Elucidating the Structures of Isomeric Silylenium Ions (SiC_3H_9^+ , $\text{SiC}_4\text{H}_{11}^+$, $\text{SiC}_5\text{H}_{13}^+$) By Using Specific Ion/Molecule Reactions

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Specific ion/molecule reactions are demonstrated that distinguish the structures of the following isomeric organosilylenium ions: $\text{Si}(\text{CH}_3)_3^+$ and $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$; $\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)^+$ and $\text{SiH}(\text{C}_2\text{H}_5)_2^+$; and $\text{Si}(\text{CH}_3)_2(i\text{-C}_3\text{H}_7)^+$, $\text{Si}(\text{CH}_3)_2(n\text{-C}_3\text{H}_7)^+$, $\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)_2^+$, and $\text{Si}(\text{CH}_3)_3(\pi\text{-C}_3\text{H}_4)^+$. Both methanol and isotopically labeled ethene yield structure-specific reactions with these ions. Methanol reacts with alkylsilylenium ions by competitive elimination of a corresponding alkane or dehydrogenation and yields a methoxysilylenium ion. Isotopically labeled ethene reacts specifically with alkylsilylenium ions containing a two-carbon or larger alkyl substituent by displacement of the corresponding olefin and yields an ethylsilylenium ion. Methanol reactions were found to be efficient for all systems, whereas isotopically labeled ethene reaction efficiencies were quite variable, with dialkylsilylenium ions reacting rapidly and trialkylsilylenium ions reacting much more slowly. Mechanisms for these reactions and differences in the kinetics are discussed. (*J Am Soc Mass Spectrom* 1991, 2, 278–291)

Both cationic and anionic organosilicon species are highly reactive in the gas phase [1–4], with a number of interesting facile rearrangements occurring. For example, collision-activated dissociation (CAD) of $\text{Si}(\text{CH}_3)_3^+$ results in significant elimination of C_2H_4 , process 1 [5]. This obviously complex reaction

may proceed by either prior rearrangement to an ethylmethylsilylenium ion, process 2, with subsequent ethene elimination or by simple extension of vibrations, process 3. In any case, the elimination of ethene is a facile

process. Schwarz, Apeloig, and co-workers [6, 7] recently studied the decomposition of a series of isomeric $\text{SiC}_5\text{H}_{13}^+$ ions and found a number of interest-

ing, facile rearrangements. Particularly intriguing was the observation that CAD of both the carbenium, $(\text{CH}_3-\text{CH}_2^+)\text{Si}(\text{CH}_3)_3$, and the corresponding silylenium, $(i\text{-C}_3\text{H}_7)\text{Si}(\text{CH}_3)_2^+$, yields identical losses, with C_2H_4 and C_3H_6 eliminations dominating in a ratio of 1.25:1 [6]. A novel hydrogen-methyl exchange reaction involving silylenium ions $(\text{SiH}_x(\text{CH}_3)_{3-x})^+$, $x = 1-3$ and propene, process 4, was reported [8]. All of these results

reflect the high proclivity of organosilicon ions to rearrange, consistent with their rich chemistry [1–4].

Except for a few notable examples [6, 7], reaction mechanisms involving organosilicon ions are poorly understood, even though labeling experiments have been exploited in many cases. Clearly, the ability to determine/distinguish isomeric ion structures would allow reaction mechanisms to be tested. Collision-activated dissociation is commonly employed for ion structure determination [9], however, the propensity for organosilicon ions toward rearrangement renders CAD a less than definitive probe of structure [6, 7]. Specific ion/molecule reactions can, however, be quite selective probes of ion structure [10, 11]. In this case, neutral reagents are selected that exploit the characteristic reactivity of an ion.

Methanol reacts with trimethylsilylenium by elimination of methane, yielding a methoxysilylenium ion,

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process 5, presumably through the intermediacy of oxonium, **1** [12]. Reactions with alcohols containing a two-carbon

or larger chain yield elimination of the corresponding olefin, forming protonated trimethyl silanol (**2**), process 6 [10]. Dialkyl ethers (R > Me) react in a similar fashion with sequential elimination of two olefins, yielding **2** [13]. Allyldimethylsilylenium reacts with alcohols by specific elimination of the allyl group as propene, forming an alkoxydimethylsilylenium, process 7 [14].

The complete absence of process 6 for allyldimethylsilylenium contrasts that for trimethylsilylenium. The above results suggest that methanol may be employed as a probe of alkylsilylenium structure. Specifically, methanol may react with a dialkylsilylenium ion, yielding competitive elimination of a corresponding alkane or dehydrogenation, each yielding a methoxysilylenium ion, process 8. For example, the SiC₃H₅⁺ isomers, Si(CH₃)₃⁺ and SiH(CH₃)(C₂H₅)⁺ (eqs 8a-8c, below), would yield distinct products upon reaction with methanol.

In this article, we demonstrate that methanol can be used to structurally distinguish isomeric alkylsilylenium ions. In addition, ethene is found to react specifically with alkylsilylenium ions containing a two-carbon or larger alkyl substituent by displacement of the corresponding olefin, process 9. By

using both methanol and ethene (isotopically labeled), various alkylsilylenium ion structures can be determined. In this article we demonstrate that the following isomeric organosilylenium ions can be structurally distinguished: Si(CH₃)₃⁺ and SiH(CH₃)(C₂H₅)⁺; Si(CH₃)₂(C₂H₅)⁺ and SiH(CH₃)₂⁺; and Si(CH₃)₂(i-C₃H₇)⁺, Si(CH₃)₂(n-C₃H₇)⁺, Si(CH₃)(C₂H₅)₂⁺, and Si(CH₃)₃(π-C₂H₄)⁺.

