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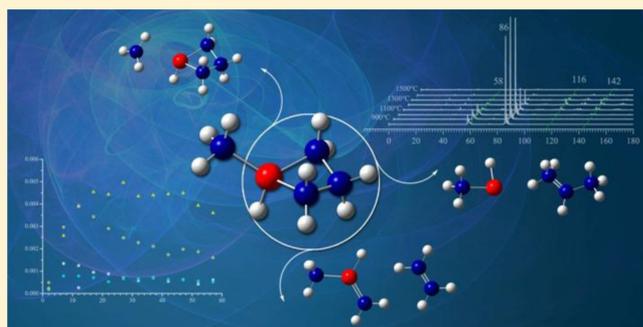
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Competition of Silene/Silylene Chemistry with Free Radical Chain Reactions Using 1-Methylsilacyclobutane in the Hot-Wire Chemical Vapor Deposition Process

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ABSTRACT: The gas-phase reaction chemistry of using 1-methylsilacyclobutane (MSCB) in the hot-wire chemical vapor deposition (CVD) process has been investigated by studying the decomposition of MSCB on a heated tungsten filament and subsequent gas-phase reactions in a reactor. Three pathways exist to decompose MSCB on the filament to form ethene/methylsilene, propene/methylsilylene, and methyl radicals. The activation energies for forming propene and methyl radical, respectively, are determined to be 68.7 ± 1.3 and 46.7 ± 2.5 $\text{kJ}\cdot\text{mol}^{-1}$, which demonstrates the catalytic nature of the decomposition. The secondary gas-phase reactions in the hot-wire CVD reactor are characterized by the competition between a free radical chain reaction and the cycloaddition of silene reactive species produced either from the primary decomposition of MSCB on the filament or the isomerization of silylene species. At lower filament temperatures of 1000–1100 °C and short reaction time ($t \leq 15$ min), the free radical chain reaction is equally important as the silene chemistry. With increasing filament temperature and reaction time, silene chemistry predominates.



INTRODUCTION

The four-membered-ring silacyclobutane (SCB) molecule and its methyl-substituted derivatives have recently attracted a lot of research interest due to their wide range of applications in chemistry¹ and material science.² The high ring strain energy leading to reduced decomposition temperatures and the ability of these molecules to produce highly reactive silene ($\text{R}_1\text{R}_2\text{Si}=\text{CH}_2$, R can be either H or alkyl group) and silylene ($:\text{SiR}_3\text{R}_4$) species upon decomposition have made them excellent choices as single-source precursors for the formation of silicon carbide thin films using chemical vapor deposition (CVD) techniques.^{3–8} In the late 1980s, a relatively new CVD technique known as hot-wire CVD⁹ or catalytic CVD¹⁰ was developed. It has since attracted much attention because high-quality thin films can be obtained at low substrate temperatures (200–450 °C), low equipment cost, high deposition rate, and high gas-utilization efficiency.¹¹ Zaharias et al. reported the use of 1,1-dimethylsilacyclobutane (DMSCB) as a source gas to form the amorphous SiC films by hot-wire CVD at a tungsten filament temperature of 1550 °C on a Si(100) substrate maintained at 250 °C.¹²

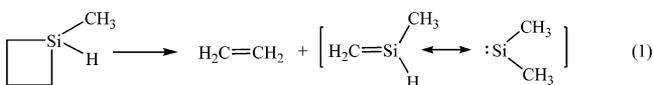
The hot-wire CVD process involves the decomposition of source gases to form radicals on the heated metal filament (typically made of tungsten or tantalum), followed by the secondary radical–radical/radical–molecule reactions in the gas phase to produce the film growth precursors that react with the substrate for ultimate film formation. Although the film formation processes in hot-wire CVD have been extensively studied, much less is known about the nature of the source gas decomposition on the filament and subsequent gas-phase reactions.

Recently, our lab has studied the gas-phase reaction chemistry of two types of organosilicon compounds, that is, open-chain alkylsilanes^{13–15} and cyclic mono/disilacyclobutanes,^{16–19} when they are used as source gases in hot-wire CVD. Examination of the parent SCB molecule has shown that competitive pathways exist for the hot-filament decomposition to produce ethene/silene and propene/silylene. It was demonstrated that the formation of ethene was favored over that of propene.¹⁶ Decomposition of DMSCB on a hot W filament was also found to favor the production of ethene and dimethylsilene.¹⁸ Furthermore, the dominance of ethene formation over propene increases significantly when using DMSCB, in which both Si–H bonds are replaced by Si–CH₃ connections. Aside from the two decomposition pathways mentioned above, the breakage of Si–CH₃ bonds in DMSCB produced a methyl radical, which initiated a short-chain reaction in the gas phase.

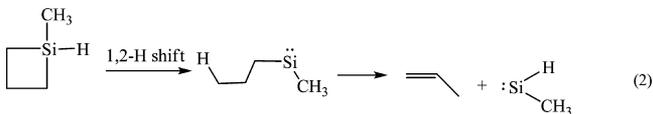
The structure of 1-methylsilacyclobutane (MSCB) is unique in that it contains both Si–H and Si–CH₃ bonds. The mechanism and kinetics of pyrolysis of MSCB have been reported in the literature.^{20–25} Conlin et al. have shown that low-pressure pyrolysis of MSCB produces methylsilene with the co-product of ethene.^{20–22} They also provided compelling evidence that methylsilene isomerizes rapidly to dimethylsilylene, as illustrated in eq 1.

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Barton et al.^{23,24} investigated the formation mechanism of propene and methylsilylene and determined that the decomposition was initiated by a 1,2-H shift from Si to the ring C atom.



