



A crossed molecular beams investigation of the reactions of atomic silicon ($\text{Si}(^3\text{P})$) with C_4H_6 isomers (1,3-butadiene, 1,2-butadiene, and 1-butyne)

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ABSTRACT

The bimolecular gas phase reactions of ground state silicon ($\text{Si}(^3\text{P})$) with the C_4H_6 isomers 1,3-butadiene, 1,2-butadiene, and 1-butyne were investigated under single collision conditions in a crossed molecular beams machine at collision energies of about 15 kJ mol^{-1} . Our data suggest each reaction proceeds indirectly via SiC_4H_6 intermediates that decompose by elimination of molecular hydrogen through tight exit transition states. In the $\text{Si}(^3\text{P})$ plus 1,3-butadiene system, multiple product channels are open as evidenced by the observation of molecular hydrogen, hydrogen deuteride, and molecular deuterium losses in experiments utilizing isotopologues of 1,3-butadiene. Non-adiabatic reaction dynamics likely dominate the reaction mechanism in each $\text{Si}(^3\text{P})$ -hydrocarbon system via intersystem crossing from the triplet to the singlet manifold. These systems are unique in that the reactions proceed at relatively low collision energies and yield products in overall exoergic reactions, unlike the reactions of $\text{Si}(^3\text{P})$ with the C1-C3 hydrocarbon which have highly endoergic product channels.

1. Introduction

Langmuir's concept of isoelectronicity, in which two molecular entities with the same number of valence electrons have similar chemistries [1,2], has been instrumental in developing modern concepts of chemical bonding and in understanding the basic principles of molecular structure and chemical reactivity of isovalent systems. Atomic carbon (C) and silicon (Si) belong to the same main group IV possessing a triplet electronic ground state ^3P ; however, when these atoms are compared in isoelectronic systems, differences in their sizes ($r(\text{C}) \sim 77 \text{ pm}$; $r(\text{Si}) \sim 111 \text{ pm}$; nonpolar covalent radii) and electronegativity ($\text{EN}(\text{C}) = 2.544$; $\text{EN}(\text{Si}) = 1.916$; Pauling units) result in carbon-carbon (C–C; $140\text{--}160 \text{ pm}$) and silicon-carbon (Si–C; $180\text{--}200 \text{ pm}$) single bonds that differ in length and stability enough to substantially influence the molecular structure resulting in low energy geometric configurations unavailable to the hydrocarbon counterparts [3–5]. These so-called organosilicon molecules, such as silylthane (H_3SiCH_3) compared to ethane (H_3CCH_3), appear in modern synthetic methods like palladium catalyzed cross-coupling reactions due in part to their low cost and low toxicity when compared to boronic acids and their derivatives [6], in medicinal chemistry where silicon-bearing functional groups may increase the tunability of certain pharmacological agents [7], and are also an important feature of astrophysical

environments, where the rotational spectra of eight molecules carrying a silicon-carbon bond have been detected in the circumstellar envelope of the carbon star IRC + 10216 (Fig. 1) [8–15]. However, despite their prominence in circumstellar environments, a gas-phase characterization of small organosilicon molecules formed from simple atomic and molecular precursors remains a work in progress for the (astro)chemistry and reaction dynamics communities.

Recently, the gas-phase synthesis of small organosilicon molecules was studied exploiting the silyldiyne (SiH) radical, produced by photodissociation of disilane (Si_2H_6) at 193 nm , with several unsaturated hydrocarbons. For the alkyne bearing hydrocarbons acetylene (C_2H_2), methylacetylene (CH_3CCH), and dimethylacetylene (2-butyne; CH_3CCCH_3), silyldiyne reactivity was localized at the π electrons of the acetylenic system resulting in the formation of cyclic reaction intermediates and eventually the products silacyclopentenylidene ($\text{c-SiC}_2\text{H}_2$) [16], methyl-silacyclopentenylidene ($\text{c-SiC}_2\text{HCH}_3$) [17], and dimethyl-silacyclopentenylidene ($\text{c-SiC}_2(\text{CH}_3)_2$) [18]. In the cummulenic and conjugated diene systems presented by allene (CH_2CCH_2) and 1,3-butadiene ($\text{CH}_2\text{CHCHCH}_2$), cyclization remained the favorable reaction mechanism. In the silyldiyne-allene system, radical addition to π system accessed SiC_3H_5 intermediates common to the SiH -methylacetylene [17] system and therefore resulted in the methyl-substituted silacyclopentenylidene ($\text{c-SiC}_3\text{H}_4$) molecule via hydrogen atom loss [19],

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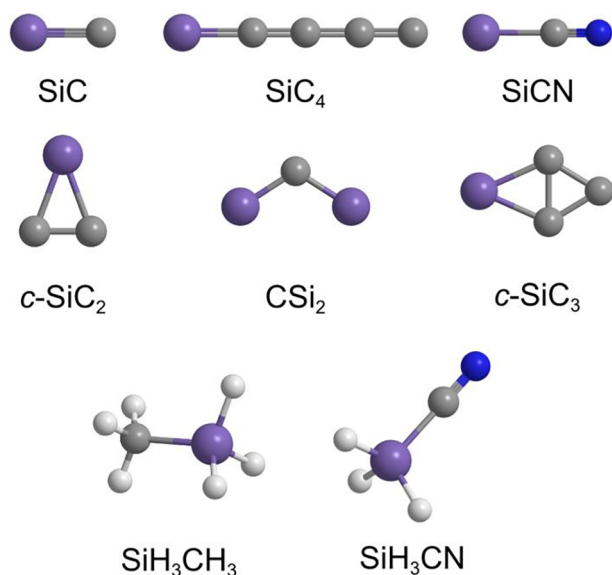


Fig. 1. Molecules carrying silicon-carbon bonds detected in the circumstellar envelope of IRC + 10216. Silicon, carbon, nitrogen, and hydrogen are indicated in purple, gray, blue, and white.

whereas silylidyne addition to methylene group of 1,3-butadiene was quickly followed by ring closure facilitated by the activated allyl group at the opposite end of the molecule forming a five membered ring forming the silole silacyclopentadiene (c-SiC₄H₆) after elimination of atomic hydrogen [20]. The silylidyne radical reaction with unsaturated hydrocarbons is therefore characterized by barrierless entrance channels followed by multiple isomerization steps and ultimately the elimination of atomic hydrogen to yield monocyclic organosilicon molecules in overall exoergic reactions. Notably, these reactions begin and end on the doublet potential energy surface (PES).

The reactivity of the silicon atom (Si(³P)) under single collision conditions has been surprisingly difficult to characterize, especially when compared with isovalent reaction systems involving the ground state carbon atom (C(³P)) whose kinetics [21–24] and chemical dynamics [25–32] in reactions with unsaturated hydrocarbons are both well known. Early kinetic studies by Basu and Husain [33,34] and Canosa *et al.* [35] suggest that Si(³P) reacts close to gas kinetics values with unsaturated hydrocarbons at rate constants of a few 10^{−10} cm³ s^{−1}. However, these studies probed only the decay kinetics of the silicon atom without identifying any of the reaction products. The reaction products are of immense interest as they provide fundamental knowledge on the reaction mechanism(s) (bimolecular versus three body reactions) and on the exotic chemical bonding typical of organosilicon molecules. From the dynamics perspective, the crossed molecular beams method was used to probe the Si(³P) plus acetylene (C₂H₂) system to determine this reaction's relevance as a precursor to the silicon-dicarbide (c-SiC₂) molecule. A relatively high collision energy (101.6 ± 1.6 kJ mol^{−1}) was required for the reaction to proceed and the only product channel detected was the endoergic (+84 ± 6 kJ mol^{−1}) hydrogen atom loss forming the linear ethynylsilylidyne (SiCCH) molecule [36]. Later experiments of Si(³P) with any hydrocarbon up to C₃, such as the C₃H₄ isomers allene (CH₂CCH₂) and methylacetylene (CH₃CCH) at the more modest collision energy of 30 kJ mol^{−1}, did not produce reactive scattering signal suggesting the presence of large and insurmountable barriers in the reaction coordinate. Very recently, crossed beam experiments revealed that Si(³P) reacted exoergically with 2-butyne (CH₃CCCH₃) producing singlet SiC₄H₄ via molecular hydrogen elimination (H₂) and suggested that critical non-adiabatic reaction dynamics underlie the reaction mechanism [37]. Therefore, the lack of reaction of unsaturated C₂ and C₃

