH_3)_2(C_2H_5)^+ \rightarrow HSi^+(CH_3)_2^+ + C_2H_4$	36 ± 3

To check for dependence of the KERDs and product ratios on initial conditions and internal energy, several tests were performed. The reactant ions $Si(CH_3)_3^+$ and $HSi(CH_3)_2^+$ were generated from a number of precursors, and the experiments were performed at two ionization energies, 50 and 70 eV. The only system that exhibited any variation was the $HSi(CH_3)_2^+$ ion. The branching ratios for the dissociation of this ion were found to vary slightly with different neutral precursors, which is reflected in the larger error bars for this ion (Table 1). The reason for this variation is unclear but may result from small amounts of isobaric contaminant ions such as $C_3H_7O^+$ in the ion beam. For all other systems studied, the KERDs and product ratios were very reproducible. This is most likely a consequence of the inherent selectivity of the MIKES experiment, which probes a relatively narrow time (and internal energy) window.

Ab initio calculations have been performed to explore the possible mechanisms for C_2H_4 loss from $Si(CH_3)_3^+$ and $HSi(CH_3)(C_2H_5)^+$ and to determine the parameters needed for statistical phase space modeling of the metastable KERDs. The global minimum on the potential energy surface for this system is the $Si(CH_3)_3^+$ ion (Figure 3). This may be compared with the results for the $SiC_2H_7^+$ potential energy surface where the global minimum is the $HSi(CH_3)_2^+$ ion[14,20] and is consistent with the finding that alkyl substituents stabilize silylenium ions relative to a hydrogen substituent.[36] The $HSi(CH_3)(C_2H_5)^+$ ion is calculated to be 0.82 eV less stable than $Si(CH_3)_3^+$. A nonclassical π-bridged structure, **I**, was found to occupy a local minimum and calculated to be 1.07 eV less stable than $Si(CH_3)_3^+$. This ion is fairly strongly bound (1.78 eV) with respect to dissociation to $H_2Si(CH_3)^+$ and C_2H_4, indicating substantial covalent character in the bridging bond. The calculated reaction endothermicity of 2.86 eV for dissociation of $Si(CH_3)_3^+$ to $H_2Si(CH_3)^+$ and C_2H_4 is in excellent agreement with the experimental value of 2.99 eV (Table 3).[36]

Altogether, five transition states were found on the $SiC_3H_9^+$ potential energy surface. Frequency analyses confirmed that these were first-order saddle points, and internal reaction coordinate (IRC) calculations were carried out to identify the minima that were connected by each transition state.

Two transition states for rearrangement of $Si(CH_3)_3^+$ were found (Figure 3). Transition state **TS1** connects $Si(CH_3)_3^+$ directly to **I**. This rearrangement involves extension of two of the Si−C bonds and the simultaneous transfer of one hydrogen from each methyl group to the silicon center. This pathway is analogous to the "extension of vibrations" pathway that was been proposed by Groenewold and Gross for ethylene elimination from trimethyl "enium" ions[16] and is also similar to the reaction pathway calculated for the $HSi(CH_3)_2^+$ reaction.[20]

A second transition state **TS2** corresponds to the α-silylcarbenium ion formed by way of a 1,2-hydrogen shift. This transition state connects $Si(CH_3)_3^+$ to $HSi(CH_3)(C_2H_5)^+$. At the HF level of theory, the α-silylcarbenium ion occupies a shallow minimum on the potential energy surface. However,