The above two decomposition pathways were also observed in the photolysis of MSCB.^{26–28} Although the primary decomposition pathways of MSCB have been well studied, much less can be found about the secondary reactions in the gas phase. These reactions are important to understand the CVD chemistry because, in practice, the deposition of SiC films by CVD with single-source organosilicon molecules typically occurs at a pressure ranging from tens of milliTorr to several Torr.^{2–7} At these pressures in a typical CVD reactor, the collision-free conditions are no longer valid, and the secondary gas-phase reactions between the primary reactive species themselves and between the radicals and the parent molecules dominate. This work aims to study both the decomposition chemistry of MSCB on a hot W filament and the gas-phase reactions under the practical deposition pressures in a hot-wire CVD reactor. To determine the decomposition pathways of MSCB on a hot filament, the chemical species formed directly from the process under collision-free conditions were probed using nonresonant single-photon ionization (SPI) with a vacuum ultraviolet (VUV) wavelength at 118 nm coupled with time-of-flight mass spectrometry (TOF). This technique is generally considered to be a “soft” ionization method with an enhanced molecular ion intensity and minimized fragmentation.^{29–31} Its ability to provide less convoluted mass spectra proves to be advantageous in diagnosis of complex reaction systems such as those characteristic of pyrolysis^{32,33} and CVD^{16,34} processes. The secondary gas-phase reaction products from a hot-wire CVD reactor held at a relatively high pressures of 0.12–0.48 Torr of MSCB were examined using the same diagnostic tool. Experiments on the decomposition of the deuterated isotopologue, 1-methyl-1-deuterio-silacyclobutane (MSCB-*d*₁), were also performed to provide insights into the mechanistic details in the reaction chemistry, which is characterized by both free radical chemistry and the reactions involving silene/silylene reactive species.

EXPERIMENTAL DETAILS

The experimental setup of the hot-wire CVD sources and the laser ionization (VUV SPI) TOF mass spectrometer used to study the gas-phase hot-wire CVD reaction chemistry has been described in detail elsewhere.^{13,16} In order to detect the primary decomposition products of MSCB from the hot W filament, a collision-free CVD source was used. Here, a resistively heated W filament (99.9+%, Aldrich; 10 cm length, 0.5 mm diameter) was placed directly in the main ionization chamber housing the TOF mass spectrometer. The filament temperature was measured by a two-color pyrometer (Chino Works). The sample gas was introduced using a mass flow controller (MFC) (MKS, type 1179A), and the pressure in the main chamber was maintained at $\sim 5 \times 10^{-6}$ Torr to ensure collision-free conditions. The base pressure was 3×10^{-7} to 5×10^{-7} Torr. A cylindrical hot-wire CVD reactor (volume, 7.1 L) was used to examine the products from the secondary gas-phase reactions. The total pressure of a

mixture of the source gas and helium in the reactor was maintained at 12 Torr using the MFC and was monitored by a capacitance manometer (MKS, Baratron, type 626A). The typical flow rate was 0.90 sccm. In the reactor setup, the collision-free conditions were voided, therefore allowing for the detection of secondary reaction products. The reactor was connected to the main ionization chamber through a pinhole (0.15 mm diameter).

The chemical species produced either from the collision-free CVD source or from the reactor was ionized by the 118 nm VUV laser radiation (10.5 eV), which was generated by frequency tripling of the 355 nm UV output from a Nd:YAG laser in a gas cell containing 210 Torr of a phase-matched 10:1 Ar/Xe gaseous mixture. A lithium fluoride (LiF) lens was used to focus the 118 nm VUV light at the center of the ion source, whereas the residual 355 nm UV beam was caused to diverge in the same region. Signals from the microchannel plate (MCP) detector were preamplified, averaged over 512 laser pulses, and saved in a computer for analysis.

MSCB and its deuterated isotopologue, MSCB-*d*₁, were synthesized by reducing 1-chloro-1-methylsilacyclobutane using LiAlH₄ (Alfa Aesar, 97%) and LiAlD₄ (CDN Isotopes, 98 atom % D), respectively.²⁴ 1-Chloro-1-methylsilacyclobutane was prepared from 3-chloropropylmethylchlorosilane (Gelest, 97%) following a procedure described by Denmark et al.³⁵ The structures and purity of MSCB (>98%) and MSCB-*d*₁ (98%) were checked by NMR and also in situ by our TOF mass spectrometer. The impurity was diethyl ether, the solvent used in the synthesis. The ¹H NMR analysis for the MSCB-*d*₁ sample showed no H attached to Si. The data obtained from our in situ analysis of the room-temperature mass spectra of MSCB-*d*₁ showed that the intensity ratio of the molecular ion peak of MSCB (*m/z* 86) to that of MSCB-*d*₁ (*m/z* 87) are $2.6 \pm 0.1\%$, indicating an isotope purity of 97% for our synthesized MSCB-*d*₁ sample. The gaseous mixture of MSCB (or MSCB-*d*₁) and He was prepared in a 2.25 L sample cylinder by entraining the room-temperature vapor from either of the two species in He (99.999%, Praxair) after degassing the respective liquid sample using several cycles of freeze–pump–thaw.

RESULTS AND DISCUSSIONS

The room-temperature VUV laser SPI mass spectrum of MSCB, shown in Figure 1, is dominated by the molecular ion

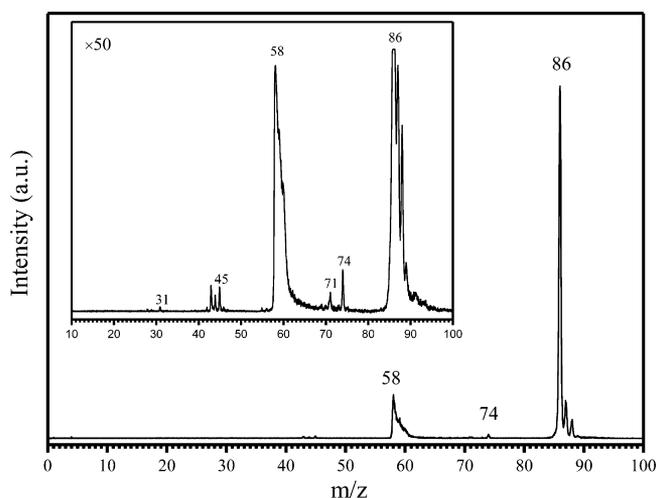


Figure 1. Room-temperature 10.5 eV SPI TOF mass spectra of MSCB. The inset is an enlarged picture in the region of 10–100 amu.