Experimental

All experiments were performed by using a modified Nicolet (Madison, WI) FTMS-1000 Fourier transform mass spectrometer (for reviews on this methodology, see [15, 16]) equipped with a 5.08 cm cubic trapping cell, 3.0 T superconducting magnet, and a 1.2 V trapping potential (a complete description of the instrument can be found in [17]). A Bayard/Alpert type ionization gauge was used to monitor pressure and was calibrated by using reactions with well-known rate constants. Pressures of reagent neutrals were subsequently corrected using ionization cross sections [18]. Uncertainties in pressure readings are less than ±30% and are the largest source for error in reaction rate constants, hence absolute reaction rate constant errors are assigned as ±30%. Replicate measurements (at least three trials) yield a precision of < ±10% of the measured rate constant (precision measured as the maximum deviation from the mean). Hence, for comparison, the relative error in rate constants for reaction of distinct ions with a particular neutral is < ±10%. Chemicals were obtained in high purity and used as supplied except for multiple freeze-pump-thaw cycles to remove noncondensable gases. Ethene-D₄ and ethene-¹³C₂ were obtained from MSD Isotopes (Montreal, Canada) with > 98% isotopic purity.

All of the authentic alkylsilylenium ions were generated by electron impact (EI) on the corresponding organosilane except for the dimethylpropylsilylenium ions that were produced by chloride abstraction from the respective chlorosilanes by Si(CH₃)₃⁺, process 10. Si(CH₃)₃(π-C₂H₄)⁺ was formed by

Table 1. Summary of reactions of specific organosilylenium ions with methanol

Reactant ion	Product ^a ions	k_{obs}^b	Efficiency ^c
$\text{Si}(\text{CH}_3)_3^+$	$\text{Si}(\text{CH}_3)_2\text{OCH}_3^+ (0.90)$ $[\text{Si}(\text{CH}_3)_3]^+ \text{HOCH}_3 (0.10)$	0.61(0.18)	0.36
$\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$	$\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{OCH}_3^+ (0.48)$ $\text{SiH}(\text{C}_2\text{H}_5)\text{OCH}_3^+ (0.22)$ $\text{SiH}(\text{CH}_3)\text{OCH}_3^+ (0.27)$ $[\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)]^+ \text{HOCH}_3 (0.03)$	1.43(0.43)	0.86
$\text{SiH}(\text{C}_2\text{H}_5)_2^+$	$\text{Si}(\text{C}_2\text{H}_5)_2\text{OCH}_3^+ (0.55)$ $\text{SiH}(\text{C}_2\text{H}_5)\text{OCH}_3^+ (0.43)$ $[\text{SiH}(\text{C}_2\text{H}_5)_2]^+ \text{HOCH}_3 (0.02)$	1.71(0.51)	1.06
$\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)^+$	$\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{OCH}_3^+ (0.49)$ $\text{Si}(\text{CH}_3)_2\text{OCH}_3^+ (0.31)$ $[\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)]^+ \text{HOCH}_3 (0.20)$	0.78(0.23)	0.49
$\text{Si}(\text{CH}_3)_2(i\text{-C}_3\text{H}_7)^+$	$\text{Si}(\text{CH}_3)(\text{C}_3\text{H}_7)\text{OCH}_3^+ (0.57)$ $\text{Si}(\text{CH}_3)_2\text{OCH}_3^+ (0.24)$ $[\text{Si}(\text{CH}_3)_2(\text{C}_3\text{H}_7)]^+ \text{HOCH}_3 (0.19)$	0.66(0.20)	0.42
$\text{Si}(\text{CH}_3)_2(n\text{-C}_3\text{H}_7)^+$	$\text{Si}(\text{CH}_3)(\text{C}_3\text{H}_7)\text{OCH}_3^+ (0.40)$ $\text{Si}(\text{CH}_3)_2\text{OCH}_3^+ (0.43)$ $[\text{Si}(\text{CH}_3)_2(\text{C}_3\text{H}_7)]^+ \text{HOCH}_3 (0.17)$	0.82(0.25)	0.52
$\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)_2^+$	$\text{Si}(\text{C}_2\text{H}_5)_2\text{OCH}_3^+ (0.22)$ $\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{OCH}_3^+ (0.60)$ $[\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)_2]^+ \text{HOCH}_3 (0.18)$	0.84(0.25)	0.53
$\text{Si}(\text{CH}_3)_3(\pi\text{-C}_2\text{H}_4)^+$	$[\text{Si}(\text{CH}_3)_3]^+ \text{HOCH}_3 (1.00)$	0.85(0.26)	0.53

^a Branching ratio for reactions are in parentheses.^b Observed bimolecular rate coefficients for disappearance of the reactant ion in units of 10^{-9} $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ with uncertainties in parentheses.^c Overall reaction efficiency = $k_{\text{obs}}/k_{\text{coll}}$ [25].

electrophilic dehydration of the corresponding alcohol, process 11. All of the

precursor organosilanes were introduced into the vacuum chamber via a pulsed solenoid inlet valve in order to prevent complicating side reactions with background organosilane [1-4]. (A detailed description of pulsed valve introduction of reagent gases in conjunction with Fourier transform mass spectrometry [FTMS] can be found in ref 19.) The pulsed valve is triggered off the quench pulse with the valve duration varied (typically between 2-3 ms) to control the amount of pulsed reagents introduced into the chamber. The ballast pressure in the pulsed valve assembly was <1 torr. A 50-ms delay follows the opening of the pulsed valve prior to EI ionization (typically 50-ms beam duration, 70 eV). A variable delay following ionization (ca. 1 s) is used to allow the pulsed reagents to be pumped from the vacuum chamber. The desired ion is isolated by swept ejection pulses [15] and subsequently allowed to react with a static pressure of a specific reagent or is collisionally activated [9, 20]. A static pressure of 1×10^{-5} torr Ar was used throughout these experiments and serves both to facilitate ion thermalization prior to reaction and also as the target for CAD.

Details concerning CAD in conjunction with FTMS have been described elsewhere [21-23]. Collision-activated dissociation breakdown curves were obtained by varying the kinetic energy of the ions (typically between 1 and 50 eV) by adjusting the duration of the CAD electric field pulse (typically between 100 and 600 μs). The CAD fragment ion intensities are plotted as a fraction of the initial parent ion intensity (no excitation) versus kinetic energy. This allows both the energy dependency for fragmentation as well as the fragmentation efficiency to be compared directly for isomeric systems. The sum of ion abundances totals less than unity at higher collision energy due to ion ejection from the cell. The CAD breakdown curves are very reproducible, with less than $\pm 3\%$ absolute variation in ion abundances. The spread in ion kinetic energy is dependent on the total average kinetic energy and is 65% at 1 eV, 19% at 10 eV, 11% at 30 eV, and 6% at 100 eV [24].