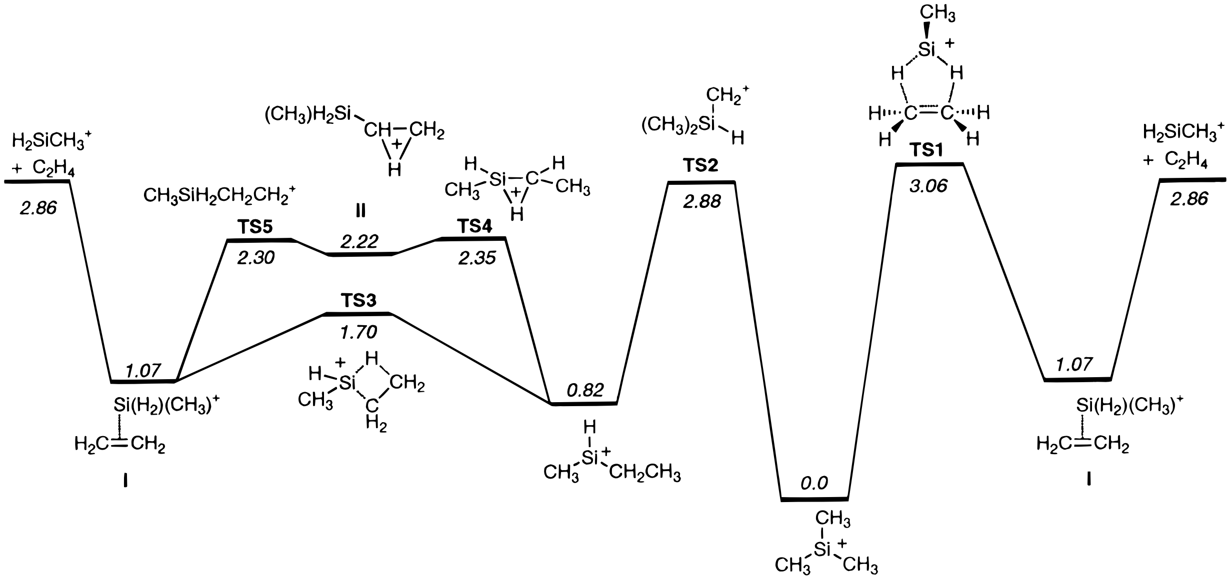

Figure 3. Calculated reaction coordinate for the rearrangement of $SiC_3H_9^+$. Energies (in eV, including zero-point energies) calculated at the MP2/6-31G(d,p) level.

TABLE 3: Reaction Thermochemistry

reaction	ΔH_{exp} (eV)	ΔH_{calc} (eV)
$HSi^+(CH_3)_2 \rightarrow H_3Si^+ + C_2H_4$	3.27[a]	3.02[b]
$(CH_3)_3Si^+ \rightarrow H_2Si^+CH_3 + C_2H_4$	2.99[c]	2.86[d]
$HSi^+(CH_3)(C_2H_5)^+ \rightarrow HSi^+CH_3 + C_2H_4$		2.04[d]
$Si(CH_3)_2(C_2H_5)^+ \rightarrow HSi(CH_3)_2^+ + C_2H_4$		1.94[d]
$Si(CH_3)_2(C_2H_5)^+ \rightarrow H_2Si(C_2H_5)^+ + C_2H_4$		2.87[d]

[a] Reference 36. [b] Reference 20, B3LYP/6-31G(d,p) corrected for zero-point vibrational energy. [c] Reference 36 and adjusted to 0 K for comparison with theory. [d] This work, calculated at the MP2/6-31G(d,p) level and corrected for zero-point vibrational energy.

TABLE 4: Relative Energies for Transition States for Rearrangement of $Si(CH_3)_3^+$ As Determined by ab Initio Calculations at Various Levels of Theory[a]

level	$Si(CH_3)_3^+$	**TS1**	**TS2**
HF/6-31G(d,p)	0	3.91	2.50
MP2/6-31G(d,p)	0	3.06	2.88
MP4/6-31(d,p)//MP2/6-31G(d,p)	0	2.92	2.70

[a] All energies are given in electronvolts and include zero-point energies. Frequency calculations were performed at HF/6-31G(d,p) for $Si(CH_3)_3^+$ and MP2/6-31G(d) for **TS1** and **TS2**.

when electron correlation is accounted for to the MP2 level, the α-silylcarbenium ion becomes a transition state and its energy relative to $Si(CH_3)_3^+$ rises by 0.4 eV. This result is consistent with experimental and theoretical studies that have shown that α-silylcarbenium ions are less stable than their silylenium ion isomers.[9,11−15] These studies have shown that nascent α-silylcarbenium ions will rearrange by a 1,2-group migration to form silylenium ions. For R = H, CH_3, or phenyl in $RSiH_2CH_2^+$, these migrations are barrierless.[15]

In their studies of the rearrangement of $SiC_3H_9^+$ isomers, Bakhtiar et al. proposed that $Si(CH_3)_3^+$ rearranges to $HSi(CH_3)(C_2H_5)^+$ prior to C_2H_4 loss and suggested this occurs by way of a concerted 1,2-hydrogen/1,2-methyl shift (dyotropic rearrangement).[19] Our attempts to locate such a transition state have been unsuccessful, but the pathway through **TS2** may be considered a stepwise version of this mechanism.