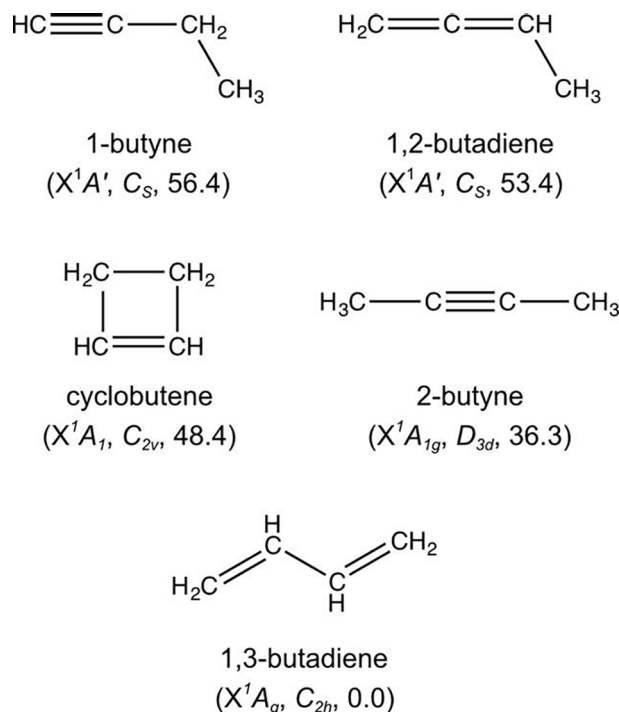


Fig. 2. Energetically low-lying structural isomers of C₄H₆. Experimental enthalpies of formation (Δ_fH(298 K) are taken from NIST and given relative to 1,3-butadiene in kJ mol^{−1}.

hydrocarbons at moderate collision energies with ground state atomic silicon, but the enhanced reactivity with unsaturated C₄ hydrocarbons still remains poorly understood. Here, we report our results of the Si(³P) reactions with the C₄H₆ isomers 1,3-butadiene, 1,2-butadiene (CH₂CCHCH₃), and 1-butyne (CH₃CH₂CCH) (Fig. 2) to gain a glimpse into the fundamental reaction mechanisms of the gas-phase silicon-carbon chemistry in the interstellar medium.

2. Experimental methods

The reactions of atomic silicon (Si(³P)) with 1,3-butadiene (≥99%; Aldrich Chemistry), 1,2-butadiene (98%; ChemSampCo), and 1-butyne (≥98%; Aldrich Chemistry) were performed in a universal crossed molecular beams machine at the University of Hawaii at Manoa [38]. In the primary source chamber, a supersonic beam of ground state silicon atoms was prepared *in situ* by ablation of silicon from a rotating silicon rod using the 4th harmonic of a Nd:YAG laser (10 ± 1 mJ per pulse; 30 Hz) [39–45], then subsequently entrained the ablated atoms in a pulsed neon (Ne; 99.999%; Specialty Gases of America) beam that was released from a piezoelectric valve operated at 60 Hz, a pulse width of 80 μs, a peak amplitude of −400 V, and a backing pressure of 4 atm. Note that the ablation laser is operated at half the frequency of the pulsed valves to allow a ‘laser on’ minus ‘laser off’ background subtraction. The neon-seeded beam of silicon atoms was skimmed and then velocity-selected by a four-slit chopper wheel (120 Hz) resulting in well-defined peak velocities (v_p) of about 1000 m s^{−1} and speed ratios (S) of about 6 for this set of experiments (Table 1). Laser induced fluorescence interrogation of our neon-seeded silicon beam indicates that all silicon atoms are in their electronic ground state (³P) [46].

In the source secondary chamber, each hydrocarbon gas was released neat by a piezoelectric valve (60 Hz, 80 μs, −400 V) with a backing pressure of 550 Torr and skimmed resulting in peak velocities and speed ratios of v_p = 777 ± 12 m s^{−1} with S = 9.5 ± 0.3, v_p = 795 ± 12 with S = 8.9 ± 0.4, and v_p = 793 ± 10 with S = 9.0 ± 0.3 for 1,3-butadiene, 1,2-butadiene, and 1-butyne,

Table 1

Peak velocities (v_p) and speed ratios (S) of the silicon (Si), 1,3-butadiene ($\text{CH}_2\text{CHCHCH}_2$), 1,2-butadiene ($\text{CH}_2\text{CCHCH}_3$), and 1-butyne ($\text{CH}_3\text{CH}_2\text{CCH}$) beams along with the corresponding collision energies (E_c) and center-of-mass angles (Θ_{CM}) for each reactive scattering experiment.

Beam	v_p (m s ⁻¹)	S	E_c (kJ mol ⁻¹)	Θ_{CM} (degree)
Si(³ P)	970 ± 30	6.0 ± 0.5	14.5 ± 0.6	57.6 ± 0.9
CH ₃ CH ₂ CCH (X ¹ A')	793 ± 10	9.0 ± 0.3		
Si(³ P)	962 ± 17	5.9 ± 0.6	14.4 ± 0.3	57.9 ± 0.6
CH ₂ CCHCH ₃ (X ¹ A')	795 ± 10	8.9 ± 0.4		
Si(³ P)	1013 ± 7	4.9 ± 0.2	15.0 ± 0.2	55.9 ± 0.4
CH ₂ CHCHCH ₂ (X ¹ A _g)	777 ± 12	9.5 ± 0.3		

respectively. The primary and secondary pulse valves were triggered at 1800 and 1820 μs, respectively, with respect to the trigger pulse ($T = 0$ μs), so that the hydrocarbon beams crossed perpendicular with the Si(³P) beam at collision energies of 14–15 kJ mol⁻¹ and center-of-mass (CM) angles of 56–58° (Table 1). Experiments with (partially) deuterated reactants were performed using the 1,3-butadiene-2,3-d₂ ($\text{CH}_2\text{CDCDCH}_2$; 98.8% atom D; CDN Isotopes) and 1,3-butadiene-1,1,4,4-d₄ ($\text{CD}_2\text{CHCHCD}_2$; 98%; Cambridge Isotopes).

The reactively scattered products were mass filtered after electron impact ionization (80 eV, 2 mA) utilizing a quadrupole mass filter and registered by a Daly-type TOF detector housed in a rotatable, triply-differentially pumped ultrahigh vacuum ($< 2 \times 10^{-11}$ Torr) chamber. 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. To acquire information on the scattering dynamics, the laboratory data were transformed into the CM frame utilizing a forward-convolution routine using an iterative method that employs a parametrized 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 averaged over a grid of Newton diagrams accounting for the apparatus functions, beam divergences, and velocity spreads. The CM functions comprise the reactive differential cross section $I(\theta, u)$, which is taken to be separable into its CM scattering angle θ and CM velocity u components, $I(u, \theta) \sim P(u) \times T(\theta)$. The differential cross section is plotted as a flux contour map that serves as an image of the reaction.

3. Theoretical methods

The geometries of likely triplet and singlet SiC₄H₄ isomers are optimized via density functional B3LYP [47–50]/cc-pVTZ calculations. The completed basis set limits [51], 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 zero-point energy corrections. The accuracy of these CCSD(T)/CBS energies are expected to be within 8 kJ mol⁻¹ [52]. GAUSSIAN09 programs [53] are facilitated in density functional and coupled cluster calculations. The minimum energy crossing point between ³i1 and ¹i1 is located with the CPMSCF/TZVPP by employing MOLPRO [54], and the CCSD(T)/CBS energy is obtained.

The Rice–Ramsperger–Kassel–Marcus (RRKM) rate constants [55] for H₂ elimination pathways on the singlet ground state are predicted at collision energy of 15 kJ/mol. The saddle-point method [55,56] is applied to evaluate the number of states and the density of states; the molecule is viewed as a collection of harmonic oscillators, of which the harmonic frequencies and energies are obtained as described above. By utilization of RRKM rate constants, the rate equations of reaction mechanism are solved with Runge–Kutta method to estimate the product branching ratios.

