

Formation of the Elusive Silylenemethyl Radical (HCSiH_2 ; X^2B_2) via the Unimolecular Decomposition of Triplet Silaethylene (H_2CSiH_2 ; a^3A'')

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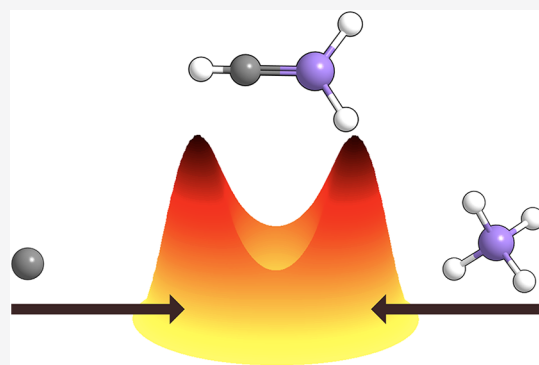


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ABSTRACT: We investigated the formation of small organosilicon molecules—potential precursors to silicon-carbide dust grains ejected by dying carbon-rich asymptotic giant branch stars—in the gas phase via the reaction of atomic carbon (C) in its 3P electronic ground state with silane (SiH_4 ; X^1A_1) using the crossed molecular beams technique. The reactants collided under single collision conditions at a collision energy of 13.0 ± 0.2 kJ mol $^{-1}$, leading to the formation of the silylenemethyl radical (HCSiH_2 ; X^2B_2) via the unimolecular decomposition of triplet silaethylene (H_2CSiH_2 ; a^3A''). The silaethylene radical was formed via hydrogen migration of the triplet silylmethylene (HCSiH_3 ; X^3A'') radical, which in turn was identified as the initial collision complex accessed via the barrierless insertion of atomic carbon into the silicon–hydrogen bond of silane. Our results mark the first observation of the silylenemethyl radical, where previously only its thermodynamically more stable methylsilylidyne (CH_3Si ; X^2A') and methylenesilyl (CH_2SiH ; X^2A') isomers were observed in low-temperature matrices. Considering the abundance of silane and the availability of atomic carbon in carbon-rich circumstellar environments, our results suggest that future astrochemical models should be updated to include contributions from small saturated organosilicon molecules as potential precursors to pure gaseous silicon-carbides and ultimately to silicon-carbide dust.



1. INTRODUCTION

Circumstellar envelopes (CSEs) of carbon-rich asymptotic giant branch (AGB) stars are host to a complex gas-phase chemistry that has required decades of interdisciplinary research effort to decode.¹ Besides the well-known combustion-like processes occurring near the stellar photosphere such as aromatic molecule formation by hydrogen-abstraction acetylene-addition^{2–5} and hydrogen-abstraction-vinylacetylene-addition sequences,^{6–8} the chemical and physical conditions within these envelopes are ideal for the production of silicon-carbide dust grains as signified by a unique absorption near $11.3 \mu\text{m}$ (885 cm^{-1}).^{9,10} Approximately 90% of the silicon-carbide grains recovered from meteorites have been connected to formation processes in CSEs of low mass carbon-rich AGB stars;^{11,12} recent dating of silicon-carbide grains revealed that in rare cases, these pre-solar materials can survive for up to a few billion years.¹³ Following their formation in CSEs, and once incorporated in cold molecular clouds, these nanometer-sized grains can accumulate icy layers of a few hundred nanometers containing predominantly water (H_2O), methanol (CH_3OH), formaldehyde (H_2CO), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and ammonia (NH_3).^{14,15} These ices can be processed by the internal ultraviolet field present even deep inside molecular

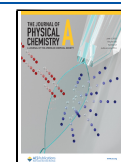
clouds and by energetic galactic cosmic rays leading to the synthesis of complex organic molecules often with biological significance such as urea [$(\text{NH}_2)_2\text{CO}$],^{16,17} sugar-related molecules such as glycerol [$\text{CHOH}(\text{CH}_2\text{OH})_2$],¹⁸ (di)-phosphates,¹⁹ aminoacids,^{20–22} and even dipeptides.^{23–26} Laboratory experiments have further suggested that silicon-carbide dust may also be linked to the formation of large fullerenes^{27,28} and polycyclic aromatic hydrocarbons.^{29,30} Despite their importance to circumstellar and interstellar chemistry, the elementary reactions leading to the formation these silicon-carbide grains remain elusive.

Gaseous molecules carrying silicon–carbon bonds in carbon-rich envelopes are considered the progenitors of silicon-carbide dust where at least eight molecules carrying a silicon–carbon bond are known to exist in the CSE of IRC +10216 (Scheme 1).^{31–38} Systematic observations of carbon-

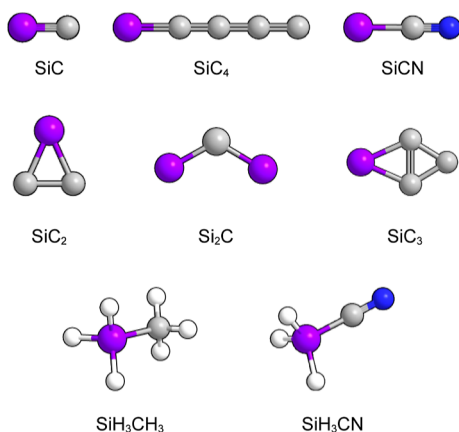
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Scheme 1. Molecules Carrying Silicon–Carbon Bonds Detected in the CSE of IRC+10216; Silicon, Carbon, Nitrogen, and Hydrogen Are Indicated in Purple, Gray, Blue, and White



rich AGB stars discovered an anti-correlation between gaseous silicon dicarbide ($c\text{-SiC}_2$) abundances and the density of the envelopes³⁹ that models suggest could be explained by the nucleation of pure gaseous silicon carbide grains leading to increasingly stable clusters and eventually solids.^{40,41} However, the inventory of gaseous molecules in CSEs is not limited to pure silicon-carbides. The presence of silylmethane (SiH_3CH_3) within IRC+10216 proposes that a chemistry involving saturated molecules such as methane (CH_4) and silane (SiH_4) could contribute to the initial formation of silicon-carbon bonds in CSEs as well. Despite this, the gas-phase characterization of small saturated organosilicon molecules formed from simple atomic and molecular precursors remains a work in progress for the (astro)chemistry and reaction dynamics communities.

A hitherto scarcely recognized pathway to silicon-carbides is the gas phase reaction of carbon atoms [$\text{C}(^3\text{P})$] with silane (SiH_4), which has an abundance of 2.2×10^{-7} relative to molecular hydrogen in IRC+10216.^{42,43} Early computational studies predicted that atomic carbon could insert into an Si–H bond of silane without an entrance barrier⁴⁴ as contrasted to the insertion of $\text{C}(^3\text{P})$ into methane (CH_4), which has a 51 kJ mol^{−1} barrier in the entrance channel.⁴⁵ Lu et al. performed the first combined experimental and computational investigation of this reaction and proposed three triplet CSiH_4 intermediates to be involved in the formation of the products CSiH_3 and CSiH_2 with branching ratios of 60 versus 40% on the triplet potential energy surface.⁴⁶ Importantly, the molecular beam contained ground and electronically excited carbon atoms which complicates the interpretation of the experimental findings. Recently, Ranka et al. approached the $\text{C}(^3\text{P}/^1\text{D})\text{--SiH}_4$ systems through a computational lens developing additional reaction pathways on the singlet potential energy surface and ultimately located an elusive $\text{C}\cdots\text{SiH}_4$ van der

Waals (vdW) complex in the entrance channel highlighting the possibility of a submerged barrier.⁴⁷ Considering the aforementioned experimental ambiguities, here, we present the results of crossed molecular beams experiments of solely ground-state carbon atoms $\text{C}(^3\text{P})$ with silane (SiH_4 ; $X^1\text{A}_1$) in an attempt to untangle the reaction dynamics initiated on the triplet CSiH_4 surface. Merged with comprehensive electronic structure calculations, our data suggest that the carbon atom undergoes barrierless insertion into the silicon–hydrogen bond of silane resulting in a triplet HCSiH_3 collision complex leading ultimately to the doublet silylenemethyl (HCSiH_2) radical. These findings motivate continued research in the area of organosilicon chemistry and provide a well-founded chemical insight into the possible formation of small saturated silicon-carbides within carbon-rich CSEs as precursors to pure silicon-carbides and ultimately silicon-carbide dust.