Results and Discussion

The reactions of silylenium ions with methanol and ethene (labeled) are summarized in Tables 1 and 2, respectively. The methanol reactions are generally quite efficient, with efficiencies varying between 1.06 ($\text{SiH}(\text{C}_2\text{H}_5)_2^+$) to 0.36 ($\text{Si}(\text{CH}_3)_3^+$) [25]. (Reaction efficiency is taken as the ratio of the experimental rate constant to the collision rate constant (i.e., $k_{\text{obs}}/k_{\text{coll}}$). Collision rate constants were calculated by using the average dipole orientation approximation for polar

Table 2. Summary of reactions of specific organosilylenium ions with ethene

Reactant ion	Neutral ^a reactant	Product ^b ions	k_{obs}^c	Efficiency ^d
$\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$	C_2H_4	$[\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+]\text{C}_2\text{H}_4(1.00)$	0.035(0.011)	0.032
$\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$	$^*\text{C}_2\text{H}_4$	$\text{SiH}(\text{CH}_3)(^*\text{C}_2\text{H}_5)^+(0.93)$ $[\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+]\text{C}_2\text{H}_4(0.07)$	0.35(0.11)	0.33
$\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$	C_2D_4	$\text{Si}(\text{CH}_3)\text{C}_2\text{H}_5\text{D}^+(0.23)$ $\text{Si}(\text{CH}_3)\text{C}_2\text{H}_4\text{D}_2^+(0.07)$ $\text{Si}(\text{CH}_3)\text{C}_2\text{H}_3\text{D}_3^+(0.11)$ $\text{Si}(\text{CH}_3)\text{C}_2\text{H}_2\text{D}_4^+(0.55)$ $[\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+]\text{C}_2\text{D}_4(0.04)$	0.48(0.14)	0.47
$\text{SiH}(\text{C}_2\text{H}_5)_2^+$	$^*\text{C}_2\text{H}_4$	$\text{SiH}(\text{C}_2\text{H}_5)(^*\text{C}_2\text{H}_5)^+(0.97)$ $[\text{SiH}(\text{C}_2\text{H}_5)_2^+]\text{C}_2\text{H}_4(0.03)$	0.47(0.14)	0.46
$\text{SiH}(\text{C}_2\text{H}_5)_2^+$	C_2D_4	$\text{SiC}_4\text{H}_{10}\text{D}^+(0.18)$ $\text{SiC}_4\text{H}_9\text{D}_2^+(0.03)$ $\text{SiC}_4\text{H}_8\text{D}_3^+(0.05)$ $\text{SiC}_4\text{H}_7\text{D}_4^+(0.65)$ $[\text{SiC}_4\text{H}_{11}]\text{C}_2\text{D}_4(0.09)$	0.70(0.21)	0.71
$\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)^+$	$^*\text{C}_2\text{H}_4$	$\text{Si}(\text{CH}_3)_2(^*\text{C}_2\text{H}_5)^+(1.00)$	0.0047(0.0014)	0.0046
$\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)^+$	C_2D_4	$\text{Si}(\text{CH}_3)_2(\text{C}_2\text{D}_4\text{H})^+(1.00)$	0.0042(0.0013)	0.0042
$\text{Si}(\text{CH}_3)_2(i\text{-C}_3\text{H}_7)^+$	C_2H_4	$\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)^+(1.00)$	0.0062(0.0019)	0.0064
$\text{Si}(\text{CH}_3)_2(i\text{-C}_3\text{H}_7)^+$	$^*\text{C}_2\text{H}_4$	$\text{Si}(\text{CH}_3)_2(^*\text{C}_2\text{H}_5)^+(1.00)$	0.0047(0.0014)	0.0047
$\text{Si}(\text{CH}_3)_2(i\text{-C}_3\text{H}_7)^+$	C_2D_4	$\text{Si}(\text{CH}_3)_2(\text{C}_2\text{D}_4\text{H})^+(1.00)$	0.0069(0.0021)	0.0071
$\text{Si}(\text{CH}_3)_2(n\text{-C}_3\text{H}_7)^+$	C_2H_4	$\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)^+(1.00)$	0.016(0.005)	0.016
$\text{Si}(\text{CH}_3)_2(n\text{-C}_3\text{H}_7)^+$	$^*\text{C}_2\text{H}_4$	$\text{Si}(\text{CH}_3)_2(^*\text{C}_2\text{H}_5)^+(1.00)$	0.018(0.005)	0.018
$\text{Si}(\text{CH}_3)_2(n\text{-C}_3\text{H}_7)^+$	C_2D_4	$\text{Si}(\text{CH}_3)_2(\text{C}_2\text{D}_4\text{H})^+(1.00)$	0.016(0.005)	0.016
$\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)_2^+$	$^*\text{C}_2\text{H}_4$	$\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)(^*\text{C}_2\text{H}_5)^+(1.00)$	0.0035(0.0011)	0.0035
$\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)_2^+$	C_2D_4	$\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{C}_2\text{D}_4\text{H})^+(1.00)$	0.0038(0.0011)	0.0039

^a... denotes ¹³C isotope.^bBranching ratio for reactions are in parentheses.^cObserved bimolecular rate coefficients for disappearance of the reactant ion in units of 10⁻⁸ cm³molecule⁻¹s⁻¹ with uncertainties in parentheses.^dOverall reaction efficiency = $k_{\text{obs}}/k_{\text{coll}}$ [25].^eReaction yielded nonlinear kinetics. See text for discussion.

neutrals.) In contrast, ethene reaction efficiencies are generally much lower with greater variability between distinct systems. For example, ethene reacts rapidly with dialkylsilylenium ions (e.g., $\text{SiH}(\text{C}_2\text{H}_5)_2^+$; eff. = 0.71), however, the efficiencies with trialkylsilylenium ions are nearly two orders of magnitude lower. In addition to the primary reaction products listed in Tables 1 and 2, many subsequent reactions were observed. For example, methanol reacts sequentially with $\text{Si}(\text{CH}_3)_3^+$, ultimately yielding trimethoxysilylenium, process 12. As a

consequence, reaction branching ratios were obtained when less than 25% of the ion of interest has reacted and are the average of three trials. Uncertainties in branching ratios are $< \pm 10\%$. Branching ratios for reaction with C_2D_4 are reported only for products with greater than 2% abundance, due to the small isotopic impurities in the label.