peak at m/z 86 along with a peak at m/z 58 from its photofragment ion, $[(\text{CH}_3)\text{HSi}=\text{CH}_2]^+$, whose intensity is $12.0 \pm 0.2\%$ of that of the molecular ion. The weak peak at m/z 74 is from the diethyl ether (DEE) impurity, in agreement with the NMR analysis. The intensity of the peak at m/z 74 is found to be $0.91 \pm 0.03\%$ of that of the MSCB ion peak, consistent with a MSCB purity of $>98\%$. The isotope peaks of the MSCB ion due to ^{28}Si , ^{29}Si , and ^{13}C were observed; however, those from the fragment ion peak at m/z 58 were not. This is due to the broadening of the latter peak that originated from the slow dissociation of the MSCB ion.^{36,37} Other weak peaks were also observed at m/z 28, 29, 31, 42–45, and 71, of which the ones at m/z 29 and 31 were from the photofragmentation of the DEE impurity. Aside from these two, the room-temperature mass spectrum of DEE also showed two other peaks at m/z 45 and 59. On the basis of the comparison of the percentage intensity of the peak at m/z 45 to that of the DEE molecular ion peak at m/z 74 from the neat DEE sample ($5.2 \pm 0.6\%$) and from the synthesized MSCB with DEE as the impurity ($46.1 \pm 1.9\%$), it is determined that the majority of the peak intensity at m/z 45 is from the photofragmentation of the MSCB molecular ion.

1. Primary Decomposition of MSCB on the Hot W Filament. The gas mixtures of MSCB in helium with different concentrations of 4, 8, 20, and 100% were examined in the experiments to detect the chemical species formed under collision-free conditions. For each mixture, filament temperatures (T_f) ranging from 900 to 2400 °C were tested at an increment of 100 °C. The experiments were repeated three times for each mixture. The filament was etched between each run of experiments by heating the filament to 2000 °C for 2 h using a 10% H_2 in He mixture under a total pressure of 2×10^{-6} Torr. Figure 2 shows the mass spectra in the region of

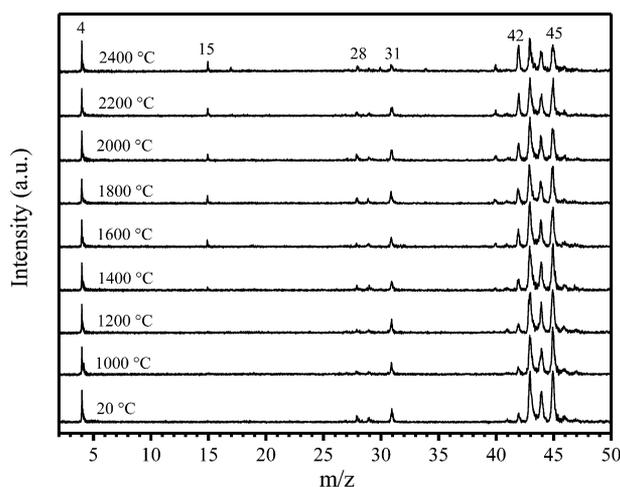


Figure 2. The 10.5 eV SPI TOF mass spectra of MSCB in the region of 2–50 amu at filament temperatures ranging from 1000 to 2400 °C at a chamber pressure of 5×10^{-6} Torr.

2–50 amu of 4% MSCB recorded at a chamber pressure of 5×10^{-6} Torr at various filament temperatures. A new mass peak at m/z 15, representing the methyl radical, started to appear after the filament was turned on, and its intensity kept increasing with T_f . This was true for all mixtures tested. The same peak at m/z 15 was not observed during a control experiment using 4% DEE in He, indicating that the methyl radical was produced exclusively from MSCB rather than the DEE impurity. It was also noted that the peak intensity ratio of m/z 71 ($[\text{M}-\text{CH}_3]^+$)

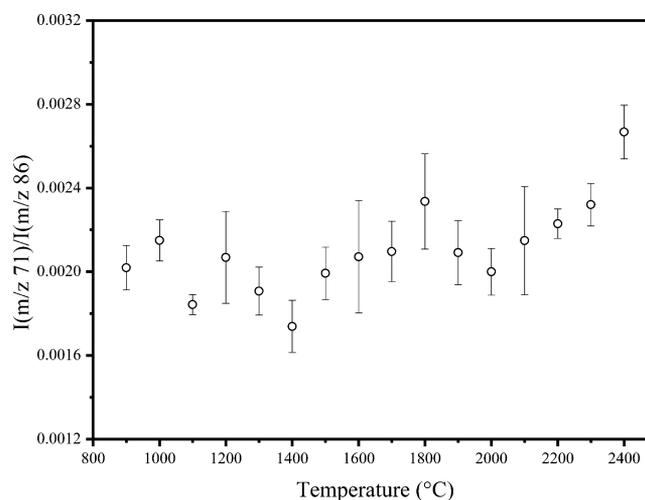
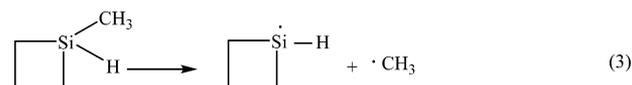


Figure 3. The intensity ratio of the SiC_3H_7^+ ($[\text{M}-\text{CH}_3]^+$, m/z 71) peak to that of $\text{SiC}_4\text{H}_{10}^{+\bullet}$ ($\text{M}^{+\bullet}$, m/z 86) as a function of the filament temperature for a 4% MSCB in He sample at a chamber pressure of 5×10^{-6} Torr.

to m/z 86 (the molecular ion, $\text{M}^{+\bullet}$) increased with T_f as shown in Figure 3. Therefore, it is determined that MSCB decomposed on the hot W filament to produce methyl and silacyclobutane-1-yl radicals according to eq 3.



This reaction was not observed in previous pyrolysis^{20–25} and photolysis^{26–28} of MSCB and hence represents a new decomposition channel when MSCB is exposed to hot W filament.