2. METHODS

2.1. Experimental Section. The reaction of atomic carbon with silane (Voltaix; 99.9999%) was performed utilizing a crossed molecular beams machine at the University of Hawaii.^{48,49} The carbon atoms were produced in their electronic ground state by ablation of a rotating graphite rod using the focused fourth harmonic of a Nd:YAG laser operating at a reduced output energy of 10 mJ per pulse.^{50–55} The ablated carbon atoms were subsequently entrained in a pulsed beam of neon gas (99.999%; Specialty Gases of America), skimmed, and then velocity-selected using a four-slot chopper wheel rotating at 120 Hz. This part of the pulse was characterized by a peak velocity v_p of 1505 ± 10 m s^{−1} and a speed ratio S of 3.3 ± 0.1 ; note that under these experimental conditions, dicarbon (C_2) is also produced with the same beam properties.⁵⁶ A neat silane beam ($v_p = 841 \pm 10$ m s^{−1}; $S = 10.2 \pm 0.3$) was spatially and temporally aligned to intersect perpendicularly the carbon atom beam resulting in a nominal collision energy of 13.0 ± 0.2 kJ mol^{−1} and a center-of-mass angle (CM) of $56.1 \pm 0.4^\circ$ (Table 1). The reactively scattered products entered a triply differentially pumped universal detector rotatable in the plane defined by the reactant beams. The products were ionized at 80 eV and filtered according to their mass-to-charge (m/z) ratio using a quadrupole mass spectrometer. Ions of the desired m/z impinged upon an aluminum target floated at a negative voltage of 25 kV; this generated a cascade of secondary electrons that struck an aluminum coated scintillator whose photons were registered by a photomultiplier tube. The resulting signal was collected by a multichannel scaler in discrete bins according to the time of arrival to produce a time-of-flight (TOF) spectrum. The laboratory data are forward-convoluted to the CM frame and the resulting CM translational energy $P(E_T)$ and angular $T(\theta)$ flux distributions are analyzed to inform the reaction dynamics.^{57,58} Errors of the $P(E_T)$ and $T(\theta)$ functions are determined within the 1σ error

Table 1. Peak Velocities (v_p) and Speed Ratios (S) of the Carbon (C), Dicarbon (C_2), and Silane (SiH_4) Beams along with the Corresponding Collision Energies (E_C) and CMs (Θ_{CM})

beam	v_p (m s ^{−1})	S	E_C (kJ mol ^{−1})	Θ_{CM} (deg)
SiH_4 ($X^1\text{A}_1$)	841 ± 10	10.2 ± 0.3		
C (^3P)	1505 ± 10	3.3 ± 0.1	13.0 ± 0.2	56.1 ± 0.4
C_2 ($X^1\Sigma_g^+/\text{a}^3\Pi_u$)	1505 ± 10	3.3 ± 0.1	20.4 ± 0.2	36.7 ± 0.4

limits of the accompanying LAB angular distribution while maintaining a good fit of the laboratory TOF spectra.

2.2. Computational. On both adiabatic triplet and singlet potential energy surfaces of CSiH_4 , the geometries of various CSiH_4 , CSiH_3 , and CSiH_2 isomers and transition states are optimized, and the 1-D barrierless reaction paths are mapped out via IRC (intrinsic reaction coordinate calculation) by coupled cluster^{59,60} CCSD/cc-pVTZ calculations. The complete basis set limits,⁶¹ CCSD(T)/CBS energies for stationary points, are then obtained by extrapolating the CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ energies, with CCSD/cc-pVTZ zero-point energy corrections. The accuracy of these CCSD(T)/CBS energies is within 8 kJ mol⁻¹.⁶² GAUSSIAN09 programs⁶³ are facilitated in coupled cluster calculations. The minimum energy crossing point between the triplet (³1) and singlet (¹1) silylmethylene is located with the CPMSCF/TZVPP by employing MOL-PRO,⁶⁴ and the CCSD(T)/CBS energy is also computed.

3. RESULTS

3.1. Laboratory Frame. Carbon atoms in their electronic ground state (³P) underwent reactive collisions with silane (SiH_4) at a collision energy of 13.0 ± 0.2 kJ mol⁻¹; distinct TOF spectra were recorded at mass-to-charge ratios $m/z = 43$ (CSiH_3^+) and $m/z = 42$ (CSiH_2^+). The presence of singly ionized carbon dioxide (CO_2^+) in the detector prevented the collection of TOFs at $m/z = 44$ of ionized $^{13}\text{C}^{28}\text{SiH}_3/^{12}\text{C}^{29}\text{SiH}_3$ or $^{12}\text{C}^{30}\text{SiH}_2$ formed via atomic or molecular hydrogen loss(es) and/or as an adduct ($^{12}\text{C}^{28}\text{SiH}_4$). The TOF spectra (Figure 1a) recorded at m/z

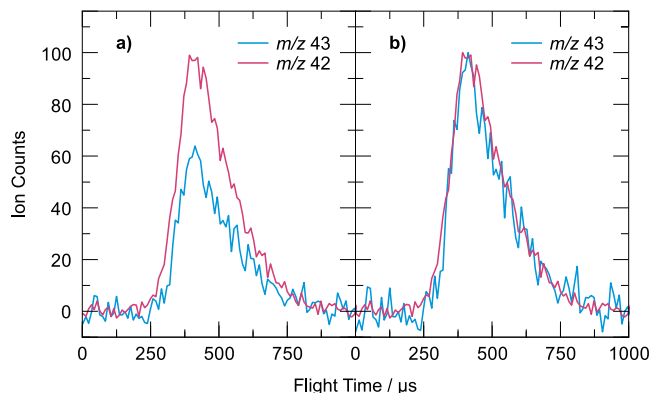
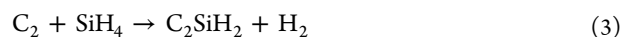


Figure 1. TOF spectra recorded at the CM for $m/z = 43$ (CSiH_3^+) and $m/z = 42$ (CSiH_2^+). The left and right panels depict raw and normalized TOF spectra, respectively.

$= 43$ and $m/z = 42$ were superimposable (Figure 1b) and therefore have a common origin owing to the atomic hydrogen loss channel(s): C (12 amu) + SiH_4 (32 amu) \rightarrow CSiH_3 (43 amu) + H (1 amu) (reaction 1); signal at $m/z = 42$ stems from dissociative electron impact ionization of the neutral CSiH_3 species within the ionizer. Given that the multichannel nature of this reaction had been both observed and predicted previously,^{46,47} we extracted the full laboratory angular distribution for both CSiH_3^+ ($m/z = 43$) [Figure 2 (top)] and CSiH_2^+ ($m/z = 42$) [Figure 3 (left)] by recording TOF spectra at discrete angles in 5° intervals. Up to 7.3×10^5 and 6.9×10^5 TOF spectra were recorded at $m/z = 43$ [Figure 2 (bottom)] and $m/z = 42$ [Figure 3 (right)] at each angle, respectively. These data were then integrated and normalized

to produce the laboratory angular distributions presented in Figures 2 (top) and 3 (left).