SiC_3H_9 + Isomers

The CAD breakdown curves for $\text{Si}(\text{CH}_3)_3^+$ and $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ are illustrated in Figures 1 and 2. As can be seen, both ions yield similar losses, with C_2H_4 elimination dominating, process 13. At higher collision energy some SiCH_3^+ is also observed. Triple mass spectrometry [26] revealed that SiCH_3^+ is formed primarily

by sequential $\text{C}_2\text{H}_4/\text{H}_2$ loss instead of direct C_2H_6 elimination. These results are in accord with a high energy CAD study of $\text{Si}(\text{CH}_3)_3^+$ [5]. Although both SiC_3H_9^+ isomers yield the same fragmentations, differences are observed in both the overall efficiency and energy dependency. The higher energy requirement from fragmentation of $\text{Si}(\text{CH}_3)_3^+$ is due in part to its increased thermal stability over $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ (ca. 17 kcal/mol). (The enthalpy of formation of $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ is estimated as 164 kcal/mol by assuming that the following reaction is thermoneutral and by using the following thermochemical infor-

Figure 1. Variation of ion abundances as a function of kinetic energy (laboratory frame) for dissociation of collisionally activated $\text{Si}(\text{CH}_3)_3^+$. $\bullet = \text{Si}(\text{CH}_3)_3^+$; $\diamond = \text{SiCH}_2^+$; $\blacktriangle = \text{SiCH}_3^+$.

Figure 2. Variation of ion abundances as a function of kinetic energy (laboratory frame) for dissociation of collisionally activated $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$. $\bullet = \text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$; $\diamond = \text{SiCH}_2^+$; $\blacktriangle = \text{SiCH}_3^+$.

mation:

$\Delta H_f^\circ(\text{SiH}(\text{CH}_3)_2^+) = 172 \text{ kcal/mol}$ and $\Delta H_f^\circ(\text{Si}(\text{CH}_3)_3^+) = 147 \text{ kcal/mol}$, from [27a]. Auxiliary thermochemical information is taken from ref 27b). In addition, substantial rearrangement is required for C_2H_4 elimination from $\text{Si}(\text{CH}_3)_3^+$. C_2H_4 elimination from $\text{Si}(\text{CH}_3)_3^+$ may involve a dyotropic rearrangement; yielding $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ followed by C_2H_4 extrusion by β -hydride migration (see below). The differences in the CAD efficiencies and energy dependencies for the SiC_3H_9^+ isomers are structurally diagnostic; however, it would be difficult for CAD to distinguish a mixture of the two silylenium isomers.

$\text{Si}(\text{CH}_3)_3^+$ reacts with methanol, yielding elimination of methane, process 5, generating a dimethylmethoxysilylenium ion along with a small amount of condensation (Table 1) [12]. Reaction with CH_3OD yields exclusive elimination of CH_3D . In contrast, three different neutral losses are observed for $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ with methanol, reactions 14-16, below, along with some condensation (Table 1). All three processes can be viewed as originated from an

oxonium intermediate analogous to **1** with competitive eliminations. Dehydrogenation is clearly the favored process, however, significant alkane eliminations are also observed. Interestingly, elimination of ethane is favored over methane elimination and this trend holds for all ethylmethylsilylenium isomers (Table 1). The reaction efficiency of the dialkyl isomer is approximately double that for the trialkyl isomer, and this general trend persists throughout this study (Table 1). The reduced efficiency of the trialkylsilylenium reaction may simply be a consequence of steric crowding around the silicon atom, making formation of adduct **1** more difficult.

$\text{Si}(\text{CH}_3)_3^+$ is inert with labeled ethene (^{13}C or D labeled), however, ethene- $^{13}\text{C}_2$ reacts rapidly with $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$, yielding thermoneutral displacement of an unlabeled ethene, process 17, along with condensation (Table 2). The product of reaction 17 undergoes exclusive, slow condensation

with ethene- $^{13}\text{C}_2$. The rate constant for condensation with unlabeled ethene, process 18, is $3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ yielding an efficiency of

0.032 [25]. The corresponding condensation process is absent with $\text{Si}(\text{CH}_3)_3^+$. Observation of condensation, process 18, suggests that the ion/molecule collision complex is long lived and, as a consequence, is stabilized by either infrared radiative emission [28, 29] or collisional stabilization with argon (ca. 6 ms/collision).

In contrast to the clean displacement reaction (process 17), ethene- D_4 yields substantial H/D exchange, processes 19-23, below, along with condensation (Table 2). Figure 3 illustrates the mass spectra obtained for reaction of $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ with C_2D_4 at various reaction times and clearly illustrates that only six hydrogens are exchangeable. We refer to Figure 3d as "exhaustive" H/D exchange, allowing the number of exchangeable hydrogens for an ion to be counted. In addition to H/D exchange, simple condensation is also observed (Figure 3). Isolation of the product of reaction 19 followed by additional trapping yields reactions 24-28, below. These results are very similar to the $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ system, however, some additional H/D scrambling is observed. Due to poor signal-to-noise ratios the relative uncertainty in these branching ratios is $\pm 30\%$. The predominance of process 27, however, suggests that the exchanged hydrogen in process 19 is primarily unscrambled with the ethyl hydrogens. Absence of isotopic exchange for $\text{Si}(\text{CH}_3)_3^+$ is consistent with a recent report involving CAD of a $\text{C}_2\text{D}_4/\text{Si}(\text{CH}_3)_3^+$ adduct ion where exclusive loss of C_2D_4 was observed

[30]. This result is also in accord with the lack of scrambling of the methyl hydrogens for $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$. The above ion molecule reactions clearly distinguish the two SiC_3H_5^+ isomers.