The other three transition states located on the $SiC_3H_9^+$ surface are involved in the rearrangement of $HSi(CH_3)(C_2H_5)^+$ to **I** by one of two pathways (Figure 3). The first mechanism involves the formation of **I** by hydrogen migration from the β carbon of the ethyl group to the silicon center. The transition state for this rearrangement is a four-membered ring structure **TS3**. This reaction pathway is the reverse of an olefin insertion β-hydrogen migration that is observed in organometallic chemistry[37] and is similar to the mechanism proposed for the dissociation of $H_2Si(C_2H_5)^+$.[14] The second dissociation pathway involves two steps. In the first step, a hydrogen from the α-carbon atom of the ethyl group is transferred to the silicon center through a three-center transition state **TS4**, resulting in the formation of the α-silylcarbenium ion, $H_2Si(CH_3)(CH^+CH_3)$ (**II**). The second step is a 1,2-hydrogen shift resulting in the formation of **I**. This interconversion goes through **TS5**, which is very similar in energy to **TS4**. The relatively low barrier heights for β-hydrogen and α-hydrogen migration (0.88 and 1.53 eV, respectively, relative to $HSi(CH_3)(C_2H_5)^+$) are consistent with the observation of facile H/D exchange in reactions of $HSi(CH_3)_2^+$ and $H_2Si(CH_3)^+$ with C_2D_4.[17,18]

The effect of including electron correlation for these calculations is significant. As mentioned previously, the α-silylcarbenium ion resulting from a 1,2-hydrogen shift in $Si(CH_3)_3^+$ is a minimum at the HF level of theory but becomes a transition state (**TS2**) with inclusion of electron correlation. Unlike **TS2**, the isomeric α-silylcarbenium ion **II** remains a minimum when electron correlation is included. However, the structure of this ion changes from a classical form at the HF level, with the positively charged carbon center apparently sp^2 hybridized, to a bridged structure at the correlated level. This nonclassical structure is analogous to the bridged structure of the ethyl cation[9] and $H_3Si(CH^+CH_3)$.[20] On going from the HF to the MP2 level, the energies for both α-silylcarbenium ions **TS2** and **II** increase by approximately 0.4 eV relative to the $Si(CH_3)_3^+$ species (Table 4). However, the energy of **TS1** relative to $Si(CH_3)_3^+$ decreases by 0.85 eV when correlation is included. These large changes in relative energy suggest that the level of theory or size of basis set may not be adequate for accurate description of the transition states involved in these reactions. To examine the sensitivity of the calculated results to the level of correlation, we carried out single-point MP4/6-31G(d,p) energy calculations on the MP2/6-31G(d,p) geometries for **TS1**, **TS2**, and $Si(CH_3)_3^+$. The energies for these transition states decreased by 0.14 and 0.18 eV, respectively, relative to $Si(CH_3)_3^+$. In contrast to this

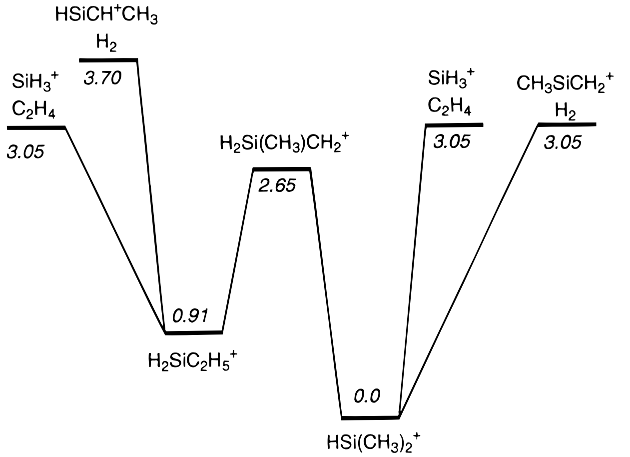

Figure 4. Potential energy surface used in the phase space theoretical modeling for the $SiC_2H_7^+$ system. All energies are given (in eV, including zero-point energies) at the MP2/6-31G(d,p) level. The energy of the $CH_3Si(CH_2)^+$ and H_2 products was treated as a variable.