The resulting distributions of the ion counts of CSiH_3^+ ($m/z = 43$) and CSiH_2^+ ($m/z = 42$) are both very broad and asymmetric, covering a range of more than 50° in the laboratory frame; each distribution peaks nearly 10° below the CM angle of the $\text{C}(\text{P})\text{--SiH}_4$ system (Table 1). Both distributions terminate at 69° due to limitations in the machine configuration that prevents scanning at larger angles. To account for these broad and asymmetric distributions, a second reaction channel arising from dicarbon (C_2)—a known byproduct of graphite ablation^{56,65}—and silane was required. In the selected part of the beam, the dicarbon (C_2) to atomic carbon (C) ratio of $0.5 \pm 0.05:1$ was determined, that is, a fraction of about 33%. The chemical dynamics of the $\text{C}_2\text{--SiH}_4$ system were untangled earlier in our laboratory;⁶⁶ these experiments revealed the existence of a single reaction channel leading to $\text{C}_2^{28}\text{SiH}_2$ isomer(s) (54 amu) (hereafter: C_2SiH_2) along with molecular hydrogen (2 amu) (reaction 3). Here, acceptable fits of the signal obtained at $m/z = 43$ and $m/z = 42$ could be obtained by the inclusion of the $\text{C}_2\text{--SiH}_4$ reactions that lead to molecular hydrogen loss products of 55 ($\text{C}_2\text{H}_2^{29}\text{Si}$)/54 ($\text{C}_2\text{H}_2^{28}\text{Si}$) amu, respectively, with fragments from dissociative electron impact ionization arising at $m/z = 43$ and $m/z = 42$. This gives a maximum near the CM angle of the $\text{C}_2\text{--SiH}_4$ system of $36.7 \pm 0.4^\circ$ (Figures 2 and 3). At higher laboratory angles, the reactive scattering data could be fit with a single channel, namely, C (12 amu) + SiH_4 (32 amu) \rightarrow CSiH_3 (43 amu) + H (1 amu), resulting in a nearly symmetric distribution about CM angle of $56.1 \pm 0.4^\circ$. The CM functions used to fit the data recorded at $m/z = 43$ —discussed in the next section—could also be used to fit the data recorded at $m/z = 42$. Most importantly, these findings support the carbon versus hydrogen atom exchange pathway, but they do not support the formation of molecular hydrogen loss products where inclusion of a molecular hydrogen loss product channel results in extremely narrow TOF distributions.

3.2. Center-of-Mass Frame. To elucidate the chemical dynamics of the bimolecular reactions of the $\text{C}\text{--SiH}_4$ system, the experimental data were transformed from the laboratory into the CM reference frame to obtain the CM translational energy $P(E_T)$ and angular $T(\theta)$ flux distributions (Figure 4).⁶⁷

3.2.1. $m/z = 43$. The TOFs and laboratory angular distribution at $m/z = 43$ (Figure 2) could be replicated via a two-channel fit: (i) the reaction C (12 amu) + $^{28}\text{SiH}_4$ (32 amu) \rightarrow $\text{C}^{28}\text{SiH}_3$ (43 amu) + H (1 amu) (reaction 1), and (ii) dissociative electron impact ionization of the $m/z = 55$ ($\text{C}_2^{29}\text{SiH}_2^+$) formed in the reaction $\text{C}_2 + ^{29}\text{SiH}_4 \rightarrow \text{C}_2^{29}\text{SiH}_2$ (55 amu) + H_2 (reaction 3). The overall branching ratios for the channels (i) and (ii) are 67 ± 5 and $33 \pm 3\%$, respectively, with the CM functions of the molecular hydrogen loss channel for the $\text{C}_2\text{--SiH}_4$ system extracted from Rettig et al.⁶⁶ For the dominant channel, (i) the reaction C (12 amu) + $^{28}\text{SiH}_4$ (32 amu) \rightarrow $\text{C}^{28}\text{SiH}_3$ (43 amu) + H (1 amu) (reaction 1), the best-fit $P(E_T)$ reveals that the maximum translational energy for the hydrogen atom loss channel leading to CSiH_3 product(s) is 105 ± 15 kJ mol⁻¹; this corresponds to the

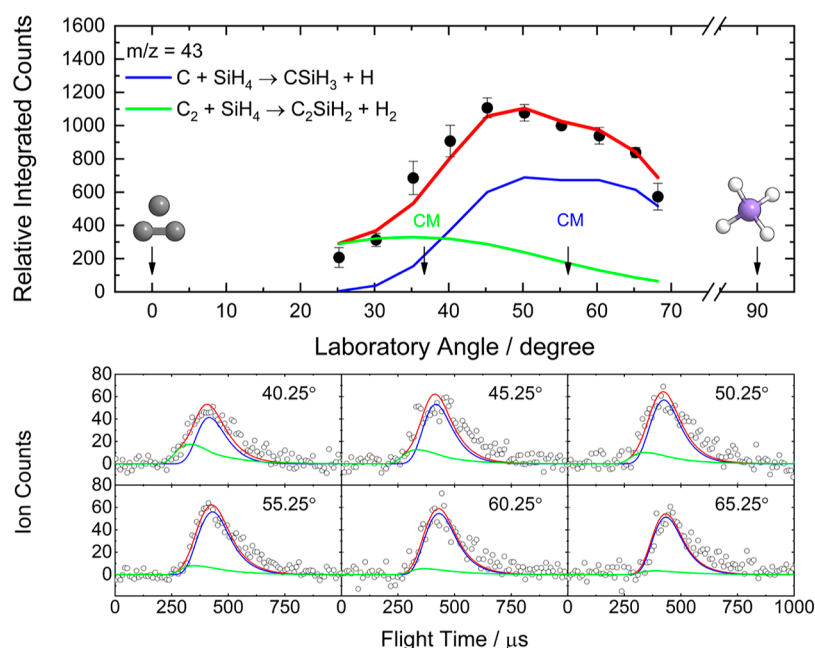


Figure 2. Laboratory angular distribution (top) and TOF spectra (bottom) recorded at $m/z = 43$ for the reaction of atomic carbon and dicarbon with silane. The data were fit with two channels (i) ^{12}C (12 amu) + $^{28}\text{SiH}_4$ (32 amu) \rightarrow $^{12}\text{C}^{28}\text{SiH}_3$ (43 amu) + H (1 amu) (blue), (ii) dissociative electron impact ionization of the $m/z = 55$ ($^{12}\text{C}_2^{29}\text{SiH}_2^+$) formed in the reaction $^{12}\text{C}_2$ (24 amu) + $^{29}\text{SiH}_4$ (33 amu) \rightarrow $^{12}\text{C}_2^{29}\text{SiH}_2$ (55 amu) + H_2 (2 amu) (green). The black circles depict the experimental data, colored lines the fits (red corresponding to the total fit), and error bars the 1s standard deviation. Colors of the atoms: silicon, purple; carbon, gray; and hydrogen, white.