The temperature profile of the normalized intensity of CH_3^+ showed Arrhenius behavior between 1100 and 1900 °C, from which the apparent activation energy can be derived. The normalized intensity is obtained by multiplying the intensity of CH_3^+ at one specified temperature, T_j , by the ratio of the intensity of the molecular ion peak (m/z 86, the base peak) at room temperature to that at T_j . The effect of varying the concentration of MSCB on the activation energy (E_a) was found to be minimal. The averaged value of E_a for producing methyl radicals from MSCB was determined to be $46.7 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}$. The fact that this activation energy is significantly lower than the Si–CH₃ bond dissociation energy ($368.6 \text{ kJ}\cdot\text{mol}^{-1}$ ³⁸) strongly suggests that the formation of methyl radical from hot filament decomposition of MSCB is a catalytic process. This supports the conclusions from previous studies on hot filament decomposition of SiH_4 ^{39,40} and organosilicon compounds.^{12,14,15,18}

As mentioned in the Introduction, the ring opening of MSCB leading to the formation of ethene (m/z 28) and methylsilene (m/z 58) (eq 1) is the major decomposition route in both pyrolysis and photolysis. In our experiments, the room-temperature mass spectrum of MSCB showed a very weak peak at m/z 28. After the filament was turned on, no consistent increase in the intensity ratio of $I(m/z$ 28)/ $I(m/z$ 86) was noted. This is mainly due to the high ionization energy (IE) of ethene (10.51 eV ⁴¹), which lies on the threshold of the photon energy in the ionization source used in this work. The small ionization cross section obscured the observation of the additional ethene species produced from eq 1. The peak at m/z 58 is the main photofragment ion from the MSCB molecular ion

when using the 10.5 eV photon for ionization. However, it was observed that the intensity ratio of $I(m/z\ 58)/I(m/z\ 86)$ increased with T_f . This trend occurred at all MSCB concentrations studied. Figure 4 shows the profile of the intensity

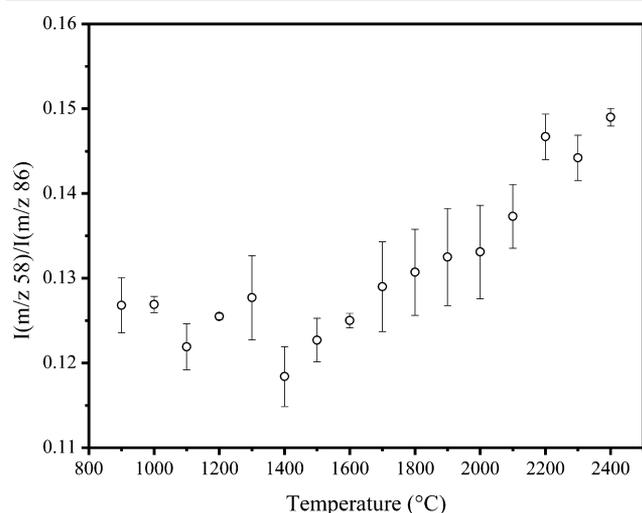


Figure 4. The intensity ratio of the SiC_2H_6^+ ($m/z\ 58$) peak to that of $\text{SiC}_4\text{H}_{10}^{+\bullet}$ ($M^{+\bullet}$, $m/z\ 86$) as a function of the filament temperature for a 4% MSCB in He sample at a chamber pressure of 5×10^{-6} Torr.

ratio of the $\text{SiC}_2\text{H}_6^{+\bullet}$ ($m/z\ 58$) peak to that of $\text{SiC}_4\text{H}_{10}^{+\bullet}$ ($M^{+\bullet}$, $m/z\ 86$) as a function of T_f for 4% MSCB in a He sample at a chamber pressure of 5×10^{-6} Torr. This indicates that MSCB also decomposes to form ethene and methylsilene on a hot W filament.

It is clear from Figure 2 that the intensity of the peak $m/z\ 42$ increases with T_f under collision-free conditions. The trend becomes more obvious when plotting the temperature distribution of the intensity ratio of $I(m/z\ 42)/I(m/z\ 86)$, as shown in Figure 5. At the same time, an examination of the

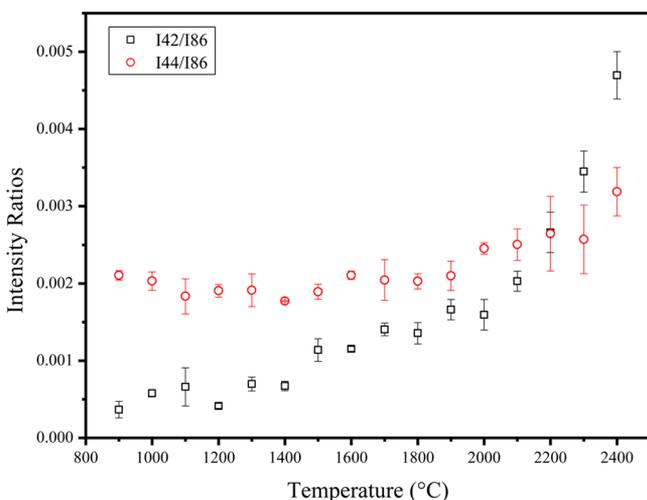


Figure 5. The intensity ratio of (a) the $\text{C}_3\text{H}_6^{+\bullet}$ ($m/z\ 42$) peak to that of $\text{SiC}_4\text{H}_{10}^{+\bullet}$ ($M^{+\bullet}$, $m/z\ 86$) and (b) the SiCH_3^+ ($m/z\ 44$) peak to that of $\text{SiC}_4\text{H}_{10}^{+\bullet}$ ($M^{+\bullet}$, $m/z\ 86$) as a function of the filament temperature for a 4% MSCB in He sample at a chamber pressure of 5×10^{-6} Torr.

intensity ratio of $I(m/z\ 44)/I(m/z\ 86)$ also revealed an increase with T_f (Figure 5). This implies the formation of propene from the hot filament decomposition of MSCB along with its

concomitant product of methylsilene. The peak intensity at $m/z\ 42$ is relatively weak, despite the fact that its IE ($9.73\ \text{eV}^{42}$) lies lower than the ionization photon energy used. This is consistent with the results from previous studies that eq 2 is a minor channel for the decomposition of MSCB via ring opening. Further investigation of the temperature dependence of the net increase in the peak intensity at $m/z\ 42$, $I(m/z\ 42)$, normalized, shows that it also follows the Arrhenius behavior in the T_f range of 1200–2400 °C. The value of $I(m/z\ 42)$ was calculated using the following formula

$$I(m/z\ 42) = I(m/z\ 42)_T - \left(\frac{I(m/z\ 42)}{I(m/z\ 86)} \right)_{\text{off}} \times I(m/z\ 86)_T \quad (4)$$

where T is the filament temperature ranging from 900 to 2400 °C and the subscript “off” means the room temperature when the filament is off. The normalized intensity was obtained using the same method as that mentioned before. The apparent E_a for propene formation was determined to be $68.7 \pm 1.3\ \text{kJ}\cdot\text{mol}^{-1}$. Comparison with the reported E_a value of $242 \pm 3\ \text{kJ}\cdot\text{mol}^{-1}$ for the same reaction in the MSCB pyrolysis process in a previous study²³ demonstrates unambiguously that the formation of propene from MSCB on a hot filament is also catalytic in nature.