sensitivity, the relative energies of the stable isomeric ions $Si(CH_3)_3^+$ and $HSi(CH_3)(C_2H_5)^+$ and the dissociation products $H_2Si(CH_3)^+$ and C_2H_4 were not sensitive to the inclusion of correlation and are in good agreement with experimental data.[36]

The experimental KERDs observed for ethylene loss from $SiC_2H_7^+$ and $SiC_3H_9^+$ (eqs 4−7) have been modeled with statistical phase space theory. For dissociation of the $SiC_2H_7^+$ isomers, loss of H_2 is a major reaction channel that competes with the reaction of interest and, therefore, must be included in the model. Loss of H_2 is also observed in the dissociation of $H_2Si(CH_3)^+$,[38] and molecular orbital calculations indicate that the lowest energy pathways are 1,1-elimination from the silicon atom yielding $SiCH_3^+$ and 1,2-elimination yielding $HSi(CH_2)^+$.[13] The former pathway involves a significant barrier (about 35 kcal/mol with respect to the separated products), whereas the latter has only a small barrier (about 3 kcal/mol with respect to the products). The shape of the experimental KERDs in the present study suggests there is little or no barrier in excess of the reaction endothermicity in the H_2 elimination reaction, and for $HSi(CH_3)_2^+$, only 1,2-elimination is possible. Therefore, we make the simplifying assumption that H_2 loss occurs through a 1,2-elimination mechanism for both isomers.

Thus, the model used for reactions 4 and 5 is a relatively simple one that incorporates a double-well potential and dissociation by 1,2-elimination of H_2 or by C_2H_4 loss (Figure 4). It has been shown experimentally that the H/D exchange of SiH_3^+ with C_2D_4 is extremely rapid, even at elevated collision energies,[6] and that near the C_2H_4 dissociation threshold, $HSi(CH_3)_2^+$ and $H_2Si(C_2H_5)^+$ interconvert rapidly.[19] Our phase space calculations show that the barrier height for the α-silylcarbenium ion can be no more than 2.65 eV above $HSi(CH_3)_2^+$ if isomerization is to dominate over dissociation. This barrier height is in excellent agreement with the ab initio results of Ketvirtis et al.[14] For the modeling of the KERDs, the barrier height was thus set at 2.65 eV. The 1,2-elimination products from $H_2Si(C_2H_5)^+$ (i.e., $HSi(CHCH_3)^+$ and H_2) are shown in Figure 4 and were calculated to be 0.65 eV higher in energy than the SiH_3^+ and C_2H_4 products. Phase space calculations show that this reaction pathway is too high in energy to be important in our experiment. Because of the observed sensitivity of the calculated energies for the α-silylcarbenium ions, the energy of the 1,2-elimination pathway yielding $(CH_3)Si(CH_2)^+$ and H_2 was treated as a variable and optimized to reproduce the experimental product ratio for elimination of C_2H_4 or H_2.

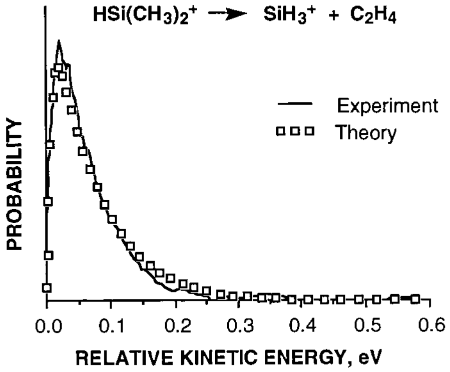

Figure 5. Comparison of experimental and calculated KERD for the dissociation of $HSi(CH_3)_2^+$.

