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J. Phys. Chem. Lett., **Just Accepted Manuscript** • DOI: 10.1021/acs.jpclett.8b01422 • Publication Date (Web): 30 May 2018

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Are Non-Adiabatic Reaction Dynamics the Key to Novel Organosilicon Molecules? The Silicon (Si(^{3}P)) – Dimethylacetylene ($C_4H_6(X^1A_{1g})$) System as a Case Study

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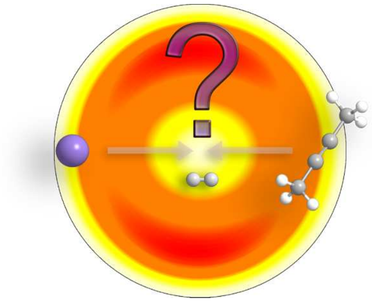
ABSTRACT: The bimolecular gas phase reaction of ground state silicon (Si; ^3P) with dimethyl-acetylene (C_4H_6; X^1A_{1g}) was investigated under single collision conditions in a crossed molecular beams machine. Merged with electronic structure calculations, the data propose non-adiabatic reaction dynamics leading to the formation of singlet SiC_4H_4 isomer(s) and molecular hydrogen (H_2) via indirect scattering dynamics along with intersystem crossing (ISC) from the triplet to the singlet surface. The reaction may lead to distinct energetically accessible singlet SiC_4H_4 isomers (**^{1}p8** to **^{1}p24**) in overall exoergic reaction(s) ($-107\,^{+12}_{-20}$ kJ mol^{-1}). All feasible reaction products are either cyclic, carry carbene analogous silylene moieties, or carry C-Si-H or C-Si-C bonds that would require extensive isomerization from the initial collision complex(es) to the fragmenting singlet intermediate(s). The present study demonstrates the first successful crossed beams study of an exoergic reaction channel arising from bimolecular collisions of silicon, Si(^3P), with a hydrocarbon molecule.

Table of Contents Graphic:



Langmuir's concept of isoelectronicity, in which two molecular entities with the same number of valence electrons have similar chemistries,[1-2] along with Lewis' and Kasha's notion of intersystem crossing (ISC),[3] defined then as a radiationless process involving a transition between two electronic states with different spin multiplicities,[4] have been instrumental in developing modern concepts of chemical bonding and in understanding basic principles of molecular structure and chemical reactivity of isovalent systems. Isovalent species such as the elements of main group 14 are expected to reveal valuable consistencies and predictabilities in their chemical bonding and chemical dynamics upon reactions with hydrocarbons with differences in the stability of carbon-silicon single versus double bonds resulting in major effects on the molecular structure.[5-7] Particular interest has been dedicated to the chemistries and reaction dynamics of the isovalent carbon (C) and silicon (Si) atoms. For instance, on the singlet C_3H_2 potential energy surface (PES), a substitution of a single carbon atom by silicon leads to a novel C_{2v} symmetric silacyclopropyne (c-C_2SiH_2) molecule,[8-9,10] whose isovalent singlet cyclopropyne (c-C_2CH_2) analog represents a transition state to propadienylidene (H_2CCC) automerization (Scheme 1).[11] Also, compared to the 'light' carbon atom, the incorporation of a 'heavier' silicon atom in molecular systems is expected to favor spin-orbit coupling, and thus intersystem crossing (ISC) is anticipated to be more common in organosilicon molecules as compared to their isovalent hydrocarbon analogs. Therefore, reactions of ground state carbon $C(^3P_j)$ and silicon $Si(^3P_j)$ with hydrocarbons define critical benchmarks to elucidate the similarities, but also critical differences in chemical bonding, molecular structures, and (non-) adiabatic reaction dynamics of organosilicon and hydrocarbon systems.

Whereas the kinetics[12-15] and chemical dynamics[16-22] of reactions of ground state carbon atoms with unsaturated hydrocarbons have been thoroughly explored, a systematic investigation of isovalent organosilicon systems and the potential role of intersystem crossing is missing from the emerging dialogue surrounding silicon-hydrocarbon reactivity.[12-15, 23-27] Interestingly, kinetic studies by Basu and Husain[28-29] and Canosa *et al.*[30] suggest that ground state silicon, $Si(^3P_j)$, should react fast, close to gas kinetics values, with unsaturated hydrocarbons revealing rate constants of a few 10^{-10} $cm^3\ s^{-1}$. However, these studies probed solely the decay kinetics of the silicon atom, and reaction products could not be assigned. An identification of these reaction products would be of immense interest to the reaction dynamics and physical organic chemistry communities as these information provide fundamental knowledge on the reaction mechanism(s) and also on exotic chemical bonding in (cyclic) organosilicon molecules and how they differ from isovalent hydrocarbon molecules.