4. Results

4.1. Laboratory

Reactive scattering signal was monitored at mass-to-charge ratios (m/z) 84–79 to probe the existence of adducts along with atomic and molecular hydrogen loss channels. Considering the natural abundances of three silicon isotopes (³⁰Si (3.1%), ²⁹Si (4.7%), ²⁸Si (92.2%)) and carbon (¹³C (1.1%), ¹²C (98.9%)), no signal was detected at m/z 84 and 83 revealing the absence of adducts (³⁰SiC₄H₆⁺/²⁹SiC₄H₆⁺) and the non-existence of the atomic hydrogen loss channel (³⁰SiC₄H₅⁺). Signal was observed at m/z 82, 81, and 80. In principle, ion counts at m/z 82 could arise from a reaction adduct (²⁸SiC₄H₆⁺), the atomic hydrogen loss (²⁹SiC₄H₅⁺), and the molecular hydrogen loss channel (³⁰SiC₄H₄⁺); signal at m/z = 81 might be linked to the atomic hydrogen loss pathway (²⁸SiC₄H₅⁺) or to a molecular hydrogen loss (²⁹SiC₄H₄⁺); finally, counts at m/z 80 can originate from the molecular hydrogen emission channel (²⁸SiC₄H₄⁺). 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 ³⁰SiC₄H₄, ²⁹SiC₄H₄, and ²⁸SiC₄H₄ (hereafter: SiC₄H₄), respectively. Lastly, signal at m/z 79 can be attributed to dissociative electron impact fragmentation of neutral SiC₄H₄ to SiC₄H₃⁺. Therefore, the laboratory data provide strong evidence of the *molecular hydrogen loss* pathway forming SiC₄H₄ isomers in the reaction of Si(³P) with each of the C₄H₆ isomers 1,3-butadiene, 1,2-butadiene, and 1-butyne.

For each reaction system, up to 2×10^5 TOF spectra for the molecular hydrogen loss channel (m/z 80; SiC₄H₄⁺) were recorded in 2.5° steps. The TOF spectra are relatively broad and peak between 400 μs and 500 μs, and have a slight bimodality, the extent of which increases in the order of 1,3-butadiene, 1,2-butadiene, the 1-butyne (Fig. 3). The normalized laboratory angular distributions span at least 35° and depict a maximum at their respective CM angles (Fig. 4). There is an apparent symmetry about the CM angle which is suggestive of an indirect reaction mechanism involving at least one SiC₄H₆ intermediate that eliminates molecular hydrogen (H₂) to form the SiC₄H₄ isomer(s). While the laboratory data present compelling evidence for the formation of molecular hydrogen loss products with molecular formulas SiC₄H₄, interpreting the data in the center-of-mass frame can yield more specific details such as reaction energetics and can also reveal features of the reaction coordinate such as the presence of intermediate complexes and exit geometries as revealed below.

Having established the molecular hydrogen-loss channel as the source of reactive scattering signal in the silicon plus 1,3-butadiene reaction, we used the 1,3-butadiene-2,3-d₂ ($\text{CH}_2\text{CDCDCH}_2$; 56 amu) and 1,3-butadiene-1,1,4,4-d₄ ($\text{CD}_2\text{CHCHCD}_2$; 58 amu) isotopologues to determine if the hydrogen atoms comprising molecular hydrogen are lost from the methylene (CH₂) or methylidyne (CH) groups, or from a combination thereof. For the Si(³P) plus 1,3-butadiene-2,3-d₂ reaction, measurements were taken at m/z 82 (SiC₄H₂D₂⁺), 81 (SiC₄H₃D⁺), and 80 (SiC₄H₄⁺). Reactive scattering signal was detected at m/z 82 and 81, indicating the presence of both molecular hydrogen (H₂) and hydrogen deuteride (HD) channels to form SiC₄H₂D₂ and SiC₄H₃D, respectively (Fig. 5a). A TOF signal for the molecular deuterium (D₂) loss channel is not discernible at the current signal-to-noise level. Accounting for the natural abundance of silicon and carbon in the detected HD-loss channel, from ²⁹SiC₄H₃D and Si¹³CC₃H₃D, we observe the H₂ and HD fractions as 61 ± 9% and 39 ± 9% (Table 2). For the Si(³P) plus 1,3-butadiene-1,1,4,4-d₄ system we monitored reactive scattering signal at m/z 84 (SiC₄D₄⁺), 83 (SiC₄HD₃⁺), and 82 (SiC₄H₂D₂⁺). Distinct TOFs are detectable at each m/z ratio corresponding to H₂, HD, and D₂ loss products (Fig. 5b). The H₂-loss channel probed at m/z 84 has contributions from the HD-loss channel via isotopes Si¹³CC₃D₃H and ²⁹SiC₄D₃H, as well as from the D₂-loss channel from isotopes ²⁹Si¹³CC₃D₂H₂ and ³⁰SiC₄D₂H₂. Similarly, the HD-loss channel recorded

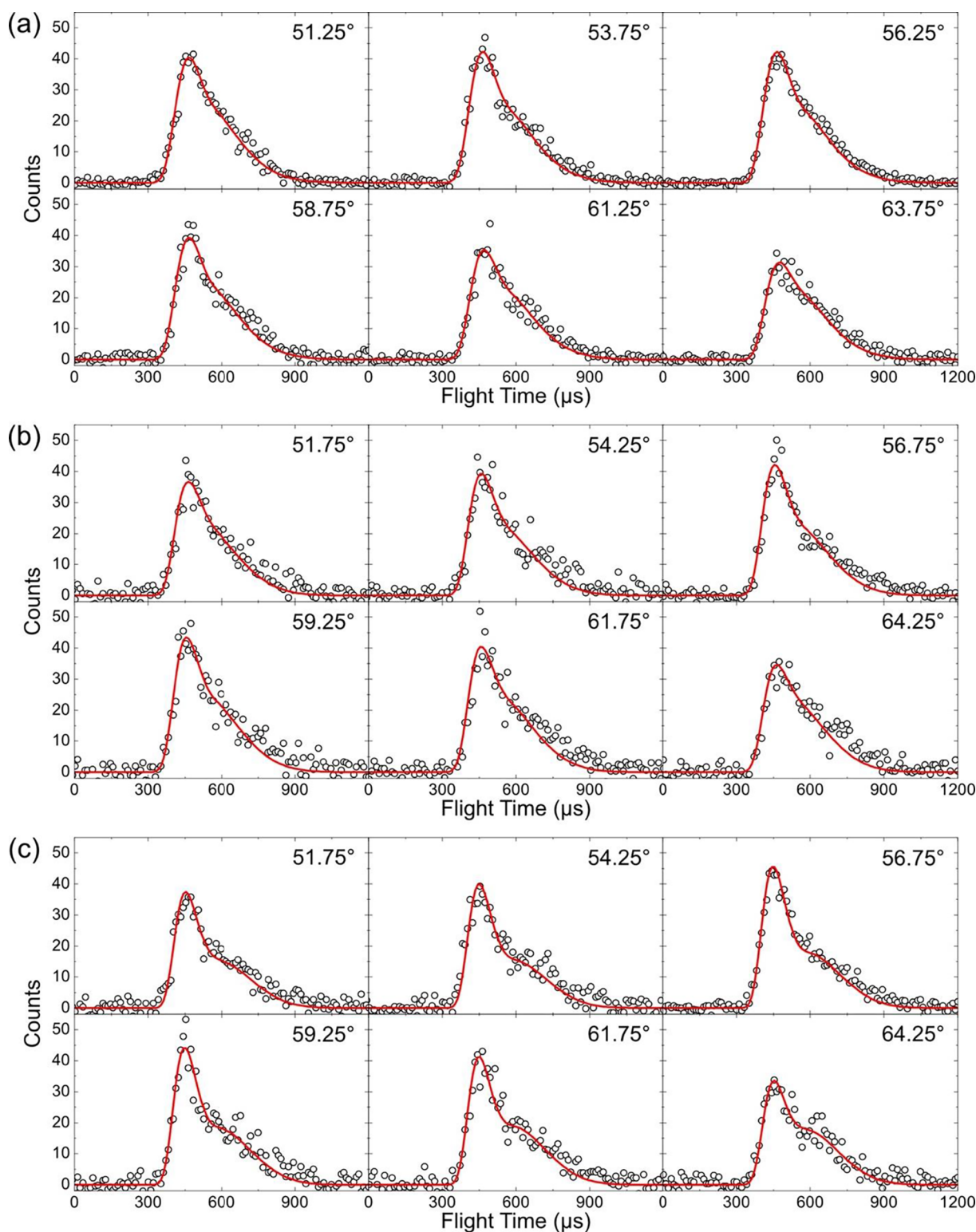


Fig. 3. Time-of-flight (TOF) spectra recorded at mass-to-charge (m/z) 80 (SiC_4H_4^+) from the reaction of ground state atomic silicon ($\text{Si}(^3\text{P})$) with (a) 1,3-butadiene ($\text{CH}_2\text{CHCHCH}_2$), (b) 1,2-butadiene ($\text{CH}_2\text{CCHCH}_3$), and (c) 1-butyne ($\text{CH}_3\text{CH}_2\text{CCH}$). The open circles are experimental data and the red lines the best fits.

at m/z 83 contains signal from the D_2 -loss channel via the $\text{Si}^{13}\text{CC}_3\text{D}_2\text{H}_2$ and $^{29}\text{SiC}_4\text{D}_2\text{H}_2$ isotopes. Accordingly, we find the H_2 , HD, and D_2 branching ratios to be $4^{+9}_{-4}\%$, $48 \pm 9\%$, and $48 \pm 9\%$, respectively (Table 2). The TOFs from each isotopic experiment are fit using the CM functions derived from the $\text{Si}(^3\text{P}) - 1,3\text{-butadiene}$ ($\text{CH}_2\text{CHCHCH}_2$) system.