The kinetics of both isotopic (H/D) exchange and ethene displacement yield insights into the mechanism involved in scrambling as well as details on the potential energy surface for the scrambling processes [31]. The high efficiency for the labeled ethene reactions suggest low barriers for the thermoneutral displacement, process 17, as well as H/D scrambling [31]. A proposed mechanism for the isotopic ethene results for $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ is presented in Scheme I. The initial ion/molecule collision complex, 3, freely converts to either the bisected open carbenium, 4, with stabilization due to hyperconjugation of the developing empty 2p orbital on the β -carbon and the bisected C-Si σ -bonding orbital [6, 7, 32], or the silicon bridged structure, 5 [33, 34]. Hyperconjugation in the bisected open carbenium is maximized for an HC $^+$ CSi dihedral angle of 90° [6, 7, 32]. Ab initio calculations predict that the bridged structure is only slightly (ca. 4 kcal/mol) less stable than the corresponding β -carbenium, 4, with little or no barrier for their interconversion [32a]. Species 4 and 5 are activated by the ethene binding energy, which is ca. 20-25 kcal/mol [30, 35]. Facile ethene insertion into an Si-H bond forms the diethyl complex, 6, yielding two equivalent ethyl groups. Subsequent β -hydrogen migration-ethene elimination (β -hydrogen elimination) completes the displacement process [8, 36-40]. Rapid, reversible H/D exchange has been observed for both SiH_3^+ (three exchangeable Hs) [36] and $\text{Si}(\text{CH}_3)_2\text{H}^+$ (one exchangeable H) [8] with C_2D_4 . Rapid, reversible ethene insertion/ β -hydrogen migration would yield an efficiency of 0.5 for process 17, which is within the experimental error of the observed efficiency. Hence, the mechanism in Scheme I must have low barriers for the ethene displacement process. The mechanism in Scheme I predicts that

Figure 3. Reaction of $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ with 5.7×10^{-8} torr of C_2D_4 . (a) Isolation of $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$, m/z 73; (b) 1.0 s reaction with C_2D_4 ; (c) 3.0 s reaction with C_2D_4 ; (d) 5.0 s reaction with C_2D_4 .

$\text{SiD}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ (simple H/D exchange) and $\text{SiH}(\text{CH}_3)(\text{C}_2\text{D}_4\text{H})^+$ to be the initial products. Subsequent collisions with C_2D_4 result in additional H/D exchange yielding ions containing five and six deuterium with the sixth H/D exchange the terminal process (Figure 3).

Scheme I, however, does not account for the H/D scrambling in processes 20 and 21. This additional H/D scrambling must occur within the collision complex and may be explained by invoking multiple reversible ethene insertion/ β -hydrogen migrations. This may proceed as depicted in Scheme II, where an initial ethene insertion/ β -deuterium migration yields **7**, which undergoes a second β -hydrogen migration generating the hypervalent di-ethene species, **8** [41]. **8**

Scheme II

rapidly collapses to the diethyl, 10, via 9. Subsequent β -hydrogen migration/ethene insertion results in two and three H/D exchanges, processes 20 and 21. Random scrambling of the six exchangeable hydrogens in the initial collision complex, 3, prior to ethene elimination would yield the following isotopic distribution; $\text{SiC}_3\text{H}_8\text{D}^+$ (11.5%), $\text{SiC}_3\text{H}_7\text{D}_2^+$ (43.1%), $\text{SiC}_3\text{H}_6\text{D}_3^+$ (38.3%), and $\text{SiC}_3\text{H}_5\text{D}_4^+$ (7.2%). The low amount of processes 20 and 21 indicates that random H/D scrambling does not occur within the lifetime of the collision complex and that there is a significant barrier for this subsequent scrambling (Scheme II). β -Hydrogen migration in 7 presumably generates a high energy intermediate, 8, and, consequently, the rate for processes 20 and 21 would be less than that for processes 19 and 22. The H/D exchange distribution for reaction of $\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{D}^+$, formed by process 19, with ethene- D_4 suggests that the initial exchangeable hydrogen is primarily unscrambled with the ethyl hydrogens in accord with Scheme I. Finally, Scheme I predicts a ratio of 1:1.5 for processes 19 and 22. The actual ratio is 1:2.5 and is in accord with a small normal kinetic isotope effect favoring retention of the label on the ethyl group. (The lowest energy configuration for the reaction intermediate is deuterium bonded to carbon and not the silicon. The effect of the zero-point-energy differences for isotopically distinct structures is responsible for this behavior.)

A potential energy surface for Scheme I is presented in Figure 4. The relative energy of the distinct intermediates are estimated as follows. The ethene binding energy to the organosilylenium is taken as 20 kcal/mol [30, 35]. The enthalpy of formation of $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{D}^+$ is estimated to be 164 kcal/mol [27] and $\Delta H_f^\circ \text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)_2^+$ is estimated to be 131 kcal/mol by assuming that the following reaction is thermoneutral and by using auxiliary thermochemical

information from ref 27. The diethyl complex is clearly the most stable intermediate and lies in a deep potential well. The relative efficiency of the isotopic exchange/displacement reactions, processes 17, 19-22,

Figure 4. Simplified potential energy surface for reaction of $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ with ethene- D_4 .

requires a low barrier for conversion of the collision complex, 3, to the diethyl species [31]. The transition state for this conversion, process 29, is probably 11. This process is analogous to the

well-known olefin insertion/ β -hydrogen elimination process for transition metal systems where the transition state employs a zero dihedral angle between $\text{M}-\text{C}-\text{C}-\text{H}$ [42]. There are no restrictions in the corresponding organosilane species 4 and 5 from achieving this favorable geometry.

An alternative ethene exchange mechanism involving sequential 1,2-hydrogen atom migrations is presented in Scheme III. (This mechanism was proposed in refs 6 and 7 to account for the CAD results for isomeric $\text{SiC}_5\text{H}_{13}^+$ ions.) Again, initial ethene coordination generates 4 and 5. Subsequent 1,2-hydrogen migration from 4 via 4a yields carbenium 12. Facile 1,2-hydrogen migration from silicon forms the diethyl species, 13. Subsequent hydrogen migrations result in H/D exchange and ethene displacement accounting for process 19-22. Although this mechanism is consistent with the above isotopic results, it involves high energy intermediates that are energetically inaccessible upon ethene coordination. There is a substantial barrier (ca. 30 kcal/mol) for generating α -silylcar-

Scheme III

Scheme IV

benium, 12 , from 4 [6, 7]. The barrier along the $4 \rightarrow 12$ ($4a$) path results from geometric constraints for this 1,2-hydrogen migration where the empty 2p orbital on the β -carbon eclipses the C-Si σ -bonding orbital resulting in a loss of hyperconjugation [6, 7]. As there is only 20-25 kcal/mol internal energy (the ethene binding energy) [30, 35] to drive the chemistry, Scheme III is highly unlikely based on simple energetic arguments.