Here, we present for the first time results of a crossed molecular beam experiment of an exoergic reaction of ground state atomic silicon with a hydrocarbon molecule – the reaction of ground state silicon atoms (Si; ^3P) with dimethylacetylene (2-butyne; C_4H_6; X^1A_{1g}) - under single collision conditions to probe the reactivity and non-adiabatic reaction dynamics of the silicon – dimethylacetylene system and to illustrate how they differ from those reactions of isovalent carbon atoms with dimethylacetylene. Although ground state atomic silicon does not react with any C1-C3 hydrocarbon at collision energies lower than 100 kJ mol^{-1} in crossed molecular beam experiments, the C4 hydrocarbon dimethylacetylene (C_4H_6) reveals an unexpected reactivity upon collisions with ground state silicon atoms. These involve indirect scattering dynamics and intersystem crossing from the triplet to the singlet manifold, multiple isomerization steps through ring opening/closure and hydrogen migrations, and eventually molecular hydrogen loss synthesizing for the first time free SiC_4H_4 isomer(s) in the gas phase via overall exoergic reaction(s). These findings unravel an unusual silicon chemistry via silicon-carbon bond coupling and exotic non-adiabatic dynamics that are distinct compared to the isovalent hydrocarbon system.

Reactive scattering signal was monitored at mass-to-charge ratios (*m/z*) from 84 to 79 to probe the existence of adducts along with atomic and molecular hydrogen loss channels. Considering the natural abundances of three silicon isotopes (^{30}Si(3.10 %), ^{29}Si(4.67 %), ^{28}Si (92.23 %)) and carbon (^{13}C(1.1 %), ^{12}C (98.9 %)), no signal was detected at *m/z* = 84 and 83 revealing the absence of adducts ($^{30}SiC_4H_6^+$/$^{29}SiC_4H_6^+$) and the atomic hydrogen loss channel ($^{30}SiC_4H_5^+$). Signal was observed at *m/z* = 82, 81, and 80. Ion counts at *m/z* = 82 could arise from the adduct ($^{28}SiC_4H_6^+$), the atomic hydrogen loss ($^{29}SiC_4H_5^+$), and the molecular hydrogen loss channel ($^{30}SiC_4H_4^+$); signal at *m/z* = 81 might be linked to the atomic hydrogen loss pathway ($^{28}SiC_4H_5^+$) or to a molecular hydrogen loss ($^{29}SiC_4H_4^+$); finally, counts at *m/z* = 80 can originate from the molecular hydrogen emission channel ($^{28}SiC_4H_4^+$). Considering that the time-of-flight spectra at *m/z* = 82, 81, and 80 are superimposable after scaling and that signal at *m/z* = 82 and 81 is present at a level of close to 5 ± 2 %, signal at *m/z* = 82, 81, and 80 can be attributed to ionized $^{30}SiC_4H_4$, $^{29}SiC_4H_4$, and $^{28}SiC_4H_4$ (hereafter: SiC_4H_4), respectively. Lastly, signal at *m/z* = 79 can be attributed to dissociative electron impact fragmentation of SiC_4H_4 to $SiC_4H_3^+$. Hence, the laboratory data alone afford compelling evidence on the existence of the molecular hydrogen loss pathway forming SiC_4H_4 isomers in the reaction of ground state silicon atoms with dimethylacetylene. The related laboratory angular distribution obtained at *m/z* = 80 ($^{28}SiC_4H_4{}^+$) reveals a pronounced distribution maximum close to the center-of-mass (CM) angle of 56.5° ± 0.6° and extends over a range greater than 40° in the laboratory frame (Figure 1). These findings propose a complex forming reaction mechanism involving SiC_4H_6 intermediate(s) that undergo decomposition via molecular hydrogen emission to SiC_4H_4 isomer(s).