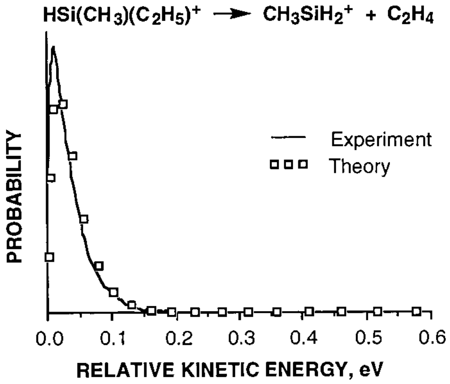

Figure 6. Comparison of experimental and calculated KERD for the dissociation of $HSi(CH_3)(C_2H_5)^+$.

Using the potential energy surface given in Figure 4, the product ratio and the theoretical KERDs for C_2H_4 and H_2 loss were calculated for several values of the relative energy of the 1,2-hydrogen elimination product from $HSi(CH_3)_2^+$. The best results were obtained when the energy for C_2H_4 loss and H_2 loss were each at 3.05 eV relative to $HSi(CH_3)_2^+$. A comparison of the experimental and calculated KERD for the loss of ethylene is shown in Figure 5. The agreement is excellent for both this and the H_2 loss channel. The energies for both of the H_2 and C_2H_4 channels relative to $HSi(CH_3)_2^+$ were calculated by ab initio methods to be 3.05 eV. Thus, the agreement between the ab initio results and the phase space results for this system is excellent. (The absence of intervening transition states in the model and the good agreement with experiment should not be construed to mean that such transition states are absent but only that they do not affect the experimental KERD.)

Loss of H_2 is only a minor dissociation channel for the $SiC_3H_9^+$ isomers and, therefore, has been neglected in the phase space model for C_2H_4 loss. The model used for these reactions is based on the results of the ab initio calculations as shown in Figure 3. Because only a modest basis set and level of correlation were used for these calculations, we allow for some inaccuracy in the calculated energetics of the transition states by varying them in the model. For the dissociation of $HSi(CH_3)(C_2H_5)^+$, two pathways are considered, as shown in Figure 3. We start with the simplest model, in which the intervening transition states are neglected, which is equivalent to assuming they have no effect on the KERD. The calculated KERD resulting from this model is shown in Figure 6 along with the experimental result. It can be seen that the agreement with experiment is excellent. When a more sophisticated model is used that includes **TS3** (*β*-H shift), **TS4** and **TS5** (sequential 1,2-H shifts), and **TS2** (rearrangement to $Si(CH_3)_3^+$) at the ab

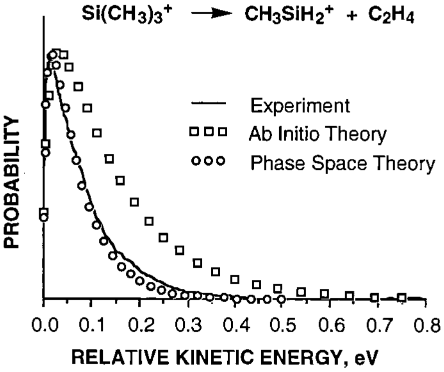

Figure 7. Comparison of experimental and calculated KERDs for the dissociation of $Si(CH_3)_3^+$.

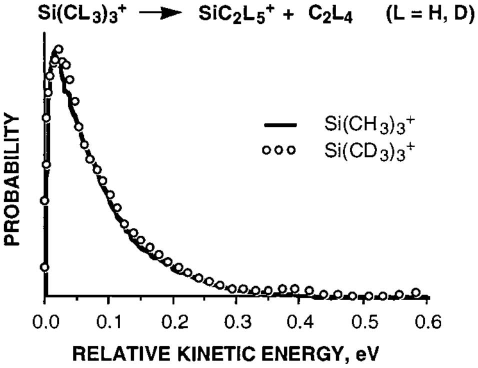

Figure 8. Comparison of the experimental KERDs for C_2H_4 loss from $Si(CH_3)_3^+$ and C_2D_4 loss from $Si(CD_3)_3^+$.