4.2. Center-of-mass functions

The center-of-mass (CM) translational energy flux $P(E_T)$ and CM angular flux $T(\theta)$ distributions were obtained utilizing the forward-convolution fitting routine. The fits for each reaction system were completed using the single reaction channel Si (28 amu) + C_4H_6

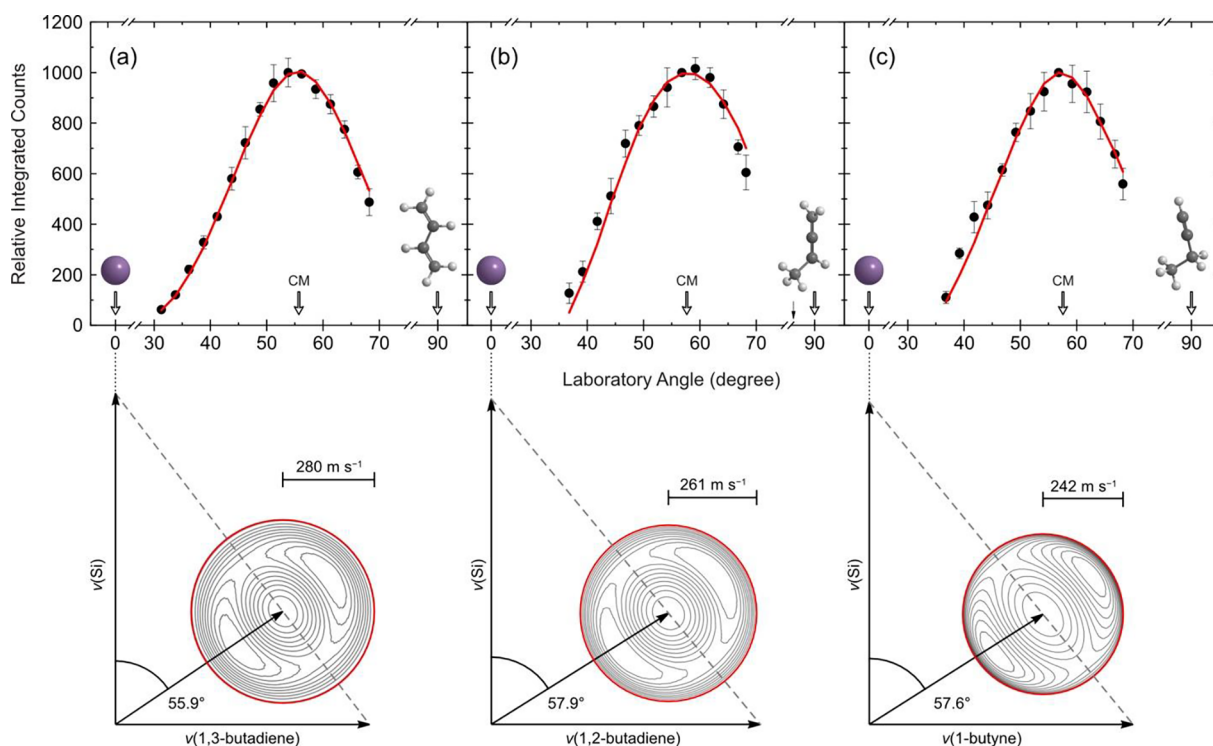


Fig. 4. Laboratory angular distributions recorded at a mass-to-charge (m/z) ratio of 80 (SiC_4H_4^+) in the reaction of ground state atomic silicon ($\text{Si}(^3\text{P})$) with (a) 1,3-butadiene ($\text{CH}_2\text{CHCHCH}_2$), (b) 1,2-butadiene ($\text{CH}_2\text{CCHCH}_3$), and (c) 1-butyne ($\text{CH}_3\text{CH}_2\text{CCH}$). The circles define the experimental data and the red lines represent the fitting based on the best-fit center-of-mass functions depicted in Fig. 5. Error bars are $\pm 1\sigma$. The CM arrow indicates the center-of-mass angle. The corresponding Newton diagrams relating the laboratory reactant and CM frame product velocities are shown below each respective angular distribution. 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 Fig. 5.

(54 amu) $\rightarrow \text{SiC}_4\text{H}_4$ (80 amu) + H_2 (2 amu), with a reaction cross section of $E_C^{-1/3}$ dependence [57]. The best-fitting CM functions are depicted as red lines in Fig. 6 with the hatched areas of the $P(E_T)$ and $T(\theta)$ functions determined within the 1σ error limits of the LAB angular distribution. The maximum energy E_{max} available to translation of

nascent SiC_4H_4 products is given by the sum of the relative translational energy of the reactants and the energy released in product formation, i.e. $E_{\text{max}} = E_C - \Delta_r G$. Therefore, the reaction energy can be determined via a conservation argument, where E_{max} is given by the $P(E_T)$, and E_C is known from the initial conditions (Table 1). Accordingly, the reactions

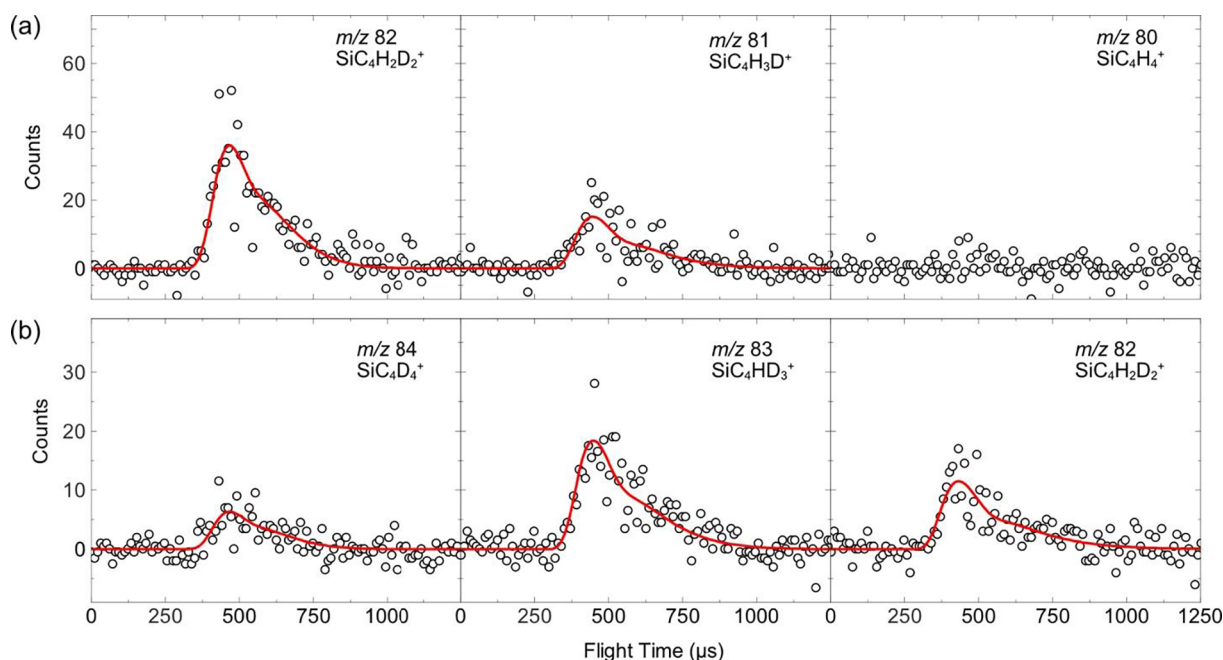


Fig. 5. Time-of-flight (TOF) spectra for the reaction of the silicon atom ($\text{Si}(^3\text{P})$) with (a) 1,3-butadiene-2,3- d_2 ($\text{CH}_2\text{CDCDCH}_2$) and (b) 1,3-butadiene-1,1,4,4- d_4 ($\text{CD}_2\text{CHCHCD}_2$) leading to H_2 -, HD -, and D_2 -loss products. The open circles represent the experimental data, and the red line represents the fit obtained from the forward-convolution routine. Terminal/internal refers to the source(s) of the departing hydrogen and/or deuterium atoms with respect to the C_4 backbone.