The goals of our study are not only to determine the molecular formula of the reaction product (SiC_4H_4), but also to expose the nature of the product isomer(s) together with the underlying formation mechanism(s) of these newly synthesized organosilicon molecules. To achieve this objective, it is critical to obtain information on the chemical dynamics. This is accomplished by utilizing a forward-convolution routine,[31] which converts the laboratory data (TOF spectra, laboratory angular distribution) of the SiC_4H_4 product(s) probed via its parent ion at $m/z = 80$ into the center-of-mass (CM) reference frame. This approach produces two 'best-fit' CM functions: the translational energy flux distribution $P(E_T)$ and the angular flux distribution $T(\theta)$ (Figure 2). A detailed examination of the CM translational energy flux distribution, $P(E_T)$, discloses a maximum translational energy (E_{max}) of $122\,^{+12}_{-20}$ kJ mol^{-1}. The $P(E_T)$ is very sensitive to the high energy cut off, and fits that terminate beyond the limit result in simulated TOFs that are too fast and too broad. For molecules born without rovibrational excitation, E_{max} represents the sum of the collision energy (15.4 ± 0.4 kJ mol^{-1}) plus the reaction exoergicity. Therefore, a subtraction of the collision energy from E_{max} discloses that the reaction forming SiC_4H_4 plus molecular hydrogen is exoergic by $107\,^{+12}_{-20}$ kJ mol^{-1}. Further, the $P(E_T)$ exhibits a broad distribution maximum from 20 to about 40 kJ mol^{-1} suggesting tight exit transition state(s) upon unimolecular decomposition of the SiC_4H_6 complex forming SiC_4H_4 isomer(s) via molecular hydrogen elimination. Finally, the center-of-mass angular flux distribution $T(\theta)$ portrays flux over the complete scattering range from 0° to 180°. The 'best-fit' $T(\theta)$ causes a nearly symmetric forward-backward scattered distribution, indicating the lifetime(s) of the decomposing complex(es) is(are) longer than its(their) rotational period(s). Moreover, the distribution maximum close to 90° suggests geometrical constraints upon fragmentation of at least one SiC_4H_6 intermediate, in which the hydrogen molecule is emitted perpendicularly to the rotational plane of the fragmenting intermediate almost parallel to the total angular momentum vector. However, an isotropic (flat) distribution can fit the data as well.

Having demonstrated that the bimolecular gas phase reaction of ground state silicon atoms with dimethylacetylene leads to the formation of SiC_4H_4 product(s) along with molecular hydrogen, we now explore the possible SiC_4H_4 isomers synthesized in this reaction (Figure 3; Supporting

Information). This is accomplished by a comparison of the experimentally determined reaction energy $107\,^{+12}_{-20}$ kJ mol^{-1} with the reaction energies obtained from our electronic structure calculations (Theoretical Methods). Considering that the SiC_4H_4 products might be formed in their singlet and/or triplet states, but the reaction is initiated on a triplet surface, both the triplet and singlet potential energy surfaces (PESs) must be considered. On the singlet surface, our calculations reveal the existence of 153 SiC_4H_4 isomers (**^{1}p1** – **^{1}p153,** Table S1), of which the energetically lowest structures are compiled in Figure 3a. Considering the experimental reaction exoergicity of $107\,^{+12}_{-20}$ kJ mol^{-1}, these energetics suggest that within the error limits, at least seventeen SiC_4H_4 isomers **^{1}p8** - **^{1}p24** can account for the experimental data and hence represent likely reaction products. The corresponding triplet states of the energetically low-lying isomers are compiled in Figure 3b (Table S2). Based on our collision energy of 15.4 ± 0.4 kJ mol^{-1}, only **^{3}p1** is energetically accessible; however, the computed exoergicity of −145 ± 5 kJ mol^{-1} does not match the experimental data of $107\,^{+12}_{-20}$ kJ mol^{-1}. Therefore, since the reaction of ground state atomic silicon with dimethylacetylene starts on the triplet surface, but the energetically accessible product(s) (**^{1}p8** - **^{1}p24**) together with molecular hydrogen have both singlet states, at least one reaction channel must involve intersystem crossing and therefore non-adiabatic reaction dynamics. A detailed inspection of the geometries of the reactants and potential products (**^{1}p8** - **^{1}p24**) reveals that the cyclic isomers **^{1}p10**, **^{1}p12**, **^{1}p16,** **^{1}p17,** and **^{1}p22** carry silylene (SiH_2), silylidyne (SiH) or acetylenic (C_2H_2) moieties, or can be represented by the silicon analogue of a carbene functional group (**^{1}p18,** **^{1}p21,** **^{1}p23,** **^{1}p24**). In isomers **^{1}p8**, **^{1}p13**, and **^{1}p20**, the silicon atom is formally inserted between carbon atom(s) and hydrogen, whereas isomers **^{1}p9**, **^{1}p11**, **^{1}p14**, **^{1}p15**, and **^{1}p19** can be rationalized as acyclic silylcarbene (Si=C=) moieties. Only four singlet products (**^{1}p11,** **^{1}p15,** **^{1}p16,** **^{1}p19**) retain a methyl group from the dimethylacetylene reactant. These findings may propose extensive isomerization from the initial collision complex(es) to the fragmenting singlet SiC_4H_6 intermediate(s) such as via hydrogen migration and ring opening/closure synthesizing the SiC_4H_4 products along with molecular hydrogen. Considering the complexity of the reaction, a complete theoretical analysis of the SiC_4H_6 and SiC_4H_4 triplet and singlet surfaces along with a full analysis of conical intersections and a statistical Rice-Ramsperger-Kassel-Marcus (RRKM) treatment is beyond the scope of this Letter, but will be conducted in the future. Nonetheless, it is interesting to consider the aromatic **^{3}p1** isomer and its formation in this reactive scattering experiment. We found two transition states on the triplet surface connecting distinct triplet SiC_4H_6 isomers to **^{3}p1** via molecular hydrogen elimination (Figure 4). Considering the collision energy of 15.4 ± 0.2 kJ mol^{-1}, the transition state located 21 kJ mol^{-1} above the Si(^{3}P) + (C_4H_6; X^1A_{1g}) entrance channel is unlikely to be passed under our experimental conditions.