total energy available E_{avail} to the reaction products (Figure 4A). The $P(E_T)$ distribution carries a most probable E_T of 22 ± 3 kJ mol $^{-1}$, while on average, 34 ± 5 kJ mol $^{-1}$ are apportioned to the translational degrees of freedom representing $33 \pm 7\%$ of the available energy. The relatively low fraction of energy used for the translation of nascent atomic hydrogen loss products along with the away-from-zero translational energy peaking of the $P(E_T)$ for each channel suggests the reaction proceeds indirectly via CSiH_4 intermediate(s) decomposing via tight exit transition state(s). For products formed without rovibrational excitation, the maximum energy cutoff of 105 ± 15 kJ mol $^{-1}$ is representative of the reaction ($\Delta_r G$) and collision energies through $E_{\text{avail}} = E_C - \Delta_r G$. Therefore, a reaction energy ($\Delta_r G$) of -92 ± 15 kJ mol $^{-1}$ can be derived based on the known experimental collision energy (E_C) of 13.0 ± 0.2 kJ mol $^{-1}$. The best-fit CM angular flux distribution $[T(\theta)]$ reveals that the reaction products are scattered at all angles (Figure 4B). Furthermore, the $T(\theta)$ distribution is symmetric about the 90° minimum which is characteristic of indirect reaction dynamics owing to CSiH_4 intermediate(s) that persists for several rotational periods such that the memory of the reactant trajectories is lost prior to dissociation to CSiH_3 plus atomic hydrogen. The minimum at 90° can arise from geometrical constraints in the exit channel where the hydrogen atom is emitted in the rotational plane of the decomposing transition state.^{68,69} These findings are also compiled in the flux contour map, which depict the reactively scattering products flux intensity as a function of the center-of-mass scattering angle (θ) and product velocity (u), providing the detailed messages on the reactive scattering process (Figure 4C).⁶⁹

3.2.2. $m/z = 42$. The two-channel fit could reproduce the experimental data at $m/z = 42$ [Figure 3 (top)] via channels i and ii along with branching ratios of 82 ± 5 and $18 \pm 8\%$, respectively [Figure 3 (top)]. Finally, we also explored if a

third channel— ^{12}C (12 amu) + $^{28}\text{SiH}_4$ (32 amu) \rightarrow $^{12}\text{C}^{28}\text{SiH}_2$ (43 amu) + H_2 (1 amu) (magenta; reaction 2) with CM functions stemmed from Lu et al.⁴⁶—could be implemented [Figure 3 (bottom)]. The overall branching ratios for the channels i, ii, and iii in the three-channel fit are 70 ± 5 , 16 ± 3 , and $14 \pm 4\%$, respectively. The fits suggest that the channels ii and iii have only minor contributions—if at all [Figure 3 (bottom)].

4. DISCUSSION

Our experiments reveal that the carbon atom reacts exoergically (-92 ± 15 kJ mol $^{-1}$) with silane to form CSiH_3 via atomic hydrogen loss in an indirect reaction involving CSiH_4 reaction intermediate(s) (Figures 5 and S1–S6 and Tables S1–S2). To understand the reaction mechanism underlying the experimental data, we introduce a comparison with electronic structure calculations to determine which structural isomers are produced. For completeness, we have considered four CSiH_3 (**p1–p4**) and three CSiH_2 isomers (**p5–p7**) as possible reaction products. The CSiH_3 isomers are the doublets silylmethylidyne [**p1** (CSiH_3 ; X^2A'')], silylene-methyl [**p2** (HCSiH_2 ; X^2B_2)], methylenesilyl [**p3** (H_2CSiH ; X^2A')], and methylsilylidyne [**p4** (CH_3Si ; X^2A'')]. Each of the three CSiH_2 isomers can be formed on both the singlet (Figure 5b) and triplet surfaces (Figure 5a). The singlet silylenecarbene [**p5** (CSiH_2 ; X^1A_1)] and silylidene [**p7** (H_2CSi ; X^1A_1)] isomers are stabilized by a carbon–silicon π -bond giving rise to carbene and silylene moieties with C_{2v} symmetry, while silaacetylene [**p6** (HCSiH ; X^1A')] is planar and supported by a Si–C triple bond of only 1.653 Å. The triplet CSiH_2 isomer **p7** (H_2CSi ; a^3A_2) has two unpaired electrons on the silicon atom, while the **p5** (CSiH_2 ; a^3A'') and **p6** (HCSiH ; a^3A'') diradicals have an unpaired electron on both the carbon and silicon atom. Considering the experimentally derived