initio calculated energies, the resulting calculated KERD is indistinguishable from the result in Figure 5, indicating that the intervening transition states do not affect the KERD. The calculations do suggest, however, that the reaction proceeds essentially exclusively by the lower energy β-hydrogen transfer (**TS3**) rather than the sequential 1,2-H shifts. This conclusion is based on a trial calculation in which **TS3** is omitted from the model but **TS4** and **TS5** are included. The calculated KERD for this model is significantly broader than experiment, indicating that **TS4** and **TS5** are high enough in energy to affect the rate of dissociation.

To explore the effect of equilibration between $HSi(CH_3)(C_2H_5)^+$ and $Si(CH_3)_3^+$ on the KERD for the metastable dissociation of $HSi(CH_3)(C_2H_5)^+$ (eq 7), the energy of **TS2** was progressively lowered and the resulting KERDs for eq 7 calculated. No effect was observed until the energy of **TS2** drops below 2.5 eV relative to $Si(CH_3)_3^+$. At lower energies, the calculated KERD becomes broader than experiment. Thus, 2.5 eV may be considered a lower bound for the energy of **TS2** relative to $Si(CH_3)_3^+$.

The model adopted for dissociation of $Si(CH_3)_3^+$ (eq 6) is based on the potential energy surface shown in Figure 3 and includes both **TS1** and **TS2** as competing pathways. When the ab initio energetics for these two transition states are used in the model, the resulting KERD is considerably broader than experiment (Figure 7, open squares). To determine the barrier heights that would be consistent with statistical dissociation leading to the experimentally observed KERD, the energy of **TS2** was lowered to the minimum allowable value of 2.5 eV determined by the previously described calculation and the energy of **TS1** was progressively lowered until the calculated KERD came into agreement with experiment (Figure 7, open circles). This occurred when **TS1** was at about 2.25 eV relative to $Si(CH_3)_3^+$.

There are a number of possible reasons for this discrepancy between energies of **TS1** and/or **TS2** in the phase space modeling compared to the ab initio results for the dissociation of $Si(CH_3)_3^+$: (1) If partial equilibration of $Si(CH_3)_3^+$ to $HSi(CH_3)(C_2H_5)^+$ occurs in the source, the experimental distribution observed would be narrowed relative to that of pure $Si(CH_3)_3^+$. If we assume the KERDs calculated using the ab initio barrier heights are the true results for hypothetical unequilibrated isomers, the $HSi(CH_3)(C_2H_5)^+$ isomer would have to make up approximately 55% of the ion population in this experiment in order to reproduce the results for the putative $Si(CH_3)_3^+$ isomer. However, this is very unlikely in that isomerization of $HSi(CH_3)(C_2H_5)^+$ to $Si(CH_3)_3^+$ must also be expected to occur, resulting in a broadening of the experimental KERD for the $HSi(CH_3)(C_2H_5)^+$ isomer, which is not observed. (2) The ab initio calculations may overestimate the relative energies of the transition states at the MP2 level of theory. On going from HF to MP2, not only does **TS2** go from being a minimum to a saddle point but the energy increases significantly from 2.3 to 2.88 eV. In contrast, the energy of **TS1** decreases dramatically, by 0.8 eV between the HF and MP2 levels. The relative energies of both of these transition states decrease further when MP4 single-point calculations were performed (Table 4), although not to values as low as predicted by the phase space modeling. (3) The observed discrepancy may be due to a dynamical effect in passing through the intervening transition state prior to dissociation or to the lifetime of intermediate **I** being too short to allow for energy randomization. Both of these situations could result in nonstatistical effects that would cause the theory and experiment to disagree, although the direction of the disagreement is difficult to predict. (4) Tunneling may be occurring through the rearrangement barriers, resulting in lower effective barriers and a narrower KERD. Passage through either **TS1** or **TS2** involves significant motion of hydrogen atoms. If tunneling is occurring, it may be inhibited by deuterium substitution, in which case a broader KERD would be expected if the ab initio barrier heights are correct. The experimental KERDs for the dissociation of $Si(CD_3)_3^+$ and $Si(CH_3)_3^+$ are compared in Figure 8. The distributions are the same within our experimental error, which indicates that there is no measurable isotope effect in this system and suggests that tunneling is not a significant process in these dissociations. We conclude that the discrepancy is most likely due to using an inadequate level of ab initio theory and/or to dynamical effects in the dissociation. In support of the latter, a similar effect has been observed for dissociations of $X^-(CH_3Y)$ complexes to give Y^- and CH_3X, where the intervening transition state is also high enough to affect the rate of dissociation.[39.40]