In conclusion, our investigation of the bimolecular gas phase reaction of ground state atomic silicon (Si; ^{3}P) with dimethylacetylene (C_4H_6; X^1A_{1g}) exposed indirect scattering dynamics involving SiC_4H_6 collision complex(es) together with a facile formation of at least one SiC_4H_4 isomer via intersystem crossing (ISC) from the triplet to the singlet surface. These non-adiabatic reaction dynamics form at least one SiC_4H_4 isomer (**^{1}p8** - **^{1}p24**) in an overall exoergic reaction (107^{+12}_{-20} kJ mol^{-1}) via a tight exit transition state. Recall that the existence of a tight exit transition state was predicted based on the off zero peaking of the center-of-mass translational energy distribution. Despite the open questions on the underlying reaction mechanisms, we provided compelling evidence on non-adiabatic reaction dynamics involved in the Si(^{3}P) - C_4H_6(X^1A_{1g}) system leading SiC_4H_4 isomer(s). This is the first successful study under single collision conditions in which reactive scattering signal of ground state atomic silicon with a closed shell hydrocarbon was observed in an overall exoergic reaction, with reactions of atomic silicon with C1 – C3 hydrocarbons revealing no evidence for bimolecular exoergic reaction channels under single collision conditions. Considering the rate constants of reactions of ground state silicon atoms with acetylene and ethylene, Smith *et al.* proposed that non-adiabatic reaction dynamics involving spin-forbidden yet exoergic molecular hydrogen loss channels are open[32] and that these reactions are initiated by a barrierless addition of atomic silicon to the π electron density of unsaturated hydrocarbons with the lifetime of the collision complex, with respect to redissociation, varying significantly between the conditions of the low temperature kinetics and crossed molecular beam studies.[33] Hence at the high collision energies used in the crossed beam experiments of up to 100 kJ mol^{-1} for the silicon – acetylene system,[34] the collision complexes likely undergo rapid redissociation rendering non-adiabatic reaction pathways non-competitive and thus difficult to observe.

It is interesting to compare these findings with the isovalent atomic carbon C(^3P_j) – dimethylacetylene[35] system thus revealing striking similarities, but also pronounced differences to the reaction of atomic silicon Si(^3P_j). Here, the reaction of atomic carbon is also initiated on the triplet surface via barrierless addition to the carbon-carbon triple bond yielding eventually a dimethylcyclopropenylidene reaction intermediate. However, the lighter carbon atom prefers adiabatic reaction dynamics by ring opening of dimethylcyclopropenylidene to dimethylpropargylene (CH_3CCCCH_3) followed by atomic hydrogen loss exclusively on the triplet surface forming the resonantly stabilized 1-methylbutatrienyl radical (CH_3CCCCH_2; X^2A'').[35] The reactivity of carbon is dictated by its preference to form carbon-carbon multiple bonds as in 1-methylbutatrienyl, whereas silicon is recognized to form exotic cyclic products or silenetype structures, which are analogous to carbenes in the carbon chemistry, as discussed above. Consequently, the comparison of the chemical dynamics of the silicon-dimethylacetylene with the isovalent carbon-dimethylacetylene effectively directs how we rationalize the chemical reactivity of silicon-containing systems and how the reaction mechanism, thermochemistry, and chemical bonding changes from silicon to carbon thus defining the silicon-dimethylacetylene system as a crucial prototype for a detailed understanding of the formation of small (organo)silicon molecules. The divergence of the chemical behavior of silicon compared to carbon is essential to our knowledge of the chemistry and will influence how we explain chemical bonding involving silicon atoms and how we think about chemical structure in the future. Further experimental and theoretical studies of these systems such as of the C_4H_6 isomers 1,3-butadiene, 1,2-butadiene, and 1-butyne under single collision conditions are merited to fully reveal the exotic reactivity of atomic silicon along with the formation of unusual organosilicon molecules to expand the understanding of their electronic structures, chemical bonding, and stability.