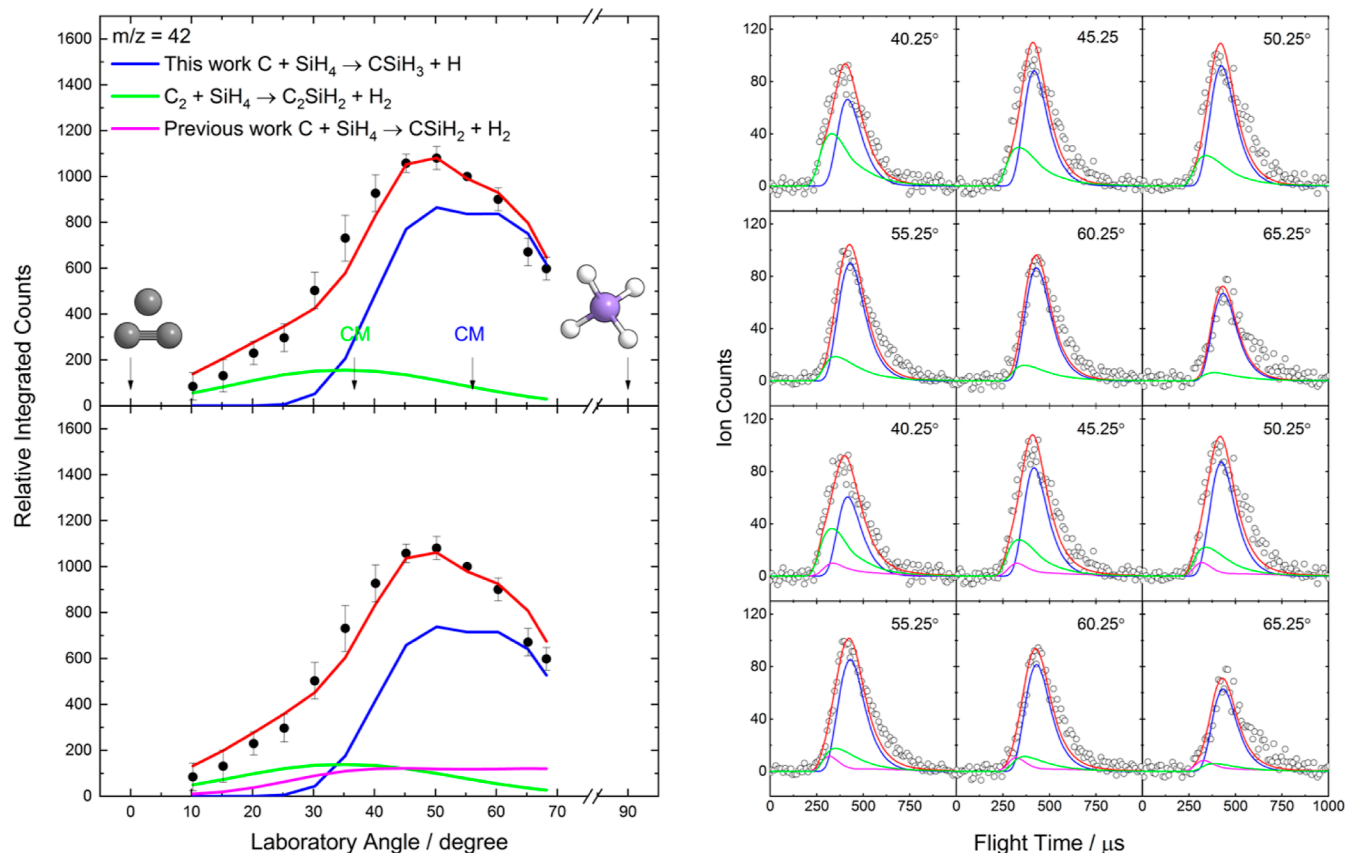


Figure 3. Laboratory angular distribution (left) and TOF spectra (right) recorded at $m/z = 42$ for the reaction of atomic carbon and dicarbon with silane. The data were fit with two channels (top) and with three channels (bottom): (i) ^{12}C (12 amu) + $^{28}\text{SiH}_4$ (32 amu) \rightarrow $^{12}\text{C}^{28}\text{SiH}_3$ (43 amu) + H (1 amu) (blue), (ii) dissociative electron impact ionization of the $m/z = 55$ ($^{12}\text{C}_2^{29}\text{SiH}_2^+$) formed in the reaction $^{12}\text{C}_2$ (24 amu) + $^{29}\text{SiH}_4$ (33 amu) \rightarrow $^{12}\text{C}_2^{29}\text{SiH}_2$ (55 amu) + H_2 (2 amu) (green) with CM functions derived from A. Rettig et al. (*J. Phys. Chem. Lett.*, **2021**, *12*, 10768–10776), and (iii) ^{12}C (12 amu) + $^{28}\text{SiH}_4$ (32 amu) \rightarrow $^{12}\text{C}^{28}\text{SiH}_2$ (43 amu) + H_2 (1 amu) (magenta) with CM functions from Lu et al. (*J. Chem. Phys.*, **2008**, *129*, 164304). The black circles depict the experimental data, colored lines the fits (red corresponding to the total fit), and error bars the 1s standard deviation. Colors of the atoms: silicon, purple; carbon, gray; and hydrogen, white.

energetics of the atomic hydrogen loss channel (-92 ± 15 kJ mol $^{-1}$) and the theoretically computed reaction energies of the four CSiH $_3$ isomers (**p1**–**p4**), the experiments and computations can be reconciled by suggesting that at least the $^2\text{p2} + \text{H}$ channel, with a computed reaction energy of -98 ± 4 kJ mol $^{-1}$, is representative of the reaction products. The formation of either $^2\text{p3}$ (H_2CSiH ; $\text{X}^2\text{A}'$) or $^2\text{p4}$ (CH_3Si ; $\text{X}^2\text{A}''$) is too exoergic, and $^2\text{p1}$ (CSiH_3 ; $\text{X}^2\text{A}''$) is energetically inaccessible at our experimental collision energy of 13.0 ± 0.2 kJ mol $^{-1}$.

The computations predict that the reaction of ground-state atomic carbon C(^3P) with silane (SiH_4) commences on the attractive triplet surface forming a vdW complex 1 kJ mol $^{-1}$ below the energy of the separated reactants (Figure S5). Similar to Ranka et al.,⁴⁷ we were unable to locate a transition state connecting this complex to any CSiH $_4$ intermediates and thus conclude that the triplet vdW complex is metastable at most and that the insertion of atomic carbon into one of the four Si–H bonds to form silylmethylene (HCSiH_3 ; $^3\text{i1}$) is essentially a barrierless process. The silylmethylene intermediate $^3\text{i1}$, despite holding two unpaired electrons on the carbon atom, is relatively low-lying (345 kJ mol $^{-1}$) and can access several reaction outcomes. First, unimolecular decomposition via elimination of molecular hydrogen from the silyl group forms *trans*-silaacetylene (HCSiH ; $^3\text{p6}$) via a barrier of 238 kJ mol $^{-1}$. Products $^2\text{p1}$ (CSiH_3) and $^2\text{p2}$ (HCSiH_2) can

be formed by the barrierless elimination of atomic hydrogen from the methyldiyne and silyl group, respectively. Second, a hydrogen atom can migrate from the silicon to the carbon atom via a barrier located 180 kJ mol $^{-1}$ below the reactants to form H_2CSiH_2 ($^3\text{i2}$). Intermediate $^3\text{i2}$ can dissociate to products $^3\text{p5}$ or $^3\text{p7}$, respectively, by the elimination of molecular hydrogen from its methylene (CH_2) or silylene (SiH_2) groups, respectively; alternatively, the elimination of molecular hydrogen sourced from both carbon and silicon centers forms $^3\text{p6}$ via a transition state 53 kJ mol $^{-1}$ above the products. Furthermore, atomic hydrogen loss products can be accessed from $^3\text{i2}$ with ejection from the methylene group yielding $^2\text{p2}$ over a relatively loose transition state located 5 kJ mol $^{-1}$ above the product channel; hydrogen atom emission from the silylene group is a barrierless process and results in $^2\text{p3}$. Third, yet another hydrogen shift from the silylene group of $^3\text{i2}$ to the carbon atom results in methylsilylene (H_3CSiH ; $^3\text{i3}$), the most stable intermediate on the triplet surface. Four products are accessible from $^3\text{i3}$: $^3\text{p6}$, $^3\text{p7}$, $^2\text{p3}$, and $^2\text{p4}$ by the elimination of molecular ($^3\text{p6}$, $^3\text{p7}$) and atomic hydrogen ($^2\text{p3}$, $^2\text{p4}$).

Following the initial insertion step, $^3\text{i1}$ can undergo intersystem crossing (ISC) to the singlet surface accessing $^1\text{i1}$ in which both electrons are paired at the carbon atom, thus representing a singlet carbene. On the singlet surface,