Another possible mechanism for the above ethene- D_4 results involves a simple 1,5-hydrogen shift in the initially formed intermediate, 4 (Scheme IV). This process, however, does not account for H/D exchange with the Si-hydrogen. In addition, Scheme IV should be rapid for ethene exchange for both dialkylsilylenium and trialkylsilylenium ions. However, trialkylsilylenium ions undergo isotopic ethene

exchange very slowly compared to the dialkylsilylenium ions (Table 2). Consequently, the direct 1,5-hydrogen shift does not appear to be important for ethene exchange in dialkylsilylenium ions.

$SiC_4H_{11}^+$ Isomers

The fragment ion abundances versus kinetic energy for CAD of $Si(CH_3)_2(C_2H_5)^+$ and $SiH(C_2H_5)_2^+$ are illustrated in Figures 5 and 6. Both isomeric ions yield nearly identical CAD spectra with sequential ethene eliminations occurring, process 30. This fragmentation pattern is consistent

with that for the $SiC_3H_9^+$ isomers which eliminate primarily ethene. Here, CAD is unable to distinguish these two silylenium isomers.

Methanol yields two primary reaction products with both $SiC_4H_{11}^+$ isomers, reactions 31-34, below, as well as direct condensation (Table 1). These reactions are

Figure 5. Variation of ion abundances as a function of kinetic energy (laboratory frame) for dissociation of collisionally activated $Si(CH_3)_2(C_2H_5)^+$. ● = $Si(CH_3)_2(C_2H_5)^+$; ◇ = $SiH(CH_3)_2^+$; ○ = SiH_3^+ .

Figure 6. Variation of ion abundances as a function of kinetic energy (laboratory frame) for dissociation of collisionally activated $SiH(C_2H_5)_2^+$. ● = $SiH(C_2H_5)_2^+$; ◇ = $Si(H)_2(C_2H_5)^+$; ○ = SiH_3^+ .

quite distinct because methane elimination occurs only with the dimethylethyl isomer whereas dehydrogenation occurs only with the diethyl isomer. As for the SiC_3H_5^+ isomers, the efficiency of the dialkyl isomer is nearly double that of the trialkyl isomer. In addition, the trialkyl isomer yields considerably more condensation than the dialkyl isomer (Table 1). Again, elimination of ethane is favored over methane elimination for the dimethylethyl isomer (correcting for the statistical factor). Each of the products formed in reactions 31-34 undergoes subsequent reactions with methanol, ultimately producing trimethoxysilylenium.

Ethene- $^{13}\text{C}_2$ reacts rapidly (eff. = 0.46) with $\text{SiH}(\text{C}_2\text{H}_5)_2^+$, yielding sequential displacement of ethene, process 35, with no $^{12}\text{C}/^{13}\text{C}$ scrambling.

Competitive with this displacement process is the corresponding condensation process (cf. reaction 18). Ethene- D_4 yields complex H/D exchange, processes 36-39, below, along with condensation (Table 2). Exhaustive H/D exchange yields all hydrogens exchangeable. These results are analogous to those for $\text{SiH}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ and are readily accounted for by invoking processes detailed in Schemes I and II.

$\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)^+$ reacts much more slowly with labeled ethene (eff. = 0.0046 for ethene- $^{13}\text{C}_2$) than the corresponding dialkylsilylenium ions (Table 2). Again, ethene- $^{13}\text{C}_2$ yields a clean displacement of unlabeled ethene, process 40, with no further exchange observed. In accord with other

trialkylsilylenium ions simple condensation is not observed. In contrast to the above dialkylsilylenium ions, only a single primary reaction product is observed

with ethene- D_4 , process 41, followed by additional slow exchange of

the remaining ethyl-H, yielding five exchangeable hydrogens in the product. Collision-activated dissociation of either $\text{Si}(\text{CH}_3)_2({}^{13}\text{C}_2\text{H}_5)^+$ (from process 40) or $\text{Si}(\text{CH}_3)_2(\text{C}_2\text{D}_5)^+$ (from exhaustive H/D exchange with ethene- D_4) yields elimination of isotopically labeled ethene with no isotopic scrambling with the methyl groups.

The simple ethene displacement without H/D scrambling may proceed by a mechanism analogous to that presented in Scheme II for the multiple H/D scrambling for dialkyl species. A proposed mechanism for the ethene- D_4 results for $\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)^+$ is presented in Scheme V. Ethene coordination forms the activated collision complex, **14**. Unlike the dialkylsilylenium species, there is not an Si-H bond into which ethene can readily insert, forming the corresponding ethyl species. Instead, ethene coordination effects a slow β -hydrogen migration, yielding hypervalent **15** which rapidly collapses to **14** or **16** followed by facile ethene elimination. The rate of ethene elimination from **14** and **16** is much greater than the rate for conversion to **15** accounting for the absence of isotopic scrambling with ethene- D_4 . Scheme V incorporates the same basic features as Schemes I and II (i.e., ethene insertion/ β -hydrogen migration). Alternatively, ethene displacement may proceed by a direct 1,5-hydrogen shift (cf. Scheme IV).

$\text{SiC}_5\text{H}_{13}^+$ Isomers

The CAD breakdown curves for the four $\text{SiC}_5\text{H}_{13}^+$ isomers ($\text{Si}(\text{CH}_3)_2(i\text{-C}_3\text{H}_7)^+$, $\text{Si}(\text{CH}_3)_2(n\text{-C}_3\text{H}_7)^+$, $\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)_2^+$, and $\text{Si}(\text{CH}_3)_3(\pi\text{-C}_2\text{H}_4)^+$) are illustrated in Figures 7-10. The CAD spectra for the two propyl species are nearly identical with competitive elimination of C_2H_4 and C_3H_6 , processes 42 and 43, below, dominating. Ethene elimination dominates at

Scheme V

low collision energy with C_3H_6 elimination more competitive at high collision energy. Elimination of C_3H_6 probably proceeds by simple β -hydrogen migration (e.g., process 29), whereas C_2H_4 elimination clearly involves a complex rearrangement [6, 7]. Rearrangement yielding C_2H_4 elimination is slightly more favorable for the *i*-propyl isomer. In contrast to the propyl species, CAD of the diethylmethyl isomer yields sequential ethene eliminations, whereas CAD of the π -ethene complex is characterized by a very efficient elimination of C_2H_4 followed by subsequent eliminations reminiscent of $Si(CH_3)_3^+$. Hence, CAD distinguishes the π -ethene complex and the diethylmethyl species from the corresponding propyl species.