Methods

Experimental Methods

The reaction of atomic silicon (Si; ^3P) with dimethylacetylene (2-butyne; C_4H_6; X^1A_{1g}) was explored in a universal crossed molecular beams machine at the University of Hawaii at Manoa.[36-40] In the primary source chamber, a pulsed beam of neon-seeded silicon atoms was prepared *in situ* by ablating a silicon target by 266 nm photons from the output of a Spectra-Physics Quanta-Ray Pro 270 Nd:YAG laser operating at 30 Hz and power of 10 ± 1 mJ per pulse.[41-43] The ablated species were seeded in neon (Ne; 99.999 %; Specialty Gases of America) at a backing pressure of 4 atm released from a piezoelectric valve operated with a repetition rate of 60 Hz, a pulse width of 80 μs, and a peak voltage of −400 V. The pulsed beam of the silicon atoms passed through a skimmer and a four-slit chopper wheel rotating at 120 Hz; the chopper wheel selected a pulse of the silicon atom beam with a well-defined peak velocity (v_p) and speed ratio (S) of 1017 ± 19 ms^{-1} and 5.3 ± 0.5, respectively. In the source secondary chamber, a pulsed beam of dimethylacetylene (99 % +, Sigma-Aldrich) was prepared by a second piezoelectric valve operating at 60 Hz, a pulse width of 80 μs, and a peak voltage of −400 V with a backing pressure of 550 Torr; this resulted in a peak velocity and speed ratio of 796 ± 8.1 ms^{-1} and 8.2 ± 0.3. After passing through the secondary skimmer, the pulsed dimethylacetylene beam crossed perpendicularly with the beam of atomic silicon resulting in a collision energy of 15.4 ± 0.4 kJ mol^{-1}

and center-of-mass (CM) angle of 56.5 ± 0.6°. The primary and secondary pulsed valves were triggered respectively at 1800 μs and 1820 μs with respect to time zero defined by the infrared diode mounted at the top of the chopper wheel, while the flash lamps of the ablation laser were fired 39 μs after the primary pulse valve with Q-switch initiated 186 μs after the flash lamp pulse. The ablation laser is operated at half the frequency of the pulsed valves to allow a 'laser on' minus 'laser off' background subtraction.

The reactively scattered products were mass filtered after ionization utilizing a quadrupole mass filter and detected by a Daly-type TOF detector housed in a rotatable, triply-differentially pumped ultrahigh vacuum chamber ($< 2 \times 10^{-11}$ Torr) after electron-impact ionization of the neutral products at an electron energy of 80 eV and an emission current of 2 mA. This detector can be rotated within the plane defined by the primary and the secondary reactant beams allowing recording of angular-resolved TOF spectra. At each angle, up to 5×10^5 TOF spectra were accumulated to obtain good signal-to-noise ratios. The recorded TOF spectra were then integrated and normalized to the intensity of the TOF at the CM angle to extract the product angular distribution in the laboratory frame. In order to acquire information on the scattering dynamics, the laboratory data were then transformed from the laboratory into the CM reference frame utilizing a forward-convolution routine. This iterative method employs a parametrized or point-form translational energy flux distribution, $P(E_T)$, and angular flux distribution, $T(\theta)$, in the CM frame. Laboratory TOF spectra as well as the angular distribution are calculated from the $P(E_T)$ and $T(\theta)$ functions, and are averaged over a grid of Newton diagrams accounting for the apparatus functions, beam divergences, and velocity spreads. For the fitting, we considered a reactive scattering cross section of an $E_T^{-1/3}$ energy dependence, where E_T defines the translational energy. This method is adopted within the line-of-center model for exoergic and barrierless entrance reactions dominated by long-range attractive forces. In addition to the mass spectrometric detection, the spin states of silicon atoms were characterized utilizing laser-induced fluorescence (LIF). Silicon atoms in their ground (triplet) and first excited (singlet) states were probed via the $3p4s\ {}^3\mathrm{P}$ — $3p^2\ {}^3\mathrm{P}$ and $3p4s\ {}^1\mathrm{P}$ — $3p^2\ {}^1\mathrm{D}$ transitions near 251 nm and 288 nm, respectively. The ${}^3\mathrm{P}$ ground state was detected for several j states. No signal was observable for the $3p4s\ {}^1\mathrm{P} \rightarrow 3p^2\ {}^1\mathrm{D}$ emission implying the absence of electronically excited silicon atoms (Si; ${}^1\mathrm{D}$) in the beam.

Theoretical Methods

The geometries of possible triplet and singlet SiC_4H_4 isomers are optimized via density functional B3LYP[44-47]/cc-pVTZ and coupled cluster[48-51] CCSD/cc-pVTZ calculations. The completed basis set limits,[52] CCSD(T)/CBS energies, are obtained by extrapolating the CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ energies, with B3LYP/cc-pVTZ or CCSD/cc-pVTZ zero-point energy corrections. The accuracy of these CCSD(T)/CBS energies are expected to be within 8 kJ mol^{-1}.[53] GAUSSIAN09 programs[54] are facilitated in density functional and coupled cluster calculations.