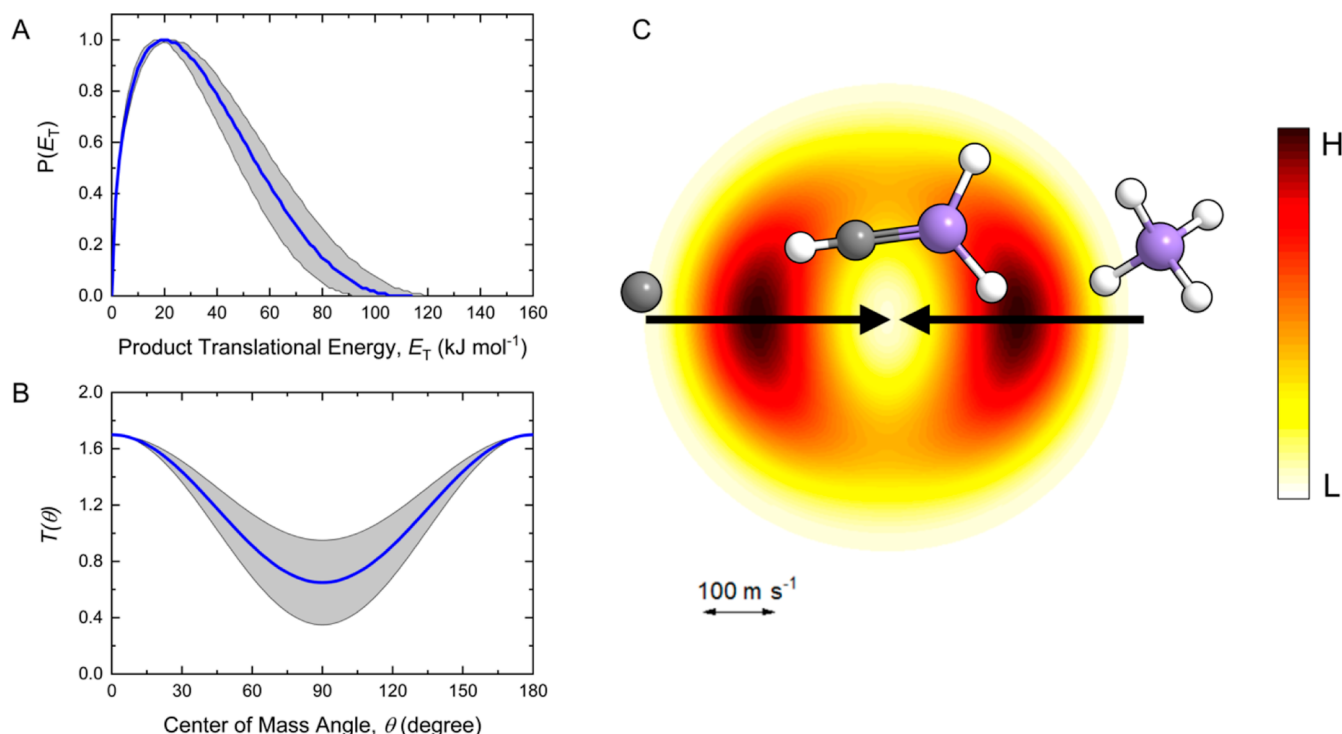


Figure 4. CM translational energy flux distribution (A), CM angular flux distribution (B), and the top view of the flux contour map (C), leading to the formation of silylenemethyl radical. Shaded areas indicate the acceptable upper and lower error limits, while the blue solid lines define the best fits. The flux contour map represents the flux intensity of the reactively scattered heavy products as a function of the CM scattering angle (θ) and product velocity (u). The color bar manifests the flux gradient from high (H) intensity to low (L) intensity. Colors of the atoms: silicon, purple; carbon, gray; hydrogen, white.

analogues of the triplet intermediates H_2CSiH_2 ($^3\text{i2}$) and H_3CSiH ($^3\text{i3}$) exists with $^1\text{i2}$ and $^1\text{i3}$ accessible via hydrogen migration. These intermediates are stabilized by 545 and 526 kJ mol⁻¹, respectively, relative to the $\text{C}(^3\text{P})$ plus SiH_4 reactants. At the CCSD/cc-pVTZ level, we locate a $^1\text{i1}$ – $^1\text{i2}$ transition state with an energy slightly higher than $^1\text{i1}$, as identified by Bartlett and co-workers.⁴⁷ However, the refined CCSD(T)/CBS energy of this transition state indicates that it is more stable than $^1\text{i1}$ and hence the electronic structure calculations suggest that silylmethylene is metastable on the singlet potential energy surface. The doublet products accessed from the singlet intermediates are formed exclusively by barrierless dissociation via hydrogen atom emission. Isomer $^2\text{p2}$ (HCSiH_2) can be accessed by hydrogen emission from the silyl group of $^1\text{i1}$ or from the methylene group of $^1\text{i2}$. Cleavage of a Si–H bond in $^1\text{i2}$ yields $^2\text{p3}$ (H_2CSiH). In $^1\text{i3}$, breaking of the silyldiyne bond results in $^2\text{p4}$ (H_3CSi); cleavage of the C–H bond forms $^2\text{p3}$. The singlet products $^1\text{p5}$, $^1\text{p6}$, and $^1\text{p7}$ are formed via molecular hydrogen loss with each involving a tight exit transition state. $^1\text{p5}$ can be formed by dissociation of $^1\text{i1}$ or $^1\text{i2}$ via Si–H or C–H bond fission, respectively. Lastly, the *trans*-silaacetylene $^1\text{p6}$ can be formed by molecular hydrogen loss from any of intermediates $^1\text{i1}$, $^1\text{i2}$, or $^1\text{i3}$, whereas silylidene $^1\text{p7}$ can only be formed by the dissociation of $^1\text{i2}$ or $^1\text{i3}$. A barrier from $^1\text{i1}$ to $^1\text{i2}$ was located at the CCSD/cc-pVTZ level of theory but vanishes at the CCSD(T)/CBS level. Therefore, we may conclude that $^1\text{i1}$ is metastable and rearranges rapidly to $^1\text{i2}$ rather than decomposing to $^1\text{p5}$, $^2\text{p2}$, and/or $^1\text{p6}$.

With the identification of at least the $^2\text{p2}$ (HCSiH_2 ; X^2B_2) isomer silylenemethyl through atomic hydrogen loss, we are

merging now the experimental and computational data in an attempt to propose the underlying reaction dynamics. For this, it is helpful to reduce the complex potential energy surface (Figure 5) to a reduced surface by eliminating the unobserved molecular hydrogen loss products and also pathways involving transition states which are higher than our collision energy of 13.0 ± 0.2 kJ mol⁻¹. This reduced surface is presented in Figure 6. $^2\text{p2}$ (HCSiH_2 ; X^2B_2) can be formed on the triplet surface via hydrogen atom emission from the silyl group of $^3\text{i1}$ or by C–H bond rupture in $^3\text{i2}$. On the singlet surface, both $^1\text{i1}$ and $^1\text{i2}$ can also undergo unimolecular decomposition via loose exit transition states leading to $^2\text{p2}$ (HCSiH_2 ; X^2B_2). Considering that the CM translational energy distribution peaks away from zero translational energy, at least one of the exit channels should be reflected in a transition state located above the energy of the separated products, that is, the transition state involved in the unimolecular decomposition of $^3\text{i2}$. Consequently, at least one channel involves the reaction sequence $^3\text{i1} \rightarrow ^3\text{i2} \rightarrow ^2\text{p2} + \text{H}$ and hence a hydrogen shift from the silicon to the carbon atom and existence of triplet silaethylene ($^3\text{i2}$). Thus, the lifetime of $^3\text{i1}$ has to be sufficiently long enough to allow this hydrogen migration to occur on the triplet surface.

Our experimental results stand in contrast to those obtained by Lu et al. who observed strongly exoergic reaction products CH_3Si ($^2\text{p4}$) and H_2CSi ($^3\text{p7}$) via atomic and molecular hydrogen loss pathways, respectively.⁴⁶ Besides, the theoretical calculations for the $\text{C}(^3\text{P}) + \text{SiH}_4$ reaction were also performed and suggested the dominant hydrogen atom loss channel along with the minor molecular hydrogen loss channel.^{47,70} The branching ratio is found to be about 1.66,⁷⁰ which is very

