Metastable and Collision-Induced Fragmentation Studies of All $C_4H_{12}Si^+$ Isomers; A Systematic Study of Structure-Reactivity Relations

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Metastable ion (MI) and collision-induced dissociation (CID) mass spectra have been recorded and compared for all nine $C_4H_{12}Si^+$ isomers. The $(Me)_4Si^+$, $t-BuSiH_3^+$, $s-BuSiH_3^+$, and $(Me)_2EtSiH^+$ isomers have unique MI and CID mass spectra. The MI mass spectra, including the kinetic energy release values, of $(Me)(i-Pr)SiH_2^+$ and $(Me)(n-Pr)SiH_2^+$ are identical, which implies isomerization. MI data also suggest that a fraction of the $Et_2SiH_2^+$ ions rearrange into branched $(Me)_2EtSiH^+$ ions and a fraction of the $n-BuSiH_3^+$ ions rearrange into branched $s-BuSiH_3^+$ ions. A comparison with the isomeric C_5H_{12} pentanes reveals a crucial difference: H_2 loss occurs for $n-BuSiH_3^+$, $i-BuSiH_3^+$, $s-BuSiH_3^+$, $(Me)(n-Pr)SiH_2^+$, $(Me)(i-Pr)SiH_2^+$, and $Et_2SiH_2^+$, but not for any of the C_5H_{12} isomers. Generation of four- or five-membered silicon containing rings is suggested for H_2 loss from the $C_4H_{12}Si^+$ silanes. (*J Am Soc Mass Spectrom* 1994, 5, 537-543)

Silanes and their organo-derivatives are of interest as precursors in chemical vapor deposition (CVD) processes used to prepare epitaxial films. Choice of precursor would be made more effective if it proved possible to relate precursor composition and structure to the mechanisms of thermal decomposition in the CVD process. This work is part of a larger effort in which the pyrolysis and film behavior of a complete set of organosilane isomers are being examined in an effort to understand the influence of precursor structure on CVD behavior. Initial results indicate a correspondence between the type of fragments produced by thermal decomposition and those generated by electron impact in a mass spectrometer for some silanes [1]. If the correlations between mass spectral data and pyrolysis behavior for these compounds are general, and can be subsequently related to particular features of epitaxial films, it should then prove possible to predict the CVD characteristics of a precursor from an examination of its mass spectra.

Over the past two decades mass spectrometry has distinguished itself as an extremely powerful technique for distinguishing isomeric ions. Two complementary approaches are available to determine the structure of ions: (1) ion/molecule reactions [2] and (2) metastable and collision-induced dissociation (CID) [3]. The latter approach was used to examine the gas phase

behavior of $Si(CH_3)_3^+$ ions [4]. Surprisingly, the dominant metastable process is loss of C_2H_4 , which must involve a complex rearrangement. In general, even-electron organosilicon cations commonly undergo complex rearrangement processes [4, 5]. Specific ion/molecule reactions can be used to distinguish isomers as well. For example, ion cyclotron resonance experiments showed that the reactions of the isomers $Si(CH_3)_3^+$ and $SiH(CH_3)(C_2H_5)^+$ with methanol give rise to different product ions [6]. However, the reactions of the isomers $Si(CH_3)_2(n-C_3H_7)^+$ and $Si(CH_3)_2(i-C_3H_7)^+$ with methanol produced product ions of the same mass and they could be distinguished only on the basis of their relative abundances. That collisional activation can also induce rearrangements has been shown in the case of isomerization of $Si(C_2H_5)H_2^+$ to the thermodynamically more stable isomer $Si(CH_3)_2H^+$ [7]. The ion structures were probed by ion/molecule reactions with ethene- D_4 , which showed that while $Si(C_2H_5)H_2^+$ undergoes multiple H/D exchanges, $Si(CH_3)_2H^+$ tends to undergo a single H/D exchange.