2. Gas-Phase Reactions in a Hot Wire CVD Reactor.

The gas-phase reaction chemistry in the reactor setup described in the experimental section was investigated using concentrations of 1, 2, and 4% MSCB seeded in helium. This provides MSCB partial pressures of 0.12, 0.24, and 0.48 Torr, respectively, when using a total pressure of 12 Torr. The experiments were performed at different T_f in the range of 900–2000 °C at an increment of 100 °C. Mass spectra were collected every 5 min for 1 h at a fixed temperature. The filament was etched at 2000 °C for 1 h in vacuum before each temperature was increased to ensure the cleanness of its surface. Figure 6 shows the mass spectra recorded for 0.48 Torr of MSCB after the filament was turned on for 10 min at different T_f . MSCB started to decompose at a filament temperature as low as 1000 °C, as indicated by the decrease in the MSCB molecular ion intensity and the appearance of new mass peaks in Figure 6. This temperature is comparable to those observed with SCB¹⁶ and DMSCB,¹⁸ its monosilacyclobutane analogues, as listed in Table 1. A comparison with the lowest decomposition temperature for three open-chain alkylsilanes studied in our lab^{13–15} (also listed in Table 1) shows that the four-membered ring compounds decomposed at lower temperatures. This is due to the significant ring strains⁴³ in the silacyclobutane ring structures.

It is noted that the peak intensities of the two primary decomposition products, ethene and propene, get enhanced significantly in Figure 6 as compared to the those observed from the collision-free setup due to the difference in the MSCB pressures. The peak intensity ratio of ethene to propene observed from our reactor experiments ranged from 0.2:1 to 0.8:1. After calibrating the ratio of the ionization cross section for these two species,¹⁶ the corrected intensity ratio of ethene to propene peaks was found to be between 7:1 and 29:1. Therefore, the formation of ethene (eq 1) is preferred over that of propene (eq 2) in the decomposition of MSCB on the hot W filament. This is in good agreement with the pyrolysis²³ and photolysis²⁶ studies performed previously on MSCB.

2.1. Reactions Involving Silene and Silylene Intermediates. The formation of ethene from the decomposition of MSCB

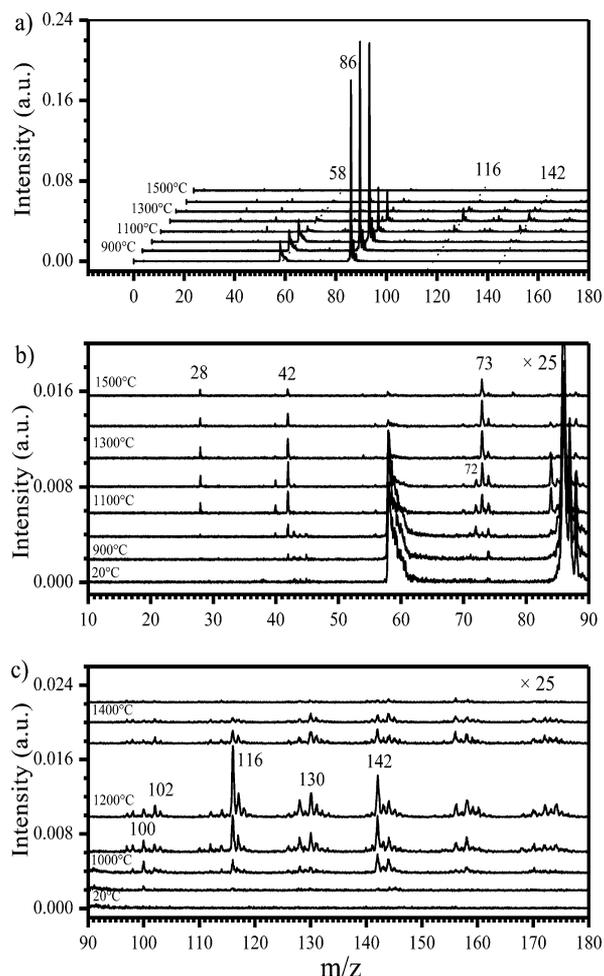


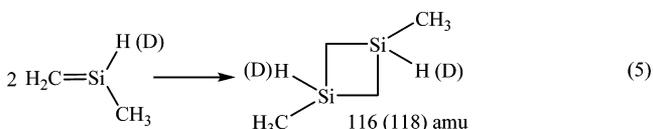
Figure 6. (a) Mass spectra of 12 Torr of 4% MSCB/He in the reactor at filament temperatures between 900 and 1500 °C. The spectrum at 20 °C was recorded when the filament was off. Enlarged spectra in regions of (b) 10–90 amu and (c) 90–180 amu.

Table 1. Lowest Decomposition Temperature and Ring Strain for Some HWCVD Precursors

precursor	lowest decomposition temperature (°C)	ring strain (kJ·mol ⁻¹)
MSCB	1000 ^a	107.8 ^g
SCB	900 ^b	107.8 ^g
DMSCB	900 ^c	108.9 ^g
trimethylsilane	1200 ^d	
tetramethylsilane	1400 ^e	
hexamethyldisilane	1400 ^f	

^aThis work. ^bReference 16. ^cReference 18. ^dReference 15. ^eReference 13. ^fReference 14. ^gReference 43.

occurs with a concomitant product, methylsilene, as illustrated in eq 1. Methylsilene, containing a Si=C double bond, is considered unstable and tends to undergo cyclodimerization to form 1,3-dimethyl-1,3-disilacyclobutane.¹