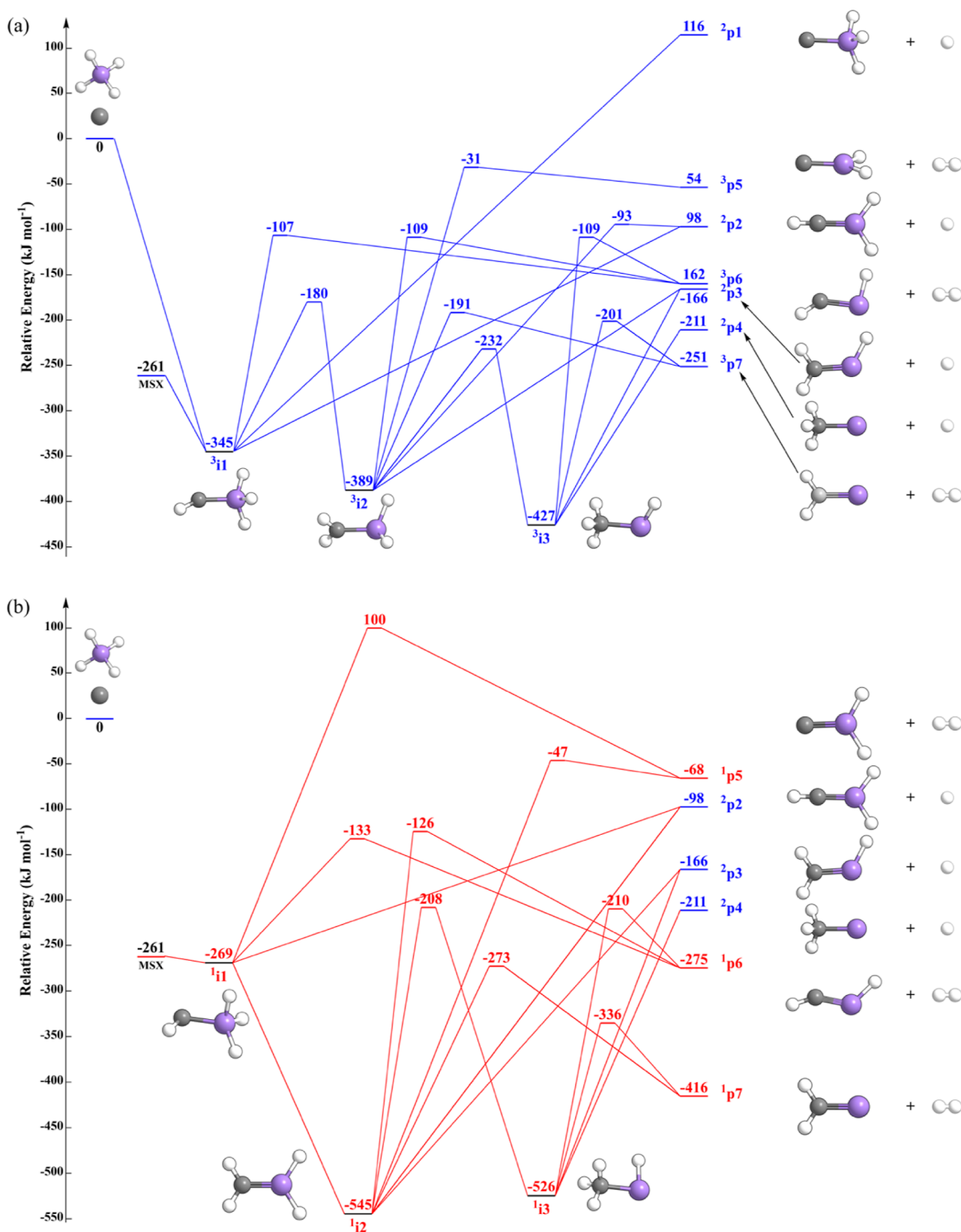


Figure 5. Pathways on the triplet (a) and singlet (b) accessed by the $\text{C}(^3\text{P}) + \text{SiH}_4(^1\text{A}_1)$ reaction leading to CSiH_3 and CSiH_2 reaction products. Energies are given in kJ mol^{-1} and are relative to the reactants, $\text{C}(^3\text{P}) + \text{SiH}_4(^1\text{A}_1)$. Singlet and triplet pathways and product channels are colored red and blue. MSX is the $^3\text{i1}-^1\text{i1}$ minimum energy crossing point (Figure S5).

comparable with the experimentally estimated value of 1.5 reported by Lu et al. One possibility for this difference could owe to the presence of electronically excited carbon atoms. Lu

et al. produced ground and electronically excited (^1D) carbon atoms by electrical discharge of CO/He or CO/H_2 mixtures, whereas our beam consists of carbon atoms solely in their

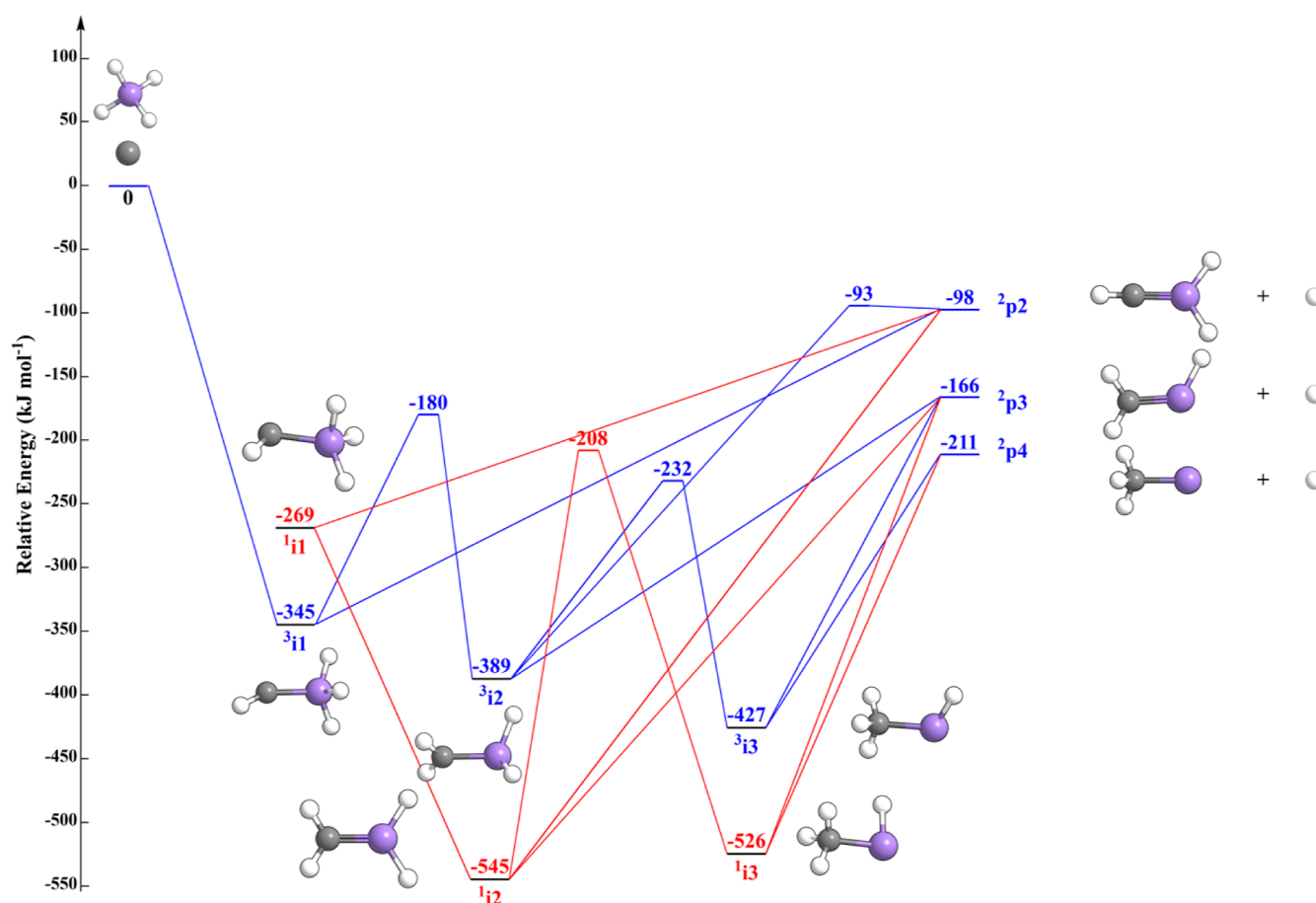


Figure 6. Simplified surface along with $\text{C}(^3\text{P}) + \text{SiH}_4(\text{X}^1\text{A}_1)$ reaction pathways leading to atomic hydrogen loss products only. Energies are given in kJ mol^{-1} and are relative to the reactants, $\text{C}(^3\text{P}) + \text{SiH}_4(\text{X}^1\text{A}_1)$. Singlet and triplet pathways and product channels are colored red and blue.