Methanol reacts with the two propyl isomers by competitive CH_4/C_3H_8 eliminations, processes 44 and 45, below, as expected, however, the branching ratios are somewhat different (Table 1). Methane loss is favored for the *i*-propyl species, whereas essentially equal amounts of methane and propane losses are observed for the *n*-propyl species. Hence, elimination of propane is favored over methane elimination for the *n*-propyl species (considering the statistical factor) as observed for the corresponding ethylmethyl isomers. However, propane and methane elimination occur with nearly equal facility for the isopropyl isomer (statistically). The reduced efficiency for propane elimination for the isopropyl system may reflect steric crowding in the incipient oxonium ion (e.g., 1) where it is more difficult to transfer the alcoholic hydrogen to a tertiary alkyl carbon than a secondary alkyl carbon. This restriction, however, is not observed for the corresponding secondary versus primary alkyl carbons (see above). The π -ethene complex reacts exclusively by elimination of ethene, process 46. This simple displacement

reaction has previously been observed in a flowing afterglow instrument [30]. Finally, methanol reacts with the diethylmethyl species by processes 47 and 48, below. Again, ethane elimination is favored over methane elimination.

Ethene reacts with the propyl isomers exclusively by propene displacement, process 49. Reaction with both ethene- D_4 and ethene- $^{13}C_2$ yields

no isotopic scrambling. Reaction of the *i*-propyl isomer with ethene yields pseudo first order kinetics with a rate constant of $6.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (eff. = 0.0061). Reaction of ethene with the *n*-propyl isomer is more complex, yielding an initial rapid reaction (relative to the *i*-propyl isomer) followed by a slow reaction (Figure 11). The initial rate constant is $1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is 2.6 times faster than that for the *i*-propyl isomer. The rate constant for the second linear portion of the kinetic plot is roughly $4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, however, the signal-to-noise ratio for the reactant ion signal is quite small at these longer reaction times, introducing additional uncertainty. This dichotomy of rate constants for the *n*-propyl isomer can be explained by invoking processes represented in Scheme VI where ethene coordination results in formation of the hypervalent complex, 17, that decomposes by three pathways: 1) elimination of propene, 2) elimination of ethene yielding an *n*-propyl complex, or 3) elimination of ethene yielding an *i*-propyl complex. As in Scheme V the decomposition of hypervalent 17 forming products is much faster than its formation accounting for the absence of isotopic scrambling. The difference in rate constants for reaction of the *n*-propyl isomer over the *i*-propyl isomer suggests that it is more difficult to form intermediate 17 from the *i*-propyl species than from the corresponding *n*-propyl species. This result, however, cannot be attributed to increased steric crowding in the *i*-propyl isomer because the corresponding ethyl species, $Si(CH_3)_2(C_2H_5)^+$, has a reaction efficiency similar to that of the *i*-propyl species (Table 2). Instead, this difference in rate constants may be due to more facile β -hydrogen migration from a secondary carbon than

Figure 7. Variation of ion abundances as a function of kinetic energy (laboratory frame) for dissociation of collisionally activated $\text{Si}(\text{CH}_3)_2(i\text{-C}_3\text{H}_7)^+$. $\bullet = \text{Si}(\text{CH}_3)_2(i\text{-C}_3\text{H}_7)^+$; $\diamond = \text{SiC}_3\text{H}_7^+$; $\blacklozenge = \text{SiC}_2\text{H}_7^+$; $\triangle = \text{SiCH}_3^+$; $\blacksquare = \text{SiCH}_3^+$; $\circ = \text{Si}^+$.

Figure 9. Variation of ion abundances as a function of kinetic energy (laboratory frame) for dissociation of collisionally activated $\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)_2^+$. $\bullet = \text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)_2^+$; $\diamond = \text{SiC}_3\text{H}_5^+$; $\triangle = \text{SiCH}_3^+$.

Figure 8. Variation of ion abundances as a function of kinetic energy (laboratory frame) for dissociation of collisionally activated $\text{Si}(\text{CH}_3)_2(n\text{-C}_3\text{H}_7)^+$. $\bullet = \text{Si}(\text{CH}_3)_2(n\text{-C}_3\text{H}_7)^+$; $\diamond = \text{SiC}_3\text{H}_7^+$; $\blacklozenge = \text{SiC}_2\text{H}_7^+$; $\triangle = \text{SiCH}_3^+$; $\blacksquare = \text{SiCH}_3^+$; $\circ = \text{Si}^+$.

Figure 10. Variation of ion abundances as a function of kinetic energy (laboratory frame) for dissociation of collisionally activated $\text{Si}(\text{CH}_3)_3(\pi\text{-C}_2\text{H}_4)^+$. $\bullet = \text{Si}(\text{CH}_3)_3(\pi\text{-C}_2\text{H}_4)^+$; $\diamond = \text{SiC}_3\text{H}_5^+$; $\triangle = \text{SiCH}_3^+$; $\blacksquare = \text{SiCH}_3^+$.

Figure 11. Temporal variation of the fractional amount of $\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)^+$ for reaction of the *n*-propyl isomer with 1.6×10^{-6} torr ethene, process 48.

a primary carbon. Hence, the *n*-propyl isomer initially reacts rapidly by process 49; however, a fraction of the *n*-propyl species is isomerized to the corresponding *i*-propyl species, which reacts more slowly.

Diethylmethylsilylenium reacts slowly with ethene— D_4 and ethene— $^{13}\text{C}_2$ exclusively by sequential displacement of unlabeled ethene, process 50, which

is analogous to that for $\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)^+$. This sequential displacement clearly distinguishes $\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)_2^+$ from the other $\text{SiC}_5\text{H}_{13}$ isomers.