Table 2

Experimental product branching ratios (%) derived from the reaction of ground state atomic silicon ($\text{Si}(^3\text{P})$) with 1,3-butadiene-2,3- d_2 (CH_2CDCH_2) and 1,3-butadiene-1,1,4,4- d_4 ($\text{CD}_2\text{CHCHCD}_2$) along with the computed branching ratios based on the RRKM rate constants.

Reaction Products	Experiment (%)	Theory (%)
$\text{Si}(^3\text{P}) + \text{CH}_2\text{CDCH}_2$		
$\text{SiC}_4\text{H}_2\text{D}_2 + \text{H}_2$	61 ± 9	0.7
$\text{SiC}_4\text{H}_3\text{D} + \text{HD}$	39 ± 9	99.3
$\text{SiC}_4\text{H}_4 + \text{D}_2$	0	0
$\text{Si}(^3\text{P}) + \text{CD}_2\text{CHCHCD}_2$		
$\text{SiC}_4\text{D}_4 + \text{H}_2$	4^{+9}_{-4}	0
$\text{SiC}_4\text{D}_3\text{H} + \text{HD}$	48 ± 9	99.95
$\text{SiC}_4\text{D}_2\text{H}_2 + \text{D}_2$	48 ± 9	0.05

of $\text{Si}(^3\text{P})$ with 1,3-butadiene, 1,2-butadiene, and 1-butyne, to form SiC_4H_4 plus molecular hydrogen, are exoergic by $114 \pm 21 \text{ kJ mol}^{-1}$, $97 \pm 17 \text{ kJ mol}^{-1}$, and $81 \pm 21 \text{ kJ mol}^{-1}$. The elimination of molecular hydrogen likely occurs via a tight transition state as evidenced by the $P(E_T)$ s each peaking at relatively high translational energies of $33 \pm 5 \text{ kJ mol}^{-1}$, $38 \pm 6 \text{ kJ mol}^{-1}$, and $46 \pm 10 \text{ kJ mol}^{-1}$ for the $\text{Si}(^3\text{P}) + 1,3\text{-butadiene}$, $\text{Si}(^3\text{P}) + 1,2\text{-butadiene}$, and $\text{Si}(^3\text{P}) + 1\text{-butyne}$ reaction systems. The $P(E_T)$ s also reveal that the SiC_4H_4 products retain $36 \pm 9\%$, $42 \pm 9\%$, and $49 \pm 15\%$ of E_{max} in their translational degrees of freedom. Hence, in each reaction, SiC_4H_4 is likely produced via one or more SiC_4H_6 intermediates that eliminate molecular hydrogen via a tight exit barrier.

For each of the three reaction systems, the best-fitting $T(\theta)$ depicts product flux over the entire angular range and is forward-backward symmetric with a maximum at 90° (sideways scattered). The symmetry of $T(\theta)$ suggests the presence of a decomposing SiC_4H_6 intermediate with a lifetime comparable to or exceeding its rotational period; the sideways scattering indicates strong geometrical constraints and a preference for molecular hydrogen elimination perpendicular to the

rotational plane of the decomposing intermediate almost parallel to the total angular momentum vector [57,58].

5. Discussion

Based on the experimental results, atomic silicon reacts exoergically with 1,3-butadiene, 1,2-butadiene, and 1-butyne leading to product(s) with the molecular formula SiC_4H_4 along with molecular hydrogen (H_2) via tight exit transition states. However, the goal of our study is 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. Possible reaction products can be deciphered by a comparison of the experimentally determined reaction energies for each system with the reaction energies obtained from electronic structure calculations [37]. At present, there are at least 153 singlet and 24 low-lying triplet SiC_4H_4 isomers predicted to be stable. Exploiting the experimental reaction energies derived in these experiments along with computed SiC_4H_4 energetics – adjusted using the enthalpies of formation ($\Delta_f H(0 \text{ K})$) of 1,2-butadiene and 1-butyne calculated at the CCSD(T)/CBS level by Li et al. [59] – the range of relevant product isomers can be narrowed to the singlet isomers $^1\text{p5}\text{--}^1\text{p44}$ as provided in Fig. 7. It is critical to highlight that only singlet isomers can account for the observed energetics. **Therefore, considering that the reaction of ground state silicon with each C_4H_6 isomer starts on the triplet surface, but the products are formed in their singlet ground states, non-adiabatic reaction dynamics and intersystem crossing (ISC) from the triplet to the singlet surface must be critical to the underlying reaction dynamics.**

Considering the complexity of the reactions, 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 dissemination but will be conducted in the future. However, it is appropriate to consider which SiC_4H_4 isomers, based on reaction energetics, are likely representative of the products formed in these crossed

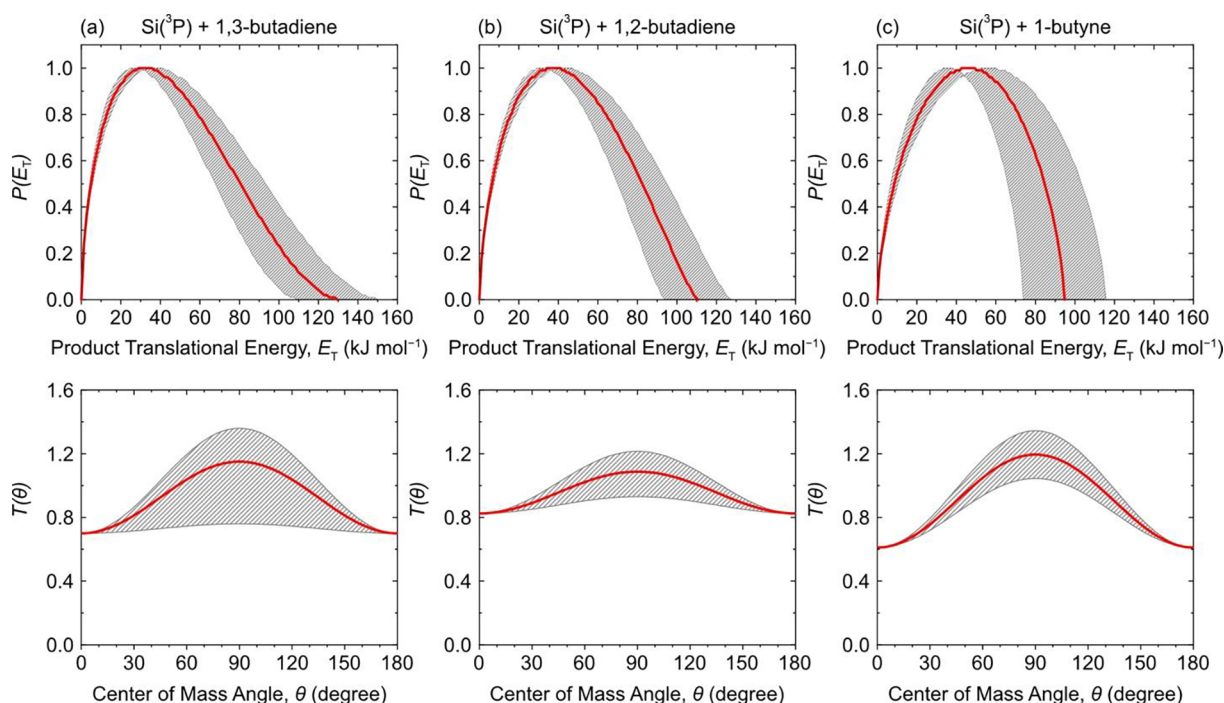


Fig. 6. Center-of-mass (CM) functions for the formation of SiC_4H_4 via molecular hydrogen loss in the reactions of ground state atomic silicon ($\text{Si}(^3\text{P})$) with (a) 1,3-butadiene ($\text{CH}_2\text{CHCHCH}_2$), (b) 1,2-butadiene ($\text{CH}_2\text{CCHCH}_3$), and (c) 1-butyne ($\text{CH}_3\text{CH}_2\text{CCH}$). The translational energy flux distributions are on the top row, and the angular flux distributions on the bottom. The hatched areas define regions of acceptable fits.