ground ^3P state. Incidentally, the ^1D state lies 122 kJ mol^{-1} above the ground state⁷¹ and could potentially account for the energy gap in the observed CSiH_3 product channels, that is, between $^2\text{p}2$ ($-98 \pm 4 \text{ kJ mol}^{-1}$) and $^2\text{p}4$ ($-211 \pm 4 \text{ kJ mol}^{-1}$). If not properly accounted for, the presence of electronically excited reactants will adversely affect the interpretation of the reactive scattering data. As a matter of fact, the photoionization efficiency curves recorded by Lu et al. detected $\text{C}(^1\text{D})$, but the contribution to the reactive scattering signal was ignored. Insertion of $\text{C}(^1\text{D})$ into the silicon–hydrogen bond of silane forms intermediate $^1\text{i}1$ that isomerizes to $^1\text{i}2$ on the singlet surface. In this scenario, the excess energy carried into the reaction coordinate by the ^1D excited state will appear as product translational energy, thereby affecting the interpretation of reaction energies, structural isomers, and ultimately reaction pathways. The involvement of the singlet surface could also account for the fact that Lu et al. observed the molecular hydrogen channel, which was not detected in our experiments; this in turn might propose that our reaction takes place on the triplet surface and does not involve ISC.

Lastly, we note that silane (SiH_4), a group 14 tetrahydride, has undergone careful studies of reactive collision in the gas phase with $\text{Si}(^3\text{P})$ ⁷² and $\text{Ge}(^3\text{P})$ as well.⁷³ The effects of the heavy atoms and the increased bond lengths they afford to molecular geometry are very apparent in structures accessed by these reactions. All CSiH_4 reaction intermediates are stabilized by covalent bonds unlike some Si_2H_4 and GeSiH_4 molecules that carry single and double hydrogen bridges and hence

multicenter bonds. Experiments observed that in the $\text{Si}(^3\text{P}) + \text{SiH}_4$ system, only the singlet disilavinylidene (SiSiH_2) molecule—the silicon analogue of vinylidene (CCH_2)—is formed by the emission of molecular hydrogen. Similarly, experimental studies of the $\text{Ge}(^3\text{P})\text{--SiH}_4$ system identified the singlet dibridged germaniumsilylene [$\text{Ge}(\mu\text{-H}_2)\text{Si}$] molecule as the nascent reaction product. Notably, the $\text{Si}(^3\text{P})$ and $\text{Ge}(^3\text{P})$ reactions with silane follow reaction coordinates underpinned by crossing from the triplet to singlet surfaces, whereas the $\text{C}(^3\text{P}) + \text{SiH}_4$ reaction occurred explicitly on the triplet surface. These differences are likely due to the heavy atom effect induced by the presence of silicon and germanium atoms.

5. CONCLUSIONS

Using the crossed molecular beams technique, we investigated the reaction of ground-state carbon atoms $\text{C}(^3\text{P})$ with silane (SiH_4) under single-collision conditions. Our experimental data suggest the formation of silylenemethyl (HCSiH_2 ; X^2B_2) via the unimolecular decomposition of triplet silaethylene (H_2CSiH_2 ; $\text{a}^3\text{A}''$). Triplet silaethylene was formed via hydrogen migration within triplet silylmethylene (HCSiH_3 ; $\text{X}^3\text{A}''$), which in turn was identified as the initial collision complex accessed via barrierless insertion of atomic carbon into the silicon–hydrogen bond of silane. Our results mark the first observation of the silylenemethyl radical where only its more stable isomers methylsilyldyne (CH_3Si) and methylenesilyl (H_2CSiH) had been detected previously in irradiated methane–silane ice mixtures;^{74,75} methylsilyldyne was also

observed in a previous crossed molecular beams experiment.⁴⁶ The silylenemethyl radical is isoelectronic with the vinyl (H_2CCH) radical yet remains distinct in its molecular geometry. The vinyl radical is planar (C_s) and the unpaired electron is stabilized in a sp^2 hybridized orbital located at the C–H group (Figure 7). Replacement of a single carbon atom

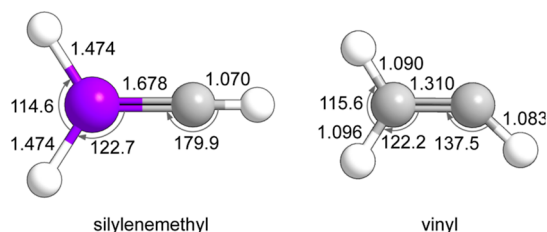


Figure 7. Molecular geometries for the isoelectronic silylenemethyl (HCSiH_2) and vinyl (HCCCH_2) radicals in their respective 2B_2 and $^2A'$ electronic ground states.

with silicon and its larger valence orbitals ultimately influences hybridization efficiency in the resulting silylenemethyl radical.^{76–78} In this configuration, the carbon atom is connected to silicon by a single σ and π bond; however, it is not sp^2 hybridized. Bonding at the carbon atom adopts sp character, resulting in a Si–C bond length of 1.678 Å midway between the double and triple bond lengths observed in organosilicon molecules. Consequently, the unpaired electron is stabilized in a nonbonding p orbital on the carbon atom perpendicular to the silicon–carbon axis.

Although CSiH_3 isomers have not been detected in the CSEs of carbon-rich AGB stars, the availability of atomic carbon and silane in these environments along with the presence of saturated molecules carrying silicon-carbon bonds such as silylmethane (SiH_3CH_3) suggest that the silylenemethyl (HCSiH_2 ; X^2B_2) radical should be present within CSEs such as IRC+10216. Therefore, silylenemethyl could be an important precursor to pure silicon-carbide gaseous molecules such as silicon carbide (SiC). Contemporary models of carbon-rich CSEs however treat silicon-carbide dust as the sole consequence of Si_xC_y nucleation and neglect the obvious chemistry involving abundant chemical species in these envelopes such as carbon and silane. Our results suggest that these models must be updated to include contributions from organosilicon molecules as potential precursors to pure gaseous silicon-carbide molecules and ultimately to silicon-carbide dust as demonstrated in the present study.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.2c01853>.

Comparison of CM functions between our study and Lu et al.; CCSD/cc-pVTZ optimized geometries of CSiH_3 and CSiH_2 isomers along with their bond lengths (angstroms), bond angles, and ground-state symmetry; CCSD/cc-pVTZ optimized structures of singlet and triplet intermediates, CPMCSCF/TZVPP optimized minimum-energy crossing point, including electronic states and point groups; CCSD/cc-pVTZ optimized geometries of the transition states for the $\text{C}(^3P) + \text{SiH}_4$ (X^1A_1) reaction on the adiabatic singlet and triplet ground-state potential energy surfaces; CCSD(T)/CBS

energies with CCSD/cc-pVTZ zero-point energy corrections of CCSD/cc-pVTZ optimized reactants, intermediates, transition states, H, and H_2 dissociation products on the adiabatic triplet and singlet ground-state potential energy surfaces of CSiH_4 ; and CCSD/cc-pVTZ optimized Cartesian coordinates of intermediates, transition states, products, and CPMCSCF/TZVPP optimized minimum-energy crossing point on the triplet and singlet CSiH_4 potential energy surfaces (PDF)

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Notes

The authors declare no competing financial interest.

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