Odd-electron alkylsilane cations have received much less attention and most studies have focused on ionization and appearance energy measurements for tetramethyl- and trimethylsilane [8-10]. These measurements allowed the determination of heats of formation of methylsilanes and other alkylsilanes. (Heats of formation of organosilicon compounds determined via static oxygen-bomb calorimetry are frequently inaccurate because of incomplete combustion and all pre-1970

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values have been rejected [11].) We report here metastable and collision-induced fragmentation studies of all nine $C_4H_{12}Si^+$ isomers. Isomerization between the various structures will be considered in detail.

Experimental

All experiments were performed using a VG Analytical ZAB-2F double focusing mass spectrometer of reversed geometry. The (volatile) samples were introduced via the septum inlet. A 100 μA beam of 70 eV electrons was used for ionization. The source temperature was 150 °C and the accelerating voltage 8 kV. Metastable ion (MI) and CID mass spectra were recorded using reported procedures [12]. The CID mass spectra were obtained using He as the target gas and the gas pressure was adjusted to give a main ion beam transmission of 80%. All MI and CID mass spectra were corrected for isotopic interference from ions of lower mass. (Natural abundances of ^{13}C , ^{29}Si , and ^{30}Si are 1.11%, 4.71%, and 3.12%, respectively.) In these experiments all slits were fully open to obtain maximum signal strength and to minimize energy resolving effects. Metastable peak shapes, however, were recorded with a main beam width of < 2 V at an accelerating voltage of 8000 V. Kinetic energy releases (based on the width at half height, $T_{0.5}$) were evaluated by established methods [13]. None of the MI peaks appeared to be composite.

All synthetic manipulations were performed in an atmosphere of dry nitrogen or argon. Solvents were dried over CaH_2 . Silanes were distilled at least twice through a 13×300 mm glass helices-packed column (8–10 theoretical plates). Fractions with a boiling point

range of less than 0.5 °C were retained for further study. The purity was verified by means of both 500 MHz ^1H NMR and high resolution mass spectrometry. Only resonances attributable to the species in question were observed. The exact mass measurements were correct for all the silanes and there were no detectable impurities.

Diethylsilane (Fluka) and dimethylethylsilane (Aldrich) were distilled twice before use. Tetramethylsilane was laboratory stock. Purchased chlorosilanes were used as supplied. Tertiary-butytrichlorosilane (Aldrich), i-butytrichlorosilane (PCR), n-butytrichlorosilane (Hüls America), and methyl-n-propyltrichlorosilane (Hüls America) were reduced with $LiAlH_4$ in refluxing dioxane [14]. A mixture of commercial (Hüls America) and synthesized methyl-i-propyldichlorosilane was reduced to the hydride. The resulting hydrides were passed through a -78 °C trap on a high vacuum line and then distilled as described above.

Secondary-butytrichlorosilane was prepared by the slow drop-wise addition of an s-BuMgCl/ Et_2O solution to an excess (1:2.5) of $SiCl_4$ (Aldrich). The resulting solution was filtered and the magnesium salts were extracted with dry hexanes. The combined filtrate and extracts were distilled, first through a 21-cm Vigreux column and then through a column of glass helices. The resulting chloride (b.p. 140–144 °C, 32% yield based upon the Grignard) was then reduced and purified as described above.

Methyl-i-propyldichlorosilane was synthesized by the slow drop-wise addition of 0.7 moles of an i-PrMgCl solution in Et_2O to a sixteenfold molar excess of $MeSi(OEt)_3$ (Aldrich) at 95–120 °C [15]. The reaction mixture was filtered, added to a 30% excess of acetyl chloride (Aldrich), and stirred for two days at room temperature. The lower boiling materials were removed by distillation (Vigreux column) and the remaining solution fractionated through a column of glass helices, yielding 50.0 g (48% based upon the Grignard) of methyl-i-propyldichlorosilane (b.p. 119–122 °C). The chloride was then reduced and the resulting hydride purified, as described above.

The yields and boiling points of the nine $C_4H_{12}Si$ silane isomers are summarized in Table 1.