The KERD for ethylene loss from $HSi(CH_3)(C_2H_5)^+$ was found to be narrower than the KERD for $Si(CH_3)_3^+$ (Figure 2). Given that the two isomers do not interconvert rapidly, the larger kinetic energy release observed for $Si(CH_3)_3^+$ can be explained in part by the relative stabilities of the two isomers, $Si(CH_3)_3^+$ being more stable than $HSi(CH_3)(C_2H_5)^+$ by 0.82 eV. According to unimolecular reaction theory, the rate of reaction is inversely proportional to the reactant density of states.[41,42] Because of the difference in stability of the two isomers, the density of states for $Si(CH_3)_3^+$ at the dissociation threshold is higher. However, the metastable dissociation experiment probes ions that dissociate at the same rates, so the internal energy of metastable $Si(CH_3)_3^+$ must be higher than that of $HSi(CH_3)(C_2H_5)^+$. Consequently, statistical partitioning of the available energy would lead to a broader KERD for $Si(CH_3)_3^+$ than for $HSi(CH_3)(C_2H_5)^+$.

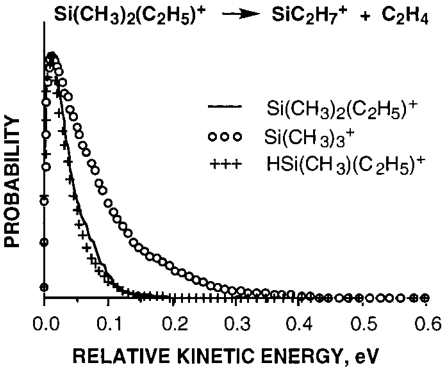

Figure 9. Comparison of the experimental KERDs for C_2H_4 loss from $Si(CH_3)_2(C_2H_5)^+$ to $HSi(CH_3)(C_2H_5)^+$ and $Si(CH_3)_3^+$.

Also examined in this study was the metastable dissociation of $Si(CH_3)_2(C_2H_5)^+$ (Table 1). We consider two possible reaction pathways for C_2H_4 loss from this ion, corresponding to the elimination of C_2H_4 from the two methyl groups (eq 8) or from the ethyl group (eq 9).

$$Si(CH_3)_2(C_2H_5)^+ \rightarrow H_2Si(C_2H_5)^+ + C_2H_4 \qquad (8)$$

$$Si(CH_3)_2(C_2H_5)^+ \rightarrow HSi(CH_3)_2^+ + C_2H_4 \qquad (9)$$

The experimental KERD for this dissociation is shown in Figure 9. Also shown are the experimental KERDs for the elimination of C_2H_4 from of $Si(CH_3)_3^+$ and $HSi(CH_3)(C_2H_5)^+$. The KERDs for the dissociations of $HSi(CH_3)(C_2H_5)^+$ and $Si(CH_3)_2(C_2H_5)^+$ are nearly identical. This suggests that the reaction mechanism that is operative is analogous to the mechanism for the dissociation of $HSi(CH_3)(C_2H_5)^+$: a rearrangement by β-hydrogen migration followed by dissociation. This corroborates the results of Bakhtiar et al. who performed collisionally activation dissociation on labeled $Si(CH_3)_2(^{13}C_2H_5)^+$. The loss of labeled $^{13}C_2H_4$ was the dominant process, which indicates that C_2H_4 comes predominantly from the ethyl group.[18] Ab initio calculations show that $HSi(CH_3)_2^+$ is more stable than $H_2Si(C_2H_5)^+$ by 0.93 eV. Thus, the conclusion that reaction 9 dominates is also consistent with the lowest energy pathway determined by ab initio methods.