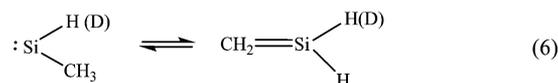


This leads to the observation of a peak at m/z 116 in Figure 6, which is one of the dominant new mass peaks produced after

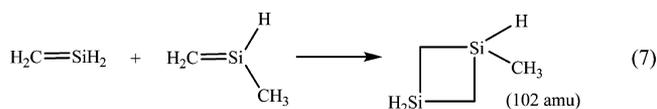
the filament is turned on. To confirm the origin of this peak, we have repeated the same experiment with 1-methyl-1-deuterio-silacyclobutane (MSCB- d_1). Figure 7 shows the mass spectrum of 12 Torr of a 4% MSCB- d_1 /He mixture recorded at a filament temperature of 1200 °C. When MSCB was replaced with MSCB- d_1 , the peak at m/z 116 was clearly shifted to m/z 118, and dominance of the peak at m/z 118 was preserved in the spectra recorded after the filament was turned on at 1200 °C. This clearly demonstrates that the peak at 116 originates from 1,3-dimethyl-1,3-disilacyclobutane, the dimer of methylsilene.

In the previous section, we have shown that decomposition of MSCB on the hot W filament also produces propene with methylsilene as its coproduct (eq 2). Barton et al.^{23,24} investigated the formation mechanism of propene and methylsilene using the deuterated isotopologue of MSCB. They determined that the decomposition was initiated by a 1,2-H shift from Si to the ring C atom with concerted ring opening to form *n*-propylmethylsilene, followed by a reversible β -insertion to form 1-methylsilacyclobutane, which then decomposed to methylsilene and propene.

Following this mechanism, the decomposition of MSCB- d_1 is expected to form propene- d_0 and - d_1 , as illustrated in Scheme 1. During our experiments with MSCB- d_1 in the reactor, a peak at m/z 43 along with the one at m/z 42 was observed. The inset in Figure 7 clearly shows this H/D scrambling. The intensity ratio of $I(m/z$ 42)/ $I(m/z$ 43) lies in the range of 0.4–2.9. Correspondingly, $:\text{SiH}(\text{CH}_3)$ and $:\text{SiD}(\text{CH}_3)$ can be formed as the coproducts of propene- d_1 and - d_0 , respectively. The interconversion of silylene and silene in the gas phase has been extensively investigated in the literature.^{44–46} The energy of silylene and silene species is found to be nearly degenerate, and the isomerization between silylene and silene is a reversible process.



The silene species formed from isomerization of methylsilene in eq 6 can undergo cycloaddition reaction with the dominant methylsilene to form 1-methyl-1,3-disilacyclobutane.



Upon replacing MSCB with MSCB- d_1 , methylsilene in eq 7 will be replaced by 1-methyl-1-deuteriosilene. Due to the H/D scrambling in methylsilene, both deuterated and undeuterated silene will be present, as represented in eq 6. As a result, the mass peak of the cycloaddition product in eq 7 will be shifted to m/z 103 and 104. This is indeed observed in Figure 7 (inset) when MSCB- d_1 is used. Therefore, the H/D scrambling pattern observed with the peak at m/z 102 provides strong evidence for the formation of methylsilene to be initiated by 1,2-H shift and its isomerization to silene species.

The cyclodimerization of silene produces 1,3-disilacyclobutane (DSCB, 88 amu). In Figure 6, the peak at m/z 88 overlaps with the isotopic peak of the parent MSCB ion (m/z 86) due to the isotopic contributions from ²⁹Si, ³⁰Si, and ¹³C. Our analysis of the intensity ratio of $I(m/z$ 88)/ $I(m/z$ 86) showed an increase with both T_f and the filament-on time. The ratio ranged from 0.067 to 0.69 for the T_f of 1100–1600 °C, as compared to the room-temperature ratio of 0.046 ± 0.003 . The significant increase in the intensity ratio of $I(m/z$ 88)/ $I(m/z$ 86)

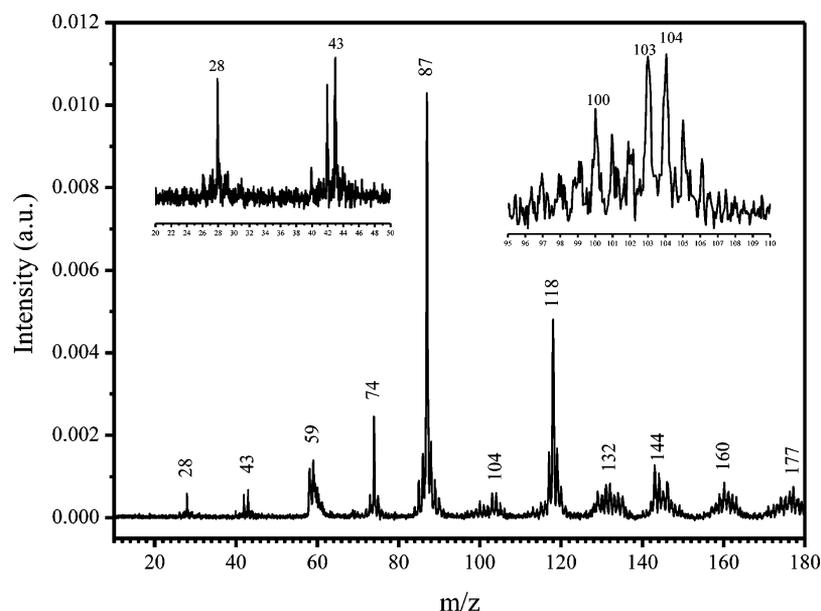
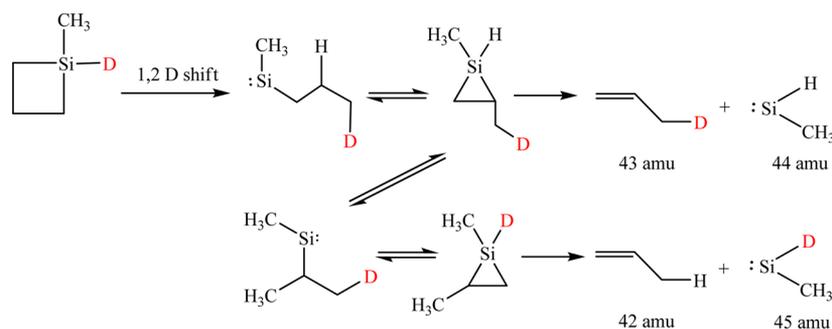


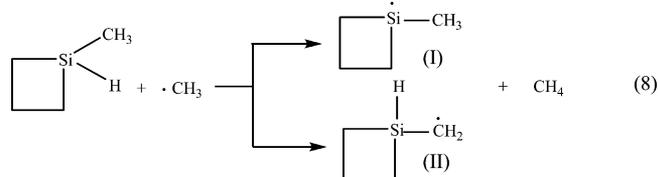
Figure 7. The mass spectrum of 12 Torr of a 4% MSCB- d_1 /He mixture recorded 10 min after the filament was turned on at 1200 °C.