Table 1. The yields and boiling points of the nine $C_4H_{12}Si$ silane isomers

Silane	boiling point, °C	yield, % ^a
$(Me)_4Si$	27.0	^b
t-BuSiH ₃	28.8	51
s-BuSiH ₃	49.0	60
i-BuSiH ₃	47.0	71
n-BuSiH ₃	56.0	77
$(Me)(i-Pr)SiH_2$	43.8	75
$(Me)(n-Pr)SiH_2$	50.3	79
Et_2SiH_2	53.8	^b
$(Me)_2(Et)SiH$	42.8	^b

^a See Experimental section for synthetic details.

^b Commercially available.

Figure 1. The structure of all neutral $C_4H_{12}Si$ isomeric silanes.

Results

The MI mass spectra of all nine C₄H₁₂Si⁺ isomers and the kinetic energy release values for the most abundant metastable processes are presented in Table 2. The first conclusion to be drawn is that, except for methyl-*n*-propyl silane and methyl-*i*-propyl silane, all the MI mass spectra are different. In those cases where the same fragment ions are generated, their relative abundances and/or their kinetic energy releases are different.

For a particular precursor the relative abundances of ions in the MI mass spectrum is governed by the energy requirement and the frequency factor of the various metastable processes. In the absence of concrete information about frequency factors, the MI mass spectra of some of the C₄H₁₂Si⁺ isomers are rationalized on the basis of thermochemical information [16]. The salient features of each spectrum are discussed and compared with those of the corresponding pentane MI mass spectra. The CID data are presented in Table 3.

Tetramethylsilane

The MI mass spectrum of tetramethylsilane ions shows loss of a methyl radical. Appearance energy measurements confirm that this is indeed the energetically most favorable process [9, 10].

The absence of CH₄ loss suggests that the heat of formation of H₂C = Si(CH₃)₂⁺ ions is at least 851 kJ·mol⁻¹, provided that there is no significant barrier for the reverse reaction ($\Delta H_f(\text{CH}_4) = -75 \text{ kJ}\cdot\text{mol}^{-1}$).

t-Butylsilane

The MI mass spectrum shows that *t*-butylsilane molecular ions lose SiH₄ predominantly and H₃Si⁺ to a lesser degree, in line with appearance energy measurements [8]. The ionization energy of *t*-butyl silane was determined to be $9.5 \pm 0.2 \text{ eV}$ and appearance energy measurements gave $9.89 \pm 0.05 \text{ eV}$ for C₄H₈⁺ and $10.25 \pm 0.02 \text{ eV}$ for C₄H₉⁺. Thus, generation of C₄H₈⁺ is 0.36 eV more favorable than C₄H₉⁺. Note that our kinetic energy release measurements suggest that both fragmentation processes occur at their thermochemical threshold; $T_{0.5}(m/z \ 56) = 2.6 \text{ meV}$ and $T_{0.5}(m/z \ 57) = 2.3 \text{ meV}$. In contrast, thermochemical data from Ref. 16 suggest that generation of C₄H₉⁺ is more favorable.

A comparison of the above thermochemical data with the appearance energies and our MI data suggests that one or more of the heats of formation for the products

Table 2. Metastable ion mass spectra of all isomeric C₄H₁₂Si⁺ molecular ions^a

Isomer -H ₄ Si	Fragment ions, mass-to-charge ratio				
	86 M ⁺ -H ₂	73 M ⁺ -H ₃ C [•]	58 M ⁺ -C ₂ H ₆	57 M ⁺ -H ₃ Si [•]	56 M ⁺ -H ₄ Si
a (Me) ₄ Si ⁺		100 (3.9)			
b <i>t</i> -BuSiH ₃ ⁺				13 (2.3)	100 (2.6)
c <i>s</i> -BuSiH ₃ ⁺	2 b	2 (17)			100 (21)
d <i>i</i> -BuSiH ₃ ⁺	100 (59)	7 (15)			
e <i>n</i> -BuSiH ₃ ⁺	100 (170)	3 (22)			11 (26)
f (Me)(<i>i</i> -Pr)SiH ₂ ⁺	100 (54)	1 (13)			
g (Me)(<i>n</i> -Pr)SiH ₂ ⁺	100 (59)	1 (15)			
h Et ₂ SiH ₂ ⁺	100 (57)		16 (7.9)		
i (Me) ₂ (Et)SiH ⁺			100 (5.8)		