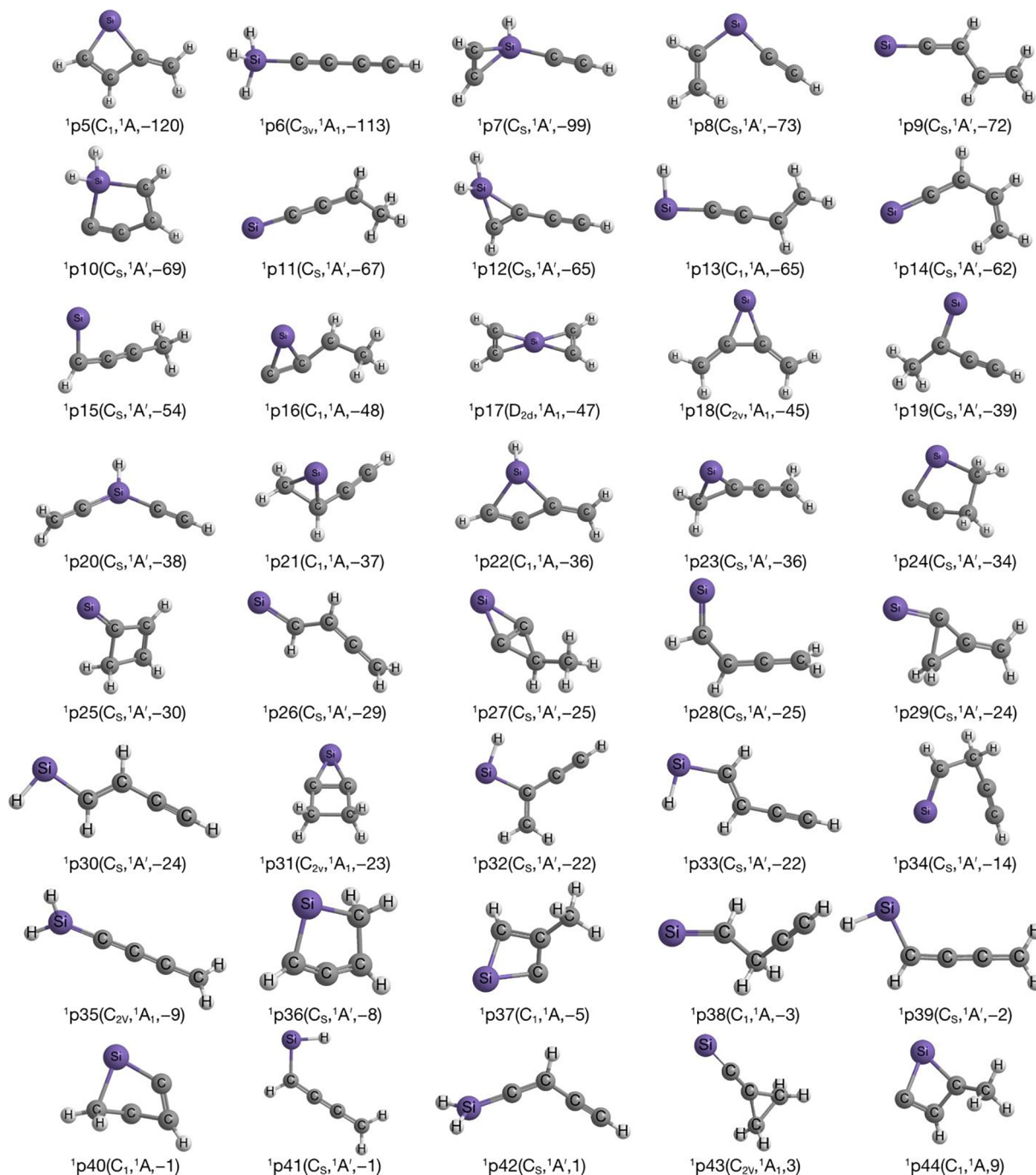


Fig. 7. Molecular structures of low-lying singlet SiC_4H_4 products $^1\text{p5} - ^1\text{p44}$, adopted from Ref. [37], along with their B3LYP//CCSD(T)/CBS relative energies in kJ mol^{-1} with respect to the separated $\text{Si}(^3\text{P})$ and 1,3-butadiene ($\text{CH}_2\text{CHCHCH}_2$) reactants, point groups, and electronic wave functions.

molecular beams studies. We therefore consider a few possibilities and note a range of SiC_4H_4 isomers that may account for the experimental data. Let us start with the $\text{Si}(^3\text{P}) - 1,3\text{-butadiene}$ system. Of the three reactions discussed herein, the $\text{Si}(^3\text{P}) - 1,3\text{-butadiene}$ bimolecular reaction leading to SiC_4H_4 plus H_2 is the most exoergic with a derived reaction energy of $-114 \pm 21 \text{ kJ mol}^{-1}$; within the error limits, at least isomers $^1\text{p5} - ^1\text{p7}$ could account for the experimental data. Formation of the triplet isomer $^3\text{p1}$ also has an agreeable computed reaction energy of $-111 \pm 5 \text{ kJ mol}^{-1}$; however, the predicted transition states for elimination of molecular hydrogen to form $^3\text{p1}$ lie at least 79 kJ mol^{-1} above the $\text{Si}(^3\text{P})$ plus 1,3-butadiene entrance channel, therefore rendering the low-lying triplet product inaccessible under our experimental conditions [37]. The SiC_4H_4 isomers $^1\text{p6}$ and $^1\text{p7}$ feature

the silicon atom formally inserted between carbon and/or hydrogen atoms that would require substantial isomerization of the initial SiC_4H_6 collision complex formed by addition of $\text{Si}(^3\text{P})$ to the π electrons of 1,3-butadiene. The planar $^1\text{p5}$, comprising a silicon atom bridging the C1 and C3 atoms to form a four-membered ring, has a computed reaction energy of $-120 \pm 5 \text{ kJ mol}^{-1}$, could be formed via a series of relatively low-energy isomerization steps as elucidated in Fig. 8 and detailed below. Although not explicitly recovered from our experimental $P(E_T)$, isomer $^1\text{p9}$ is noteworthy due to the simple addition-elimination reaction that would govern its formation, whereby elimination of the terminal methylene hydrogen atoms yields a SiC_4H_4 isomer that retains the *trans*-conjugated motif of 1,3-butadiene. Hence, this isomer, along with other high energy singlet isomers like $^1\text{p23}$ could be obscured in

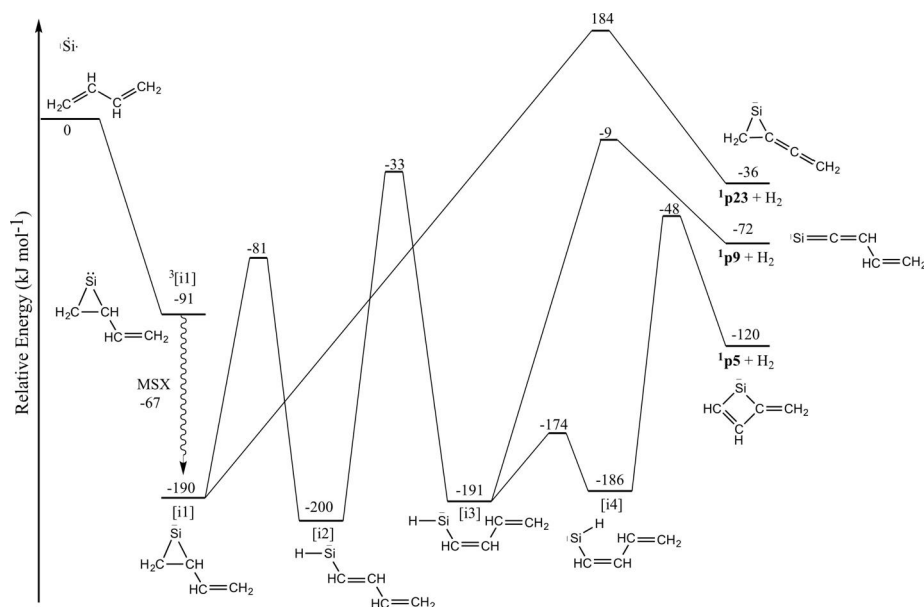


Fig. 8. Pathways accounting for the formation of molecular hydrogen (H_2) loss products in the reaction of the ground state silicon atom ($Si(^3P)$) with 1,3-butadiene ($CH_2CHCHCH_2$). The energies are obtained at the B3LYP//CCSD(T)/CBS level.

the low-energy region of our SiC_4H_4 translational energy flux distribution (Fig. 6a). The isotopic experiments reveal that molecular elimination recruits hydrogen (deuterium) atoms from all positions of the 1,3-butadiene backbone, which strongly suggests multiple product channels contribute to the reactive scattering signal recorded at m/z 80 ($SiC_4H_4^+$) in the hydrogenated system. Considering that the $Si(^3P)$ plus 1,3-butadiene-1,1,4,4- d_4 reaction gave reactive scattering signal for the molecular hydrogen (H_2), hydrogen deuteride (HD), and molecular deuterium (D_2) loss channels, isomer 1p_9 could account for the observed D_2 loss originating from the methylene- d_2 group(s), whereas the low energy isomer 1p_5 could be representative of the detected HD loss channel. The potential H_2 loss signal could then be attributed to the high energy isomer $^1p_{23}$. Potential routes leading to 1p_5 , 1p_9 , and $^1p_{23}$ in the reactions of $Si(^3P)$ with 1,3-butadiene, 1,3-butadiene-2,3- d_2 , and 1,3-butadiene-1,1,4,4- d_4 are compiled in Figs. 8 and 9.