The above specific reactions once again unequivocally distinguish the four distinct $\text{SiC}_5\text{H}_{13}^+$ isomers.

Conclusions

Specific ion/molecule reactions are demonstrated that structurally distinguish isomeric alkylsilylenium ions. These reactions involve either methanol or ethene (isotopically labeled). As a consequence of facile rearrangements, CAD, in many cases, is *not* structurally diagnostic. The insertion of an olefin into an Si—H bond of a silylenium ion, process 29, is a facile process implying a low barrier [31].

The ability to distinguish isomeric organosilyle-

nium ions will undoubtedly aid in understanding the complex chemistry of ionic organosilicon species. Structures more complex than those discussed here should also be distinguishable by these methods. In short, the ability to determine unambiguously organosilylenium ion structures in the gas phase will greatly assist the general area of ionic organosilane chemistry.

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References

- Oppenstein, A.; Lampe, F. W. In *Review of Chemical Intermediates*; Strausz, O. P., Ed.; Elsevier: Amsterdam, 1986; Vol 6, p 275.
- Schwarz, H. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rapport, Z., Eds.; Wiley: New York, 1989; p 445.
- DePuy, C. H.; Damrauer, R.; Bowie, J. H.; Seldon, J. C. *Acc. Chem. Res.* **1987**, *20*, 127.
- Bowie, J. H. *Mass Spectrom. Rev.* **1984**, *3*, 1.
- Groenewold, G. S.; Gross, M. L. *J. Organomet. Chem.* **1982**, *235*, 165.
- Apeloig, Y.; Karni, M.; Stanger, A.; Schwarz, H.; Drewello, T.; Czekay, G. *J. Chem. Soc., Chem. Commun.* **1987**, 989.
- Drewello, T.; Burgers, P. C.; Zummack, W.; Apeloig, Y.; Schwarz, H. *Organometallics* **1990**, *9*, 1161.
- Reuter, K. A.; Jacobson, D. B. *Organometallics* **1989**, *8*, 1126.
- (a) Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry*; VCH: New York, 1988. (b) McLafferty, F. W. *Tandem Mass Spectrometry*; Wiley: New York, 1983. (c) Cooks, R. G. *Collision Spectroscopy*; Plenum: New York, 1978.
- Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.
- Kascheres, C.; Cooks, R. G. *Anal. Chim. Acta* **1988**, *215*, 223.
- Blair, I. A.; Philipou, G.; Bowie, J. H. *Aust. J. Chem.* **1979**, *32*, 59.
- (a) Trenerry, V. C.; Bowie, J. H.; Blair, I. A. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1640. (b) Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Nouv. J. Chim.* **1981**, *5*, 193.
- Blair, I. A.; Trenerry, V. C.; Bowie, J. H. *Org. Mass Spectrom.* **1980**, *15*, 15.
- (a) Gross, M. L.; Rempel, D. L. *Science* **1984**, *226*, 26. (b) Wanczek, K. P. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *60*, 11. (c) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316. (d) Comisarow, M. B. *Anal. Chim. Acta* **1985**, *178*, 1.
- Fourier Transform Mass Spectrometry*; Buchanan, M. B., Ed.; American Chemical Society: Washington, DC, 1987.
- Jacobson, D. B. *J. Am. Chem. Soc.* **1989**, *111*, 1626.
- Bartmess, J. E.; Georadiadis, R. M. *Vacuum* **1983**, *33*, 149.
- Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.
- Cooks, R. G. *Collision Spectroscopy*; Plenum: New York, 1978.
- (a) Cody, R. B.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *41*, 199. (b) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96. (c) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 7436.
- McIver, R. T., Jr.; Bowers, W. D. In *Tandem Mass Spectrometry*; McLafferty, F. W., Ed.; Wiley: New York, 1983; p 287.
- Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*,

Scheme VI

- 736, 7484.
24. Comisarow, M. B. *J. Chem. Phys.* **1971**, *55*, 187.
25. Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers M. T., Ed.; Academic: New York, 1979; Vol 1, Chap 3.
26. Cody, R. B.; Burnier, R. C.; Cassady, C. J.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 2225.
27. (a) Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 900. (b) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data. Suppl.* **1988**, *17*.
28. Woodin, R. L.; Beauchamp, J. L. *Chem. Phys.* **1979**, *41*, 1.
29. Dunbar, R. C. *Int. J. Mass Spectrom. Ion. Phys.* **1983**, *54*, 109.
30. Hajdasz, D.; Squires, R. R. *J. Chem. Soc., Chem. Commun.* **1988**, 1212.
31. (a) Grabowski, J. J.; DePuy, C. H.; Van Doren, J. M.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1985**, *107*, 7384 and references therein. (b) Moylan, C. R.; Brauman, J. I. *Annu. Rev. Phys. Chem.* **1983**, *34*, 187. (c) Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 2906. (d) Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 3641. (e) Hunter, E. P.; Lias, S. G. *J. Phys. Chem.* **1982**, *86*, 2769. (f) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.
32. (a) Ibrahim, M. R.; Jorgenson, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819. (b) Wierschke, S. G.; Chandrasekhar, J.; Jorgenson, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1497.
33. Cook, M. A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *24*, 301.
34. Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.
35. Li, X.; Stone, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 5586.
36. Abernathy, R. N.; Lampe, F. W. *J. Am. Chem. Soc.* **1981**, *103*, 2573.
37. Barton, T. J.; Tillman, N. *J. Am. Chem. Soc.* **1987**, *109*, 6711.
38. (a) Rogers, D. S.; Walker, K. L.; Ring, M. A.; O'Neal, H. E. *Organometallics* **1987**, *6*, 2313. (b) Dickinson, A. P.; Nares, K. E.; Ring, M. A.; O'Neal, H. E. *Organometallics* **1987**, *6*, 2596.
39. Welsh, K. M.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1988**, *110*, 6689.
40. Gaspar, P. P. In *Reactive Intermediates*; Jones, M. J.; Moss, R. A., Eds.; Wiley: New York, 1978; Vol 3, p 333.
41. Corriu, R., In *Silicon Chemistry*; Corey, J. Y.; Corey, E. P.; Gaspar, P. P., Ed.; Wiley: New York, 1987; Chap. 22.
42. Collman, J. P.; Hegedus, L. S., *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; p 292.