^a The relative intensities are normalized to the most intense signal in the MI mass spectrum = 100. The relative intensities reflect low resolution conditions and the data are corrected for isotopic contributions from ions of lower mass. The kinetic energy releases ($T_{0.5}$ values in meV) are presented in parentheses.

^b Not determined.

Table 3. Collision-induced dissociation mass spectra of all isomeric $C_4H_{12}Si^{++}$ molecular ions^a

Isomer	Fragment Ions, Mass-to-Charge Ratio													
	87	86	73	72	71	60	59	58	57	56	55	45	44	43
a (Me) ₄ Si ⁺⁺			1000	19			11	8				9	8	
b t-BuSiH ₃ ⁺⁺					12	19	50	15	1000	555		25	10	10
c s-BuSiH ₃ ⁺⁺		20	357				89	32	249	1000		43		19
d i-BuSiH ₃ ⁺⁺	3	664	1000	11		8	21	17	7					26
e n-BuSiH ₃ ⁺⁺	49	1000	39			30	266	84	14	122	10	6	5	
f (Me)(i-Pr)SiH ₂ ⁺⁺	45	1000	61	10	4	4	18	13				12	12	7
g (Me)(n-Pr)SiH ₂ ⁺⁺	57	1000	89	13	9	12	27	23				32	28	14
h Et ₂ SiH ₂ ⁺⁺	91	891				11	237	1000	36	18	19			23
i (Me) ₂ (Et)SiH ⁺⁺	160		39	35		8	253	1000				26	11	20

^a The relative intensities are normalized to the most intense signal in the MI mass spectrum = 1000. The relative intensities reflect low resolution conditions and the data are corrected for isotopic contributions from ions of lower mass.

presented in Ref. 16 may be in error. (Indeed, recent proton affinity measurements [17] have revised the heat of formation of $(H_3C)_3C^+$ ions from 694 [16] to 711 kJ.mol⁻¹.) Interestingly, t-butylsilane molecular ions do not lose methane or a methyl radical on the time-scale of MI experiments. Unfortunately, no thermochemical data are available to explain the absence of the latter processes.

In the CID mass spectrum loss of H_3Si^+ (m/z 57), a simple cleavage reaction, is more prevalent than loss of SiH_4 (m/z 56), a rearrangement reaction.

s-Butylsilane

Generation of $C_4H_8^+$ ions is also the most abundant metastable process for s-butylsilane molecular ions. However, these $C_4H_8^+$ ions most likely have the 2-butene structure.

The absence of H_3Si^+ loss in the MI mass spectrum is in line with thermochemical data and excludes the possibility of isomerization of s-butylsilane cations into t-butylsilane cations. Table 2 shows that the kinetic energy release for loss of H_4Si is significantly larger for s-butylsilane ions than for t-butylsilane ions.

The CID mass spectrum has characteristic signals at m/z 73 (loss of H_3C^+), m/z 59 (loss of $C_2H_5^+$), and m/z 57 (loss of H_3Si^+); all of which correspond to secondary cations generated via simple bond cleavage reactions.

i-Butylsilane, n-Butylsilane, Methyl-i-Propylsilane, Methyl-n-Propylsilane, and Diethylsilane

Since H_2 loss is by far the most prominent metastable process for i-butylsilane, n-butylsilane, methyl-i-propyl

silane, methyl-n-propylsilane, and diethylsilane molecular ions, it is reasonable to assume that the corresponding fragmentation routes are the least energy-demanding for these isomers. The kinetic energy release values (> 50 meV for all five isomers) indicate that H_2 loss does not occur at its thermochemical threshold. The MI mass spectra of methyl-i-propylsilane and methyl-n-propylsilane are identical within experimental error and, therefore, isomerization between those two $C_4H_{12}Si^{++}$ isomers is likely (see below). The CID mass spectra of these two isomers are also quite close; the same signals are present in both spectra although the relative abundances vary slightly.