In detail, in discussing the possible reaction mechanism(s) governing the experimental outcome we consider the $Si(^3P)$ plus 1,3-butadiene-1,1,4,4- d_4 reaction (Fig. 9b). The silicon atom could add across the carbon-carbon double bond of the 1,3-butadiene-1,1,4,4- d_4 to yield a vinyl-substituted silacyclopropylylene ($SiC_2D_2HCHCD_2$) with a low-lying triplet $^3[i1]$ state; the latter could undergo intersystem crossing (ISC) to singlet $[i1]$ that is stabilized by 190 $kJ\ mol^{-1}$ with respect to the separated reactants. On the singlet manifold, $[i1]$ can eliminate the hydrogen atoms at the C2 and C3 atoms to form $^1p_{23-d_4}$ with an overall reaction energy of $-34 \pm 5\ kJ\ mol^{-1}$, or undergo ring-opening facilitated by deuterium atom (D) migration from the methylene- d_2 up the carbon-silicon bond to form a silylene-substituted 1,3-butadiene ($DSiCDCHCHCD_2$; $[i2]$) via a tight transition state located 77 $kJ\ mol^{-1}$ below the bimolecular entrance channel. Intermediate $[i2]$ can undergo *cis-trans* isomerization to $[i3]$. Elimination of molecular deuterium from $[i3]$ yields the $^1p_{9-d_2}$ isomer via an exit barrier located 61 $kJ\ mol^{-1}$ above the product channel, which is overall exoergic by $63 \pm 5\ kJ\ mol^{-1}$. Alternatively, $[i3]$ can further isomerize to $[i4]$ by rotation about the carbon-silicon bond which then eliminates hydrogen deuteride (HD) via a ring closing transition state to form the cyclic product $^1p_{5-d_3}$ with a calculated reaction energy of $-115 \pm 5\ kJ\ mol^{-1}$. Note that this scheme is not intended to be exhaustive and is designed to illustrate some of the possible reaction routes underlying our experimental data.

Recall that we recovered branching ratios of $4^{+9}_{-4}\%$ ($-H_2$), $48 \pm 9\%$

($-HD$), and $48 \pm 9\%$ ($-D_2$) in the $Si(^3P) - 1,3$ -butadiene-1,1,4,4- d_4 experiment, and of $61 \pm 9\%$ ($-H_2$), $39 \pm 9\%$ ($-HD$), and 0% ($-D_2$) in the $Si(^3P) - 1,3$ -butadiene-2,3- d_2 experiment. In both studies, molecular elimination from the interior methylidyne groups is nonexistent within the experimental error, which is consistent with the computed route to form $^1p_{23}$ plus H_2 possessing an exit barrier that lies 184 $kJ\ mol^{-1}$ above the entrance channel (Fig. 8) and is therefore insurmountable at the working collision energy of 15 $kJ\ mol^{-1}$ (Table 1). The formation of isomers 1p_5 and 1p_9 along with their isotopologues are certainly permissible under our experimental conditions and thus likely contribute to the reactive scattering signal recorded in the $Si(^3P)$ plus 1,3-butadiene- (d_2/d_4) experiments. Considering the accessibility of 1p_5 and 1p_9 on our deuterated potential energy surfaces, we calculated the statistical yield of each isomer at a collision energy of 15 $kJ\ mol^{-1}$ using rate constants obtained from RRKM calculations (Tables S1 and S2). For the reaction of $Si(^3P)$ with 1,3-butadiene-2,3- d_2 and 1,3-butadiene-1,1,4,4- d_4 , formation of 1p_5 by HD-loss is favored with computed branching ratios of 99.3% and 99.95%, respectively (Table 2). Within the framework of our PES, it is clear that additional pathways leading to H_2 -loss ($SiC_4H_4D_2$)/ D_2 -loss ($SiC_4H_2D_4$) products – which are formed in the experiment – are lacking, provided that the reaction system follows statistical behavior. Finally, we note that beyond the agreement between the experimentally derived and computed reaction energies, the computed geometries for the $[i3] \rightarrow ^1p_9 + H_2$ and $[i4] \rightarrow ^1p_5 + H_2$ exit transition states have the light molecule departing at 57.3° and 64.9° with respect to the SiC_4H_6 orbital plane which is agreeable with the sideways scattering depicted in $T(\theta)$ (Fig. 6a).

The formation of SiC_4H_4 via the reaction of $Si(^3P)$ with 1,2-butadiene has a derived reaction energy of $-97 \pm 17\ kJ\ mol^{-1}$ and could correspond to isomers $^1p_{14}$ – $^1p_{25}$. Seven of the molecules in this group are monocyclic, with the ring size ranging from 3 to 5 atoms, whereas $^1p_{17}$ is a bicyclic compound with a high degree of symmetry. The allenyl moiety from 1,2-butadiene is readily seen in isomers $^1p_{26}$ and $^1p_{28}$, which are slightly higher in energy at $-79 \pm 5\ kJ\ mol^{-1}$ and $-75 \pm 5\ kJ\ mol^{-1}$, respectively. For the reaction of $Si(^3P)$ with 1-butyne, the derived reaction energy of $-81 \pm 21\ kJ\ mol^{-1}$ can correspond to the formation of isomers $^1p_{17}$ – $^1p_{36}$. In the considered energy range are isomers that share common functional groups with the 1-butyne reactant such as $^1p_{32}$, $^1p_{33}$, and $^1p_{34}$ that each carry an acetylenic group. Other remnants of 1-butyne can be found in the