Supporting Information

Table S1: Structures, relative energies (E) with respect to the separated reactants, point groups, and electronic wave functions of potential singlet products ^{1}p25-^{1}p153. Table S2: Cartesian coordinates of singlet products ^{1}p1-^{1}p153. Table S3: Cartesian coordinates of potential triplet products ^{3}p1-^{3}p24.

Acknowledgements

The Hawaii group thanks the National Science Foundation (NSF) for support under award CHE-1360658. Computer resources at the National Center for High-Performance Computing of Taiwan were utilized in the calculations.

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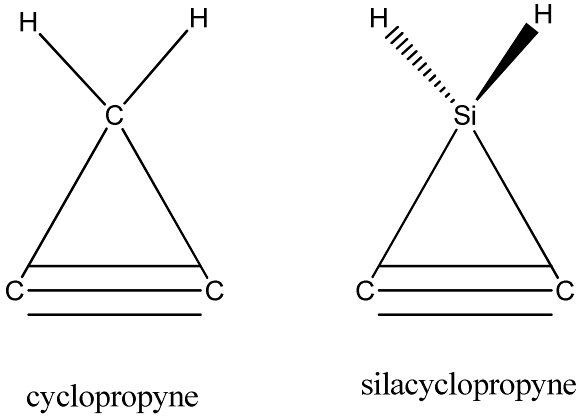

Scheme 1. Structures of cyclopropyne and silacyclopropyne. Singlet cyclopropyne represents a transition state, whereas electronic structure calculations predict that silacyclopropyne denotes a reaction intermediate.