Scheme 1. Formation of Propene and Methysilylene from MSCB- d_1



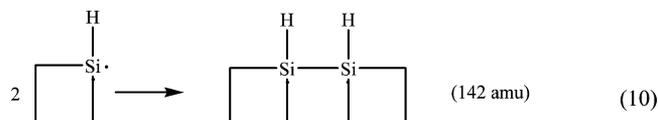
suggests that DSCB was formed in the reactor under our experimental conditions.

2.2. Free Radical Short-Chain Reactions. One of the primary decomposition channels of MSCB (eq 3) produced methyl and silacyclobutane-1-yl radicals. Methyl radical is known to be a good H abstractor, whereas the latter is a poor one due to the low strength of the Si–H bond formed as compared to the C–H bond. The abstraction of H (from either the Si–H or C–H bond) by the methyl radical was found to be the main chain propagation step in the short-chain reactions that dominate the secondary gas-phase reactions when using open-chain alkylsilanes^{13–15} in a hot wire CVD reactor. With the existence of both Si–H and C–H bonds in the abundant source molecule MSCB, it is expected that two more radicals, that is, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}^\bullet\text{-CH}_3$ (I) and $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si(H)-CH}_2^\bullet$ (II), to be produced from H abstraction by the methyl radical.



The subsequent recombination reactions between these two radicals and the two primary radicals from eq 3 terminate the short-chain reactions and also lead to the formation of stable

molecular products. The reactions involving the two primary radicals (methyl and silacyclobutane-1-yl) are shown below.



The product from the self-recombination of the silacyclobutane-1-yl radicals in eq 10, 1,1'-bis(silacyclobutane), was observed after the filament was turned on in our experiments with the reactor setup. The peak at m/z 142 was actually another dominant new peak in addition to the peak at m/z 116, as shown in Figure 6. The mass peaks for methane (eq 8) and ethane (eq 9) were not observed in our experiments. The high ionization energy (CH_4 : 12.61 eV;⁴⁷ C_2H_6 : 11.52 eV⁴⁸) and the

small quantities produced are the main reasons that these two species escape the detection by our mass spectrometer.

The two secondary radicals produced from the H abstraction reactions in eq 8 have the same mass of 85 amu. The cross recombination of each of the two radicals with methyl produces DMSCB and 1-ethylsilacyclobutane (ESCB) with the same mass (100 amu), as represented by eqs 11 and 12, respectively. A mass peak at m/z 100 was indeed observed in the mass spectra recorded after the filament was turned on, and its intensity maximized at a T_f of 1200 °C (Figure 6). The room-temperature mass spectrum recorded with the same VUV laser ionization source of the authentic DMSCB sample shows predominantly two peaks at m/z 100 (base peak) and 72.¹⁸ The peak intensity of m/z 72 is found to be 78.2% of that of the molecular ion peak at m/z 100. In Figure 6, a peak at m/z 72 was observed along with the appearance of the new peak at m/z 100, and its peak intensity also maximized at 1200 °C. Examination of the intensity ratio of $I(m/z\ 72)/I(m/z\ 100)$ for all filament-on spectra at $T_f = 1000\text{--}1400$ °C for 4% MSCB/He sample shows that it is constant at $61.4 \pm 0.3\%$. This ratio is lower than the same ratio from the room-temperature mass spectrum of DMSCB, indicating that more than one source, including DMSCB, is contributing to the peak intensity at m/z 100. Furthermore, it is noted that radical II contains a H atom originating from the Si–H bond and radical I does not. Therefore, it is expected that this structure difference carried forward in the two species, DMSCB and ESCB, formed from the radical recombination reactions 11 and 12 will reveal itself in the mass shift when using the deuterated isotopologue of MSCB, MSCB- d_1 . As can be seen in the inset picture of Figure 7, the intensity of the peak at m/z 101 is enhanced relative to the one at m/z 100 when MSCB- d_1 is used. For the T_f ranging from 1100 to 1500 °C, the intensity ratio of $I(m/z\ 101)/I(m/z\ 100)$ with MSCB- d_1 varies from 0.49 to 1.37 depending the filament-on time and T_f . This is higher than the corresponding value of 0.18–0.71 when using MSCB, with the peak at m/z 101 mainly from the (M+1) isotope peak of the one at m/z 100 and the photofragment ions of the peak at m/z 116 combined. The much enhanced intensity ratio of $I(m/z\ 101)/I(m/z\ 100)$ suggests that part of the mass peak at m/z 100 is shifted by 1 mass unit when MSCB- d_1 is used. This clearly demonstrates that both DMSCB (0 mass unit shift with MSCB- d_1) and ESCB (+1 mass unit shift with MSCB- d_1) are produced in the reactor, which in turn provides strong evidence that two H abstraction pathways as represented by eq 8 occur simultaneously.