Conclusions

All five ions studied in this work exhibit unimolecular loss of C_2H_4 on the 10^{-5} s time scale. Analysis of the kinetic energy release distributions indicates that these dissociations do not involve barriers in excess of the endothermicity of the dissociation. The $SiC_2H_7^+$ isomers were found to interconvert rapidly prior to unimolecular dissociation, yielding indistinguishable product ion kinetic energy release distributions. The results of the statistical phase space calculations for this system are in good agreement with experiment. The $SiC_3H_9^+$ isomers do not interconvert prior to unimolecular dissociation, as indicated by the significantly different KERDs for the $Si(CH_3)^+$ and $HSi(CH_3)(C_2H_5)^+$ ions. The mechanism for loss of ethylene from $Si(CH_3)_3^+$ was deduced from ab initio calculations to occur by either rearrangement to $HSi(CH_3)(C_2H_5)^+$ through an α-silylcarbenium ion, **TS2**, or direct rearrangement to the ion molecule complex, **I**, followed by dissociation. The barriers for rearrangement were found by ab initio methods to be 2.88 and 3.06 eV, respectively. The results of statistical phase space calculations, however, suggest that either these calculated barrier heights are too high or dissociation of $Si(CH_3)_3^+$ is not statistical. The results of statistical phase space also suggest that the $HSi(CH_3)(C_2H_5)^+$ ion undergoes loss of C_2H_4 by migration of a hydrogen from the β-carbon to the silicon center forming **I**, followed by dissociation. Comparison of the KERDs for the elimination of C_2H_4 from $Si(CH_3)_3^+$ and $HSi(CH_3)(C_2H_5)^+$ with the KERD for the same reaction of $Si(CH_3)_2(C_2H_5)^+$ indicates that C_2H_4 loss occurs preferentially from the ethyl group.

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Supporting Information Available: Details of the calculations and tables of the parameters that were used in the modeling (6 pages). Ordering information is given on any current masthead page.

Appendix

The experimental KERDS were modeled using statistical phase space theory.[31−34] Details of the calculations and tables of the parameters that were used in the modeling are available as Supporting Information, and only a brief summary of the most pertinent points will be given here. Parameters required for the PST calculations include vibrational frequencies and geometric mean rotational constants. These parameters were taken from literature when available,[43] but for most of the species, they were taken from the results of the ab initio calculations.

The kinetic models used to fit the data were based on the potential energy surface calculated by *ab initio* methods and have been described in the main text. Additional points of relevance are mentioned here. For the purpose of these calculations, it is imperative to include the experimental time window, and this is accomplished by weighting the microcanonical states by the probability of dissociation (eq 10). In eq

$$P_{\mathrm{diss}}(E,J) = \exp[-k_i(E,J)t_1] - \exp[k_1(E,J)t_2] \qquad (10)$$

10, t_1 and t_2 are the transit times for an ion to reach the entrance and exit, respectively, of the reaction zone and the rate constant $k_i(E,J)$ is the rate of the reaction through dissociation channel i with energy E and total angular momentum J.

In order to model the KERDS, it is necessary to integrate over the energy and angular momentum distribution, $P(E,J)$, of the reactant ion. Because the reactant ions were formed by dissociative ionization, the energy distribution of the reactant ions is unknown and must be estimated. To test for sensitivity of the calculated KERD to assumed forms of $P(E,J)$, three different energy distributions were used in the modeling. The first is a square distribution in which it was assumed that the probability was constant over the energy range in which the ions dissociate with $k \approx 10^5$ s (eq 11). The second function

$$P(E) = \text{constant} \qquad (11)$$

used was a decreasing linear function (eq 12). Several different

$$P(E) = 1.00 - mE \qquad (12)$$

values for the slope m were used in the calculations. The third function used was a Boltzmann distribution (eq 13), with $T = 425$ K. The angular momentum distribution used in the

$$P(E) = \exp(-E/kT) \qquad (13)$$

calculations is a Boltzmann distribution at a temperature of 425 K, the source temperature used for these experiments.

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