In the CID mass spectrum of i-butylsilane molecular ions the most intense signal is at m/z 73, in contrast to the MI mass spectrum. The m/z 73 ions are most likely the secondary $H_3C-C^+H-CH_2-SiH_3$ cations, generated via loss of H_3C^+ .

Diethylsilane is the only $C_4H_{12}Si^{++}$ isomer that has been previously examined in detail [9b]. The diethylsilane ionization energy has been reported as 9.8 eV with H_2 loss from the molecular ions requiring an additional 0.2 eV. The structure of the $C_4H_{10}Si^{++}$ product ions will be discussed below.

Dimethylethylsilane

The MI mass spectrum of dimethylethylsilane molecular ions is unique because it is dominated by m/z 58, that is, C_2H_6 loss. The relatively small kinetic energy release for this process, 21 meV, suggests that it may well occur relatively close to its thermochemical threshold.

[†] The appearance potential for generation of $H_3C-SiH=CH_2^+$ and H_2 from $(CH_3)_2SiH_2$ ($\Delta H_f = -95$ kJ.mol⁻¹) is 10.7 eV and the appearance potential for generation of $H_3C-SiH=CH_2^+$ and CH_4 ($\Delta H_f = -75$ kJ.mol⁻¹) from $(CH_3)_3SiH$ ($\Delta H_f = -163$ kJ.mol⁻¹) is 10.7 eV [9b]. Using these data the heat of formation of $H_3C-SiH=CH_2^+$ should be ≤ 937 kJ.mol⁻¹ and ≤ 925 kJ.mol⁻¹, respectively, i.e., ≤ 930 kJ.mol⁻¹.

The CID mass spectrum of dimethylethylsilane ions contains an m/z 58 signal and a relatively intense m/z 59 signal, due to loss of C_2H_5 .

To summarize, the MI mass spectra show that the straight chain silanes (n-butylsilane, methyl-n-propylsilane and diethylsilane) have a high tendency to lose H_2 . In contrast the branched silanes lose either H_3C^+ (tetramethylsilane), SiH_4 (t-butylsilane and s-butylsilane), or C_2H_6 (dimethylethylsilane). Interestingly, the H_2 loss behavior of i-butylsilane and methyl-i-propylsilane mimics that of the straight chain silanes.

Discussion

Isomerization

Detailed MI studies using isotopically labeled compounds indicate that n-pentane molecular ions isomerize (via 1,2-ethyl and/or 1,2-methyl shifts) into methylbutane molecular ions prior to metastable decomposition [18] because isomerization of linear to branched alkanes is energetically favorable [16]. However, there is no evidence for communication of n-pentane and methylbutane ions with dimethylpropane ions.

Similarly, the identical MI mass spectra suggest that methyl-n-propylsilane cations isomerize into the branched and therefore more stable methyl-i-propylsilane cations. Isomerization could take place via a 1,2-methyl shift or a 1,2- H_3C-SiH_2 shift. The identical kinetic energy release values for H_2 and H_3C^+ loss imply that the isomerization barrier is below the thresholds for H_2 and H_3C^+ loss.

Because the kinetic energy release values and the relative abundances of m/z 86 and 73 in the MI mass spectrum of i-butylsilane molecular ions are close to those in the MI mass spectra of ionized methyl-n-propylsilane and methyl-i-propylsilane, it is conceivable that i-butylsilane ions communicate with the methyl-propylsilane ions.