2.3. Competition between Reactions Involving Silene/Silylene and Free Radical Short-Chain Reactions. Figure 8 shows the intensity profiles of the main product peaks at m/z 100, 102, 116, and 142 as a function of time when using 4% MSCB at filament temperatures of 1100 and 1200 °C. At low filament temperatures of 1000 (not shown) and 1100 °C, the intensity of the two dominant peaks at m/z 116 and 142 are comparable in the first 15 min after the filament is turned on. Afterward, the peak at m/z 116 becomes dominant. At filament temperatures higher than 1100 °C, the dominance of the m/z 116 peak was observed through the 1 h run for each temperature. This trend was also observed when using the other two concentrations of the MSCB sample in the reactor. This suggests that at low filament temperatures, there is a competition of the free radical chain reactions and those involving silene species because the peak at m/z 142 is from the former and the one at m/z 116 is representative of the latter. With increasing temperature and reaction time, the dimerization of silene species

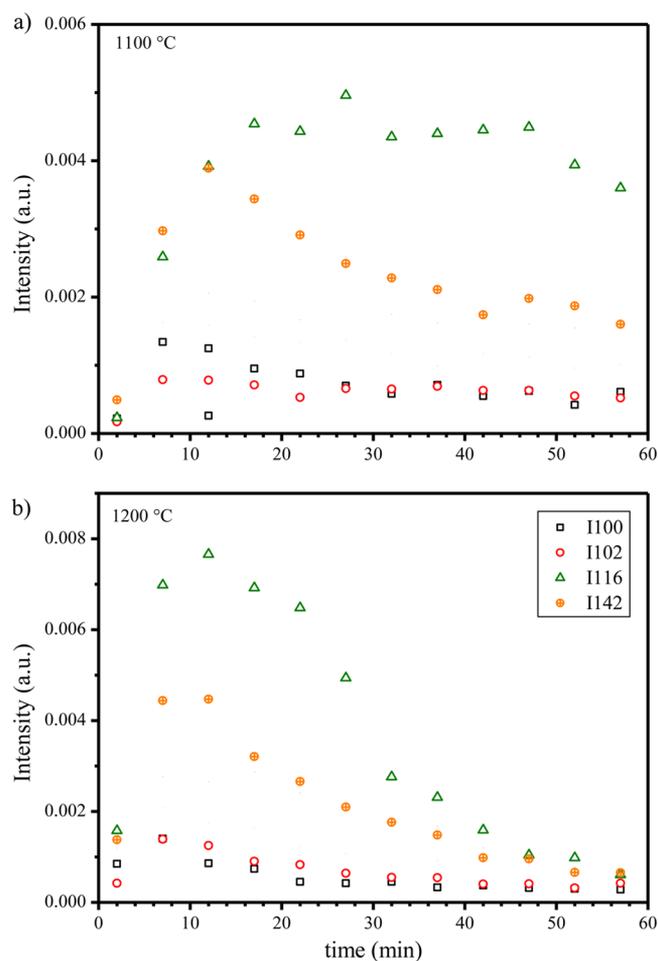


Figure 8. The intensity profile of the signals from the peaks at m/z 100, 102, 116, and 142 as a function of filament-on time at (a) 1100 and (b) 1200 °C from 12 Torr of 4% MSCB in the reactor.

becomes more prevalent. Interestingly, when comparing the peak intensities at m/z 100 from free radical reactions and those at m/z 102 from cycloaddition of silenes, it is noted that the m/z 100 peak is stronger at low T_f and short reaction time, whereas the one at m/z 102 takes over at high T_f and long reaction time. This provides further support for the conclusions drawn upon the competition between the two types of reactions.

It is noted from Figure 8 that the signals from the 1,3-dimethyl-1,3-disilacyclobutane ion (m/z 116) reached a steady state at 1100 °C. At an increased temperature of 1200 °C, its intensity first increased with time in the first 12 min but decreased thereafter. For the other main product (1,1'-bis(silacyclobutane)) peak at m/z 142, the intensity increased to a maximum at 12 min for both temperatures. This suggests that the two products, once formed, started to decompose on the filaments themselves, leading to their consumption. According to the intensity profile shown in Figure 8, the consumption rates of 1,3-dimethyl-1,3-disilacyclobutane and of 1,1'-bis(silacyclobutane) dominate over their formation rates, respectively, at 1200 and 1100 °C. It could also be argued that the decrease in the peak intensities was due to changes in the filament conditions because the filament could form alloys upon exposure to chemicals. Our previous study⁴⁹ has shown that the W filament can be carburized upon exposure to 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TDMSCB) with a decomposition temperature of 1200 °C. The carburization is mainly

due to the methyl radicals produced on the heated filament. However, the carburization was found to dominate only at higher temperatures ($T \geq 1800$ °C). The decomposition temperature of MSCB at 1000 °C is not significantly different than the one at 1200 °C¹⁷ for TMDSCB. Therefore, the W filament carburization rate with MSCB should be low at the lower temperatures of 1100 and 1200 °C examined, and its impact on the peak intensities should be minimal.

CONCLUSIONS

The decomposition chemistry of MSCB on a hot W filament and the gas-phase reactions under the practical deposition pressures in a hot wire CVD reactor were studied. Three decomposition pathways were found when exposing MSCB to a hot W filament, which form ethene/methylsilene, propene/methylsilylene, and methyl radicals. The formation of ethene was demonstrated to favor over that of propene, with a product ratio of ethene to propene ranging from 7:1 to 29:1. The formation of methyl radicals via Si-CH₃ bond cleavage represents a new decomposition channel of MSCB when exposed to the W filament. The activation energies for the formation of propene and methyl radical were determined to be 68.7 ± 1.3 and 46.7 ± 2.5 kJ·mol⁻¹, respectively. This shows unambiguously that the formation of these two species from hot filament decomposition of MSCB is a catalytic process.

The secondary gas-phase reactions under a practical deposition pressure are characterized by a free radical chain reaction and the reactions involving silene/silylene species. The free radical chain reaction is initiated by the decomposition of MSCB to form methyl radicals and propagated by H abstraction reactions. The termination steps produce several stable products, including 1,1'-bis(silacyclobutane) (m/z 142), DMSCB (m/z 100), and 1-ethylsilacyclobutane (m/z 100). The silene/silylene chemistry is represented mainly by the cycloaddition of silene and the isomerization of silylene to silene. The filament temperature and reaction time are the two major factors that influence the reaction chemistry, whereas the effect of MSCB pressure on the reaction chemistry is found to be minimal in the pressure range of 0.12–0.48 Torr tested in this work. It has been shown that silene chemistry dominates at filament temperatures higher than 1200 °C ($T_f \geq 1200$ °C). At a lower T_f of 1000–1100 °C and short reaction time ($t \leq 15$ min), free radical chain reactions compete with the silene chemistry.

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Notes

The authors declare no competing financial interest.

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