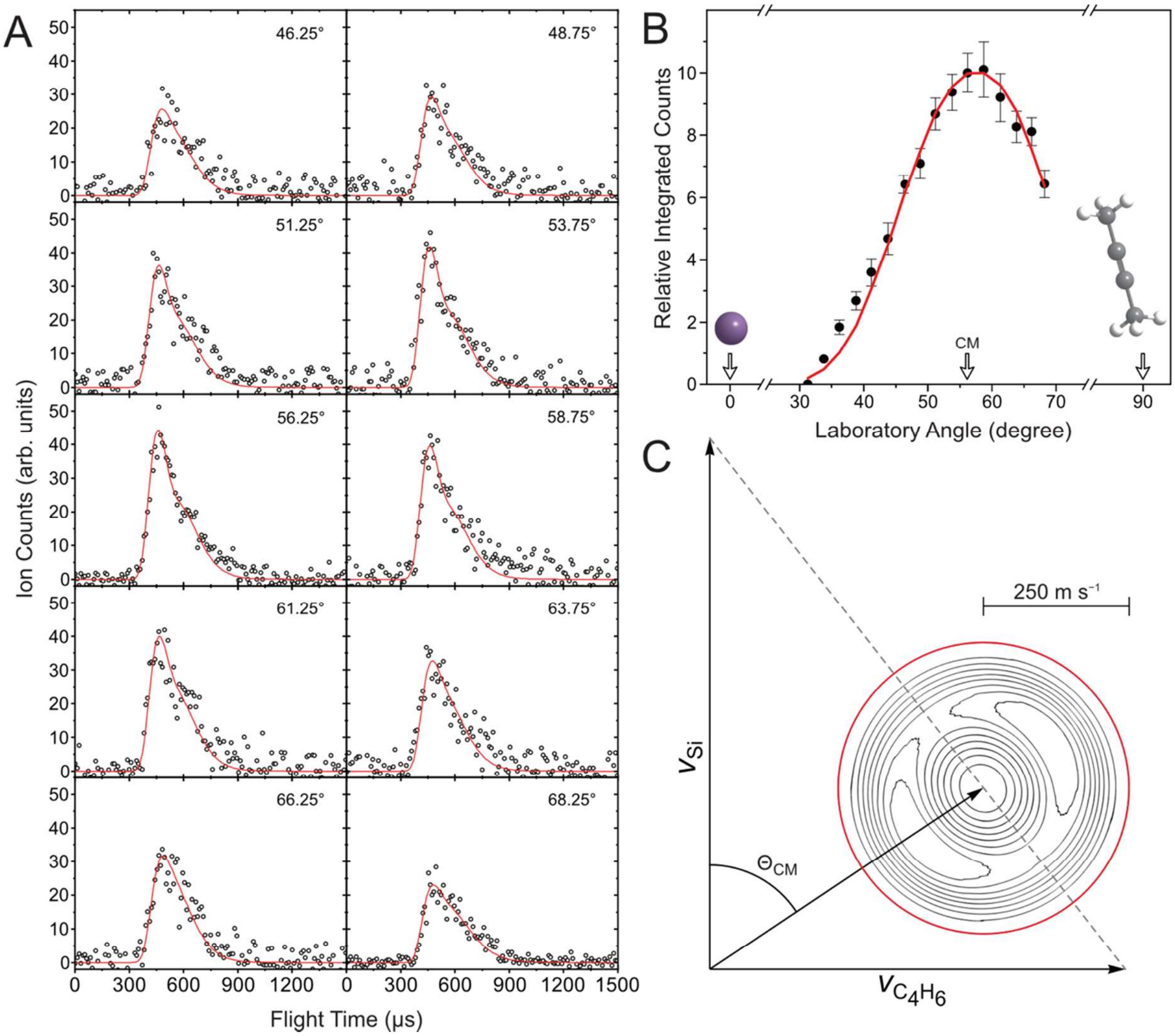

Figure 1. Time-of-flight (TOF) spectra (A) and laboratory angular distribution (B) recorded at a mass-to-charge (*m/z*) ratio of 80 ($SiC_4H_4^+$) in the reaction of ground-state atomic silicon (Si(^{3}P)) with dimethylacetylene(CH_3CCCH_3). The circles define the experimental data and the red lines represent the fitting based on the best-fit center-of-mass functions, as depicted in Figure 2. Error bars are ±1σ. The CM arrow indicates the center-of-mass angle. (C) Corresponding Newton diagram relating the laboratory reactant and CM frame product velocities. The SiC_4H_4 product flux is inlaid within the Newton circle (red), which has a radius equal to the maximum CM velocity of SiC_4H_4 as defined by the CM functions depicted in Figure 2.

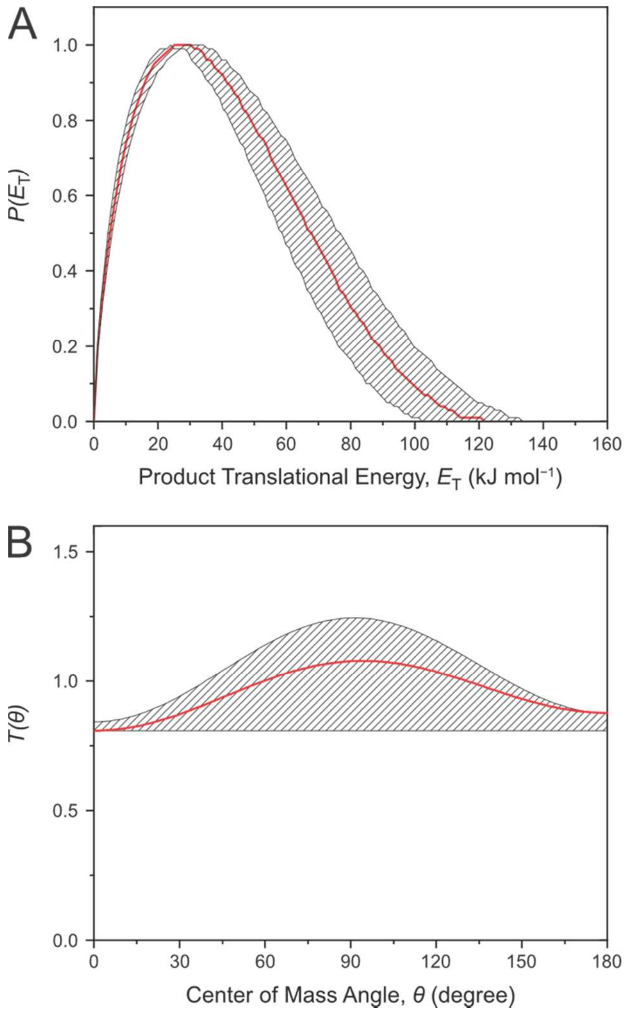

Figure 2. Center-of-mass (A) translational energy flux distribution *P*(E_T*)* and (B) angular flux distribution *T(θ)* leading to the formation of the SiC_4H_4 molecule(s) plus molecular hydrogen in the reaction of ground-state atomic silicon (Si(^{3}P)) with dimethylacetylene (CH_3CCCH_3). Hatched areas bound the acceptable upper and lower error limits of the best-fit functions denoted by red lines.