The MI spectrum of diethylsilane ions shows loss of C_2H_6 and H_2 . The former process is characteristic for dimethylethylsilane. To explain this, we propose that a small fraction of the diethylsilane cations rearrange into the more branched dimethylethylsilane cation via a 1,2-methyl shift. Because the kinetic energy release values for C_2H_6 loss from these compounds are virtually identical, 7.9 and 5.8 meV, the isomerization process is not rate determining or, if it is, the transition state is close to the threshold for C_2H_6 loss. However, the rearrangement reaction must be more energy demanding than H_2 loss, the major metastable process for the diethylsilane molecular ions. The CID mass spectra of diethylsilane and dimethylethylsilane ions are distinctly different.

The metastable loss of SiH_4 from n-butylsilane molecular ions suggests that isomerization into s-butylsilane molecular ions is possible. The latter pro-

cess would involve a 1,2-methyl and/or a 1,2-silyl shift. Since the kinetic energy release values for SiH_4 loss from n-butylsilane and s-butylsilane ions are close, 26 versus 21 meV, the isomerization reaction is probably not rate determining. The loss of a methyl radical is unexpected for straight chain n-butylsilane molecular ions and could indicate isomerization into s-butylsilane or i-butylsilane cations. Loss of a methyl radical from the latter isomers would yield energetically favorable secondary cations. Isotopic labeling will be required to delineate these isomerization processes in detail.

Comparison with Pentane Molecular Ions

The isomerization of straight chain silanes into branched silanes parallels the behavior observed for saturated hydrocarbons such as butanes and pentanes. The fundamental difference between the $C_4H_{12}Si^+$ silanes and the ionized butanes and pentanes is the abundance of metastable H_2 loss. For n-butane and methylpropane molecular ions Wolkoff et al. [19] stated that "Although elimination of H_2 is the process with the lowest energy requirement, there is no evidence that such a reaction takes place." A similar situation exists for n-pentane and methylbutane molecular ions [16, 20]. In contrast, six of the $C_4H_{12}Si^+$ silanes display loss of H_2 in their MI mass spectra and for five isomers it is the most abundant process. Clearly, the presence of silicon guides the metastable ion chemistry in this respect. This difference in behavior can ultimately be traced back to characteristic differences between the two elements themselves. Silicon's greater size (Van der Waal's radii: 117 pm for Si and 72 pm for C) and larger, more diffuse bonding orbitals, compared to carbon, lead to longer, more easily "bent" bonds, which can more readily accommodate the smaller bond angles found in cyclic structures. Thus, the presence of silicon attenuates the three major sources of strain energy in small rings: angle deformation, torsional strain, and transannular interactions [21]. As a result, silicon is more amenable to participation in small cyclic structures than carbon and generation of cyclic structures upon metastable H_2 loss should be more likely for the $C_4H_{12}Si^+$ silanes than for the $C_5H_{12}^+$ pentanes. A comparison of thermochemical data serves to illustrate this point. Information for the species of interest, $C_4H_{10}Si^+$, is not available, but thermochemical data for the higher homologue, $C_5H_{12}Si^+$, are available [16]. The unsaturated $H_2C=CHSi(CH_3)_3^+$ ions have a heat of formation of 794 $\text{kJ}\cdot\text{mol}^{-1}$, whereas the value for the cyclic isomer, 1,1-dimethyl-1-silacyclobutane $^+$, is 25 $\text{kJ}\cdot\text{mol}^{-1}$ lower, that is, 769 $\text{kJ}\cdot\text{mol}^{-1}$. For all-carbon species the situation is reversed; ring isomers have much larger heats of formation than acyclic olefinic isomers (e.g., $\Delta H_f(2\text{-pentene}^+) = 840 \text{ kJ}\cdot\text{mol}^{-1}$ versus $\Delta H_f(\text{cyclopentane}^+) = 936 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta H_f(2\text{-methyl-2-butene}^+) = 795$

$\text{kJ}\cdot\text{mol}^{-1}$ versus $\Delta H_f(\text{methylcyclobutane}^+) = 907 \text{ kJ}\cdot\text{mol}^{-1}$).

Thermochemical data suggest that generation of olefins via H_2 loss from n-pentane and methylbutane should be competitive with the observed metastable processes, but because it does not occur, loss of H_2 giving rise to olefins must have a high activation energy barrier. As suggested above, H_2 loss accompanied by generation of cyclic compounds (cyclopentane⁺ and methylcyclobutane⁺, respectively) is rather energetically unfavorable. The situation is markedly different for silicon containing compounds. Based on the above argument we suggest that H_2 loss from the $\text{C}_4\text{H}_{12}\text{Si}^+$ molecular ions might lead to silicon containing ring ions. H_2 loss accompanied by generation of an acyclic species containing a $\text{C}=\text{C}$ bond is energetically unfavorable and is probably accompanied by a large activation energy barrier (by analogy with saturated hydrocarbon ions). Acyclic species containing a $\text{Si}=\text{C}$ bond are unlikely, because they are known to be 65–120 $\text{kJ}\cdot\text{mol}^{-1}$ less stable than the corresponding $\text{C}=\text{C}$ analogues [22]. Indeed, most of the silane isomers capable of forming four or five-membered silicon containing rings (c, d, e, f, g, and h; see Figure 1) exhibit H_2 loss. (The only exception is the dimethylethylsilane molecular ion, i, which loses C_2H_6 metastably.) Those species incapable of forming such a structure (a and b) decompose via other mechanisms.

In an attempt to confirm the structure of the $\text{C}_4\text{H}_{10}\text{Si}^+$ ions, the MI mass spectra of the $\text{C}_4\text{H}_{10}\text{Si}^+$ ions from c, d, e, f, g and h were recorded; all spectra are dominated by m/z 58, that is, C_2H_4 loss. Cyclic species such as silacyclobutane and 1,1-dimethyl-1-silacyclobutane are known to lose C_2H_4 abundantly upon electron impact ionization [23]. Thermal decomposition of 1-methyl-1-silacyclobutane (a cyclic $\text{C}_4\text{H}_{10}\text{Si}$ isomer) and 1,1-dimethyl-1-silacyclobutane also results in C_2H_4 elimination [23b, 24]. However, there is no unambiguous evidence available to support a cyclic or an acyclic structure for the $\text{C}_4\text{H}_{10}\text{Si}^+$ ions.

The stated goal of relating the structures of organosilane CVD precursors to their pyrolysis and (ultimately) epitaxial film characteristics requires specific structure-reactivity relationships. As an initial step, analysis of the MI data from this work leads to the correlation of a particular fragmentation process with a specific structural feature of the silane isomer: the elimination of H_2 is favored in those compounds capable of forming a four- or five-membered silicon containing ring. Work in progress comparing the MI mass spectra of the $\text{C}_4\text{H}_{10}\text{Si}^+$ ions generated by H_2 loss with those produced by electron impact ionization of the neutral cyclic $\text{C}_4\text{H}_{10}\text{Si}$ species will provide further information on the actual structures resulting from H_2 elimination from $\text{C}_4\text{H}_{12}\text{Si}^+$ ions. The next stage will be to identify further similarities between mass spectral and pyrolysis behavior. As noted, the same decomposition pathway dominates both the pyrolytic and metastable reactions of t-butylsilane [1]. Whether a

correlation between cyclization and H_2 elimination is demonstrated pyrolytically for the silanes remains to be seen. Silicon containing organic rings are frequent products of intermediates in pyrolysis reactions of organosilanes. At high temperatures and pressures (600–700 °C, 760 Torr), continuous flow pyrolysis of methylsilanes ($\text{Me}_{4-n}\text{Si}_n$, $n = 0-3$), for example, produces a variety of cyclic carbosilanes [25]. The large number of complex consecutive reactions taking place under these conditions have not been detailed or even listed, however, and more work of a systematic nature is needed.

Acknowledgments

The authors are grateful to the AMOCO Corporation for donating their VG Analytical ZAB-2F to our facility and the National Science Foundation for major departmental instrumentation grants and a Materials Research grant. The authors also thank David F. Snyder for experimental assistance and the Chemistry Department of the University of Wisconsin-Madison for financial support.

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