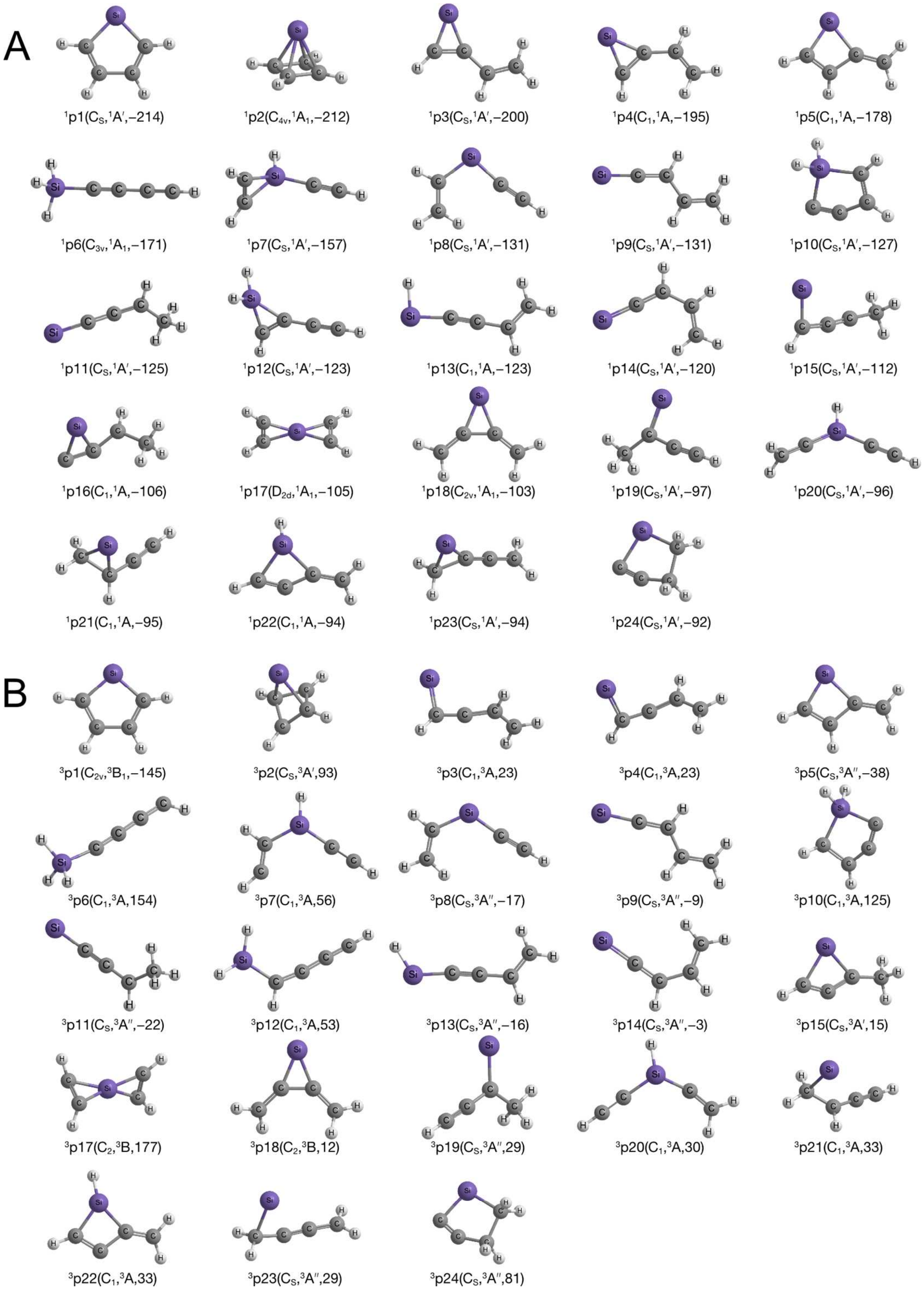

Figure 3. Molecular structures of singlet (a) and triplet (b) SiC_4H_4 products **p1-p24** along with their relative energies in kJ mol^{-1} with respect to the separated reactants, point groups, and electronic wave functions. Note that upon optimization, ^{3}**p16** collapses to ^{3}**p11**.

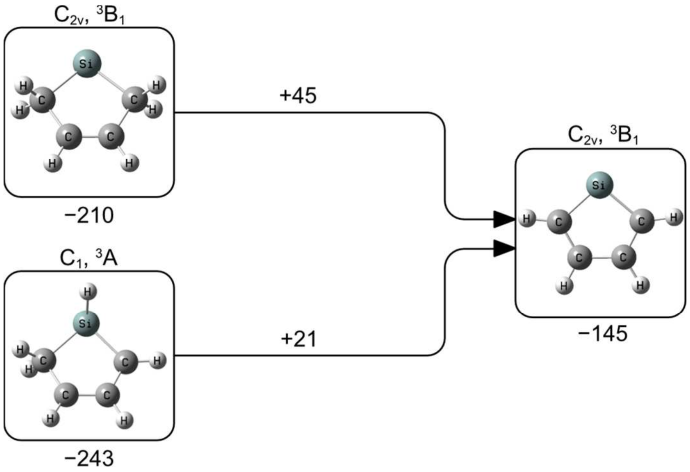

Figure 4. Reaction pathways leading to the triplet product ^{3}**p1**. Relative energies (kJ mol^{-1}), point groups, and electronic wave functions are also included.