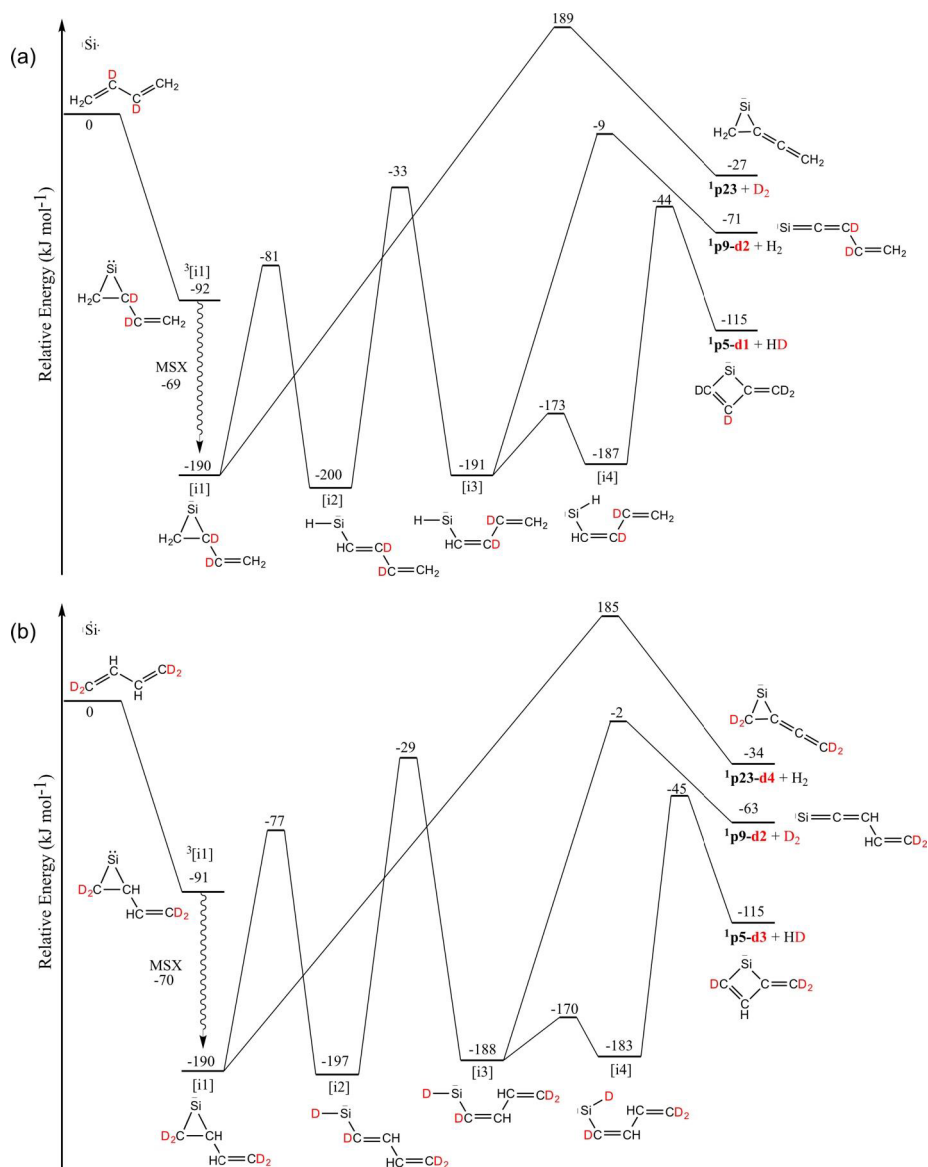


Fig. 9. Pathways accounting for the formation of molecular hydrogen (H_2), hydrogen deuteride (HD), and molecular deuterium (D_2) loss products in the reaction of the ground state silicon atom (Si^3P) with (a) 1,3-butadiene-2,3- d_2 ($\text{CH}_2\text{CDCDCH}_2$) and (b) 1,3-butadiene-1,1,4,4- d_4 ($\text{CD}_2\text{CHCHCD}_2$). The energies are obtained at the B3LYP//CCSD(T)/CBS level.

relatively high energy methyl-bearing isomers $^1\text{p}37$ and $^1\text{p}44$. Finally, isomers $^1\text{p}32$, $^1\text{p}33$, and $^1\text{p}34$ have Si–C bonds at the methylene or methyl position of 1-butyne. This activity along the alkyl group can occur only via substantial isomerization of the SiC_4H_6 complex following the addition of Si^3P to the acetylenic group. Despite these features, it is clear that the formation of these isomers does not occur by a simple addition-elimination mechanism, but instead by a rather complex series of unimolecular reactions preceding dissociation.

6. Conclusions

In this study, we revealed that ground state atomic silicon (Si^3P) reacts exoergically with the C_4H_6 isomers 1,3-butadiene ($-114 \pm 21 \text{ kJ mol}^{-1}$), 1,2-butadiene ($-97 \pm 17 \text{ kJ mol}^{-1}$), and 1-butyne ($-81 \pm 21 \text{ kJ mol}^{-1}$) via an indirect reaction mechanism forming the products SiC_4H_4 and molecular hydrogen on the singlet surface via non-adiabatic reaction dynamics involving intersystem crossing from the triplet to the singlet manifold. In the Si^3P plus 1,3-butadiene system, multiple product channels are open as evidenced by

the observation of molecular hydrogen (H_2), hydrogen deuteride (HD), and molecular deuterium (D_2) losses in experiments utilizing isotopologues of 1,3-butadiene. The methylidyne hydrogen atoms (CH) were labeled using 1,3-butadiene-2,3- d_2 , where we exposed branching ratios of $61 \pm 9\%$ and $39 \pm 9\%$ for the H_2 - and HD-loss channels, respectively. A reactive scattering signal for the D_2 loss – derived from both methylidyne-d (CD) groups of the C4 backbone – was not discernible from the noise. In a separated experiment, the methylene groups (CH_2) were deuterated using 1,3-butadiene-1,1,4,4- d_4 . The H_2 , HD, and D_2 loss channels were each observed with branching ratios of $4 \pm 9\%$, $48 \pm 9\%$, and $48 \pm 9\%$. Therefore, molecular elimination sourced from both methylidyne groups – i.e. from the C2 and C3 carbon atoms of 1,3-butadiene – is therefore nonexistent within the experimental error, whereas molecular elimination from the C1-C1, C1-C2, C1-C3, C1-C4, etc., occur with near equal probability. Logistically, we were unable to perform similar isotopic studies with isotopologues of 1,2-butadiene and 1-butyne to probe the activity of inequivalent hydrogen atoms during reaction although these data would be extremely useful in teasing out the details of the reaction mechanisms.

Considering our isotopic data, we produced potential energy surfaces (PES) accounting for the formation of three SiC_4H_4 isomers that were likely candidates for product formation in the $\text{Si}(^3\text{P})$ plus 1,3-butadiene-(d_2/d_4) experiments based on their computed reaction energies and on the expected product mass, i.e. whether dissociation of the collision complex occurred via H_2 , HD, or D_2 loss (Figs. 8 and 9). Formation of isomer $^1\text{p5}$, whose computed reaction energy ($-120 \pm 5 \text{ kJ mol}^{-1}$) is in strong agreement with the experimental reaction energy, along with $^1\text{p9}$ ($-72 \pm 5 \text{ kJ mol}^{-1}$), can account for the observed product channels in each isotopic study and therefore likely contribute to the SiC_4H_4 signal arising from the $\text{Si}(^3\text{P})$ plus 1,3-butadiene reaction. Given the immense number of predicted stable SiC_4H_4 isomers a full investigation of the singlet and triplet SiC_4H_6 PESs is merited. The PES must consider the bimolecular entrance channels for the addition of $\text{Si}(^3\text{P})$ to 1,3-butadiene, 1,2-butadiene, 1-butyne, and 2-butyne. Since the isomers formed in the low-lying product channels are singlet, the triplet SiC_4H_6 isomers facilitating intersystem crossing must also be located and characterized. RRKM analysis coupled to the *ab initio* results should render predictions for which SiC_4H_6 isomers participate in the reaction scheme and to what extent each SiC_4H_4 isomer is formed over a range of collision energies.

The present investigation along with the $\text{Si}(^3\text{P})$ – 2-butyne study carried out earlier [37] reveal that ground state silicon atoms – in strong contrast to C1 to C3 hydrocarbons – can react exoergically forming hitherto elusive and exotic SiC_4H_4 singlet isomers whose exact nature has yet been determined. Although the ligand-stabilized silacyclopentadienylidene ($\text{c-SiC}_4\text{Ph}_4$) has been isolated in a hydrocarbon matrix (77 K) [60], and later used in the synthesis of siloles and silanones [61,62], the neutral products of our $\text{Si}(^3\text{P})$ reaction with the C_4H_6 isomers represent the first free SiC_4H_4 molecules synthesized in the gas-phase. On the other hand, numerous isoelectronic C_5H_4 isomers have been synthesized and are available from commercial suppliers. Crossed molecular beam experiments combined with electronic structure calculations revealed that bimolecular reactions of ground state atomic carbon ($\text{C}(^3\text{P})$) with unsaturated C_4H_6 isomers are initiated by the barrierless addition of the carbon atom to a carbon-carbon double or triple bond followed by hydrogen migration and/or ring opening of the initial collision complex and further isomerization(s) of reaction intermediates in overall exoergic reactions [25]. These indirect scattering dynamics are predominantly dictated by atomic carbon versus atomic hydrogen replacement channels leading to an extension of the carbon skeleton in the hydrocarbon reactant by a single carbon atom forming principally acyclic resonantly stabilized free radicals (RSFR). With the exception of the carbon–acetylene system, which reveals non-adiabatic reaction dynamics on the singlet surface exhibiting both atomic and molecular hydrogen loss channels [63–67], the remaining carbon atom reactions take place solely on the triplet surface. The reactions of $\text{C}(^3\text{P})$ with the unsaturated C_4H_6 isomers 1,3-butadiene, 1,2-butadiene, 2-butyne form predominantly the doublet C_5H_5 products 1-vinylpropargyl ($\text{HCCCHC}_2\text{H}_3$), 3-vinylpropargyl ($\text{H}_2\text{CCCC}_2\text{H}_3$), and 1-methylbutatrienyl ($\text{H}_2\text{CCCCCH}_3$), respectively, alongside atomic hydrogen. The crossed molecular beams study of the $\text{C}(^3\text{P})$ – 1-butyne system remains outstanding, although its reaction dynamics are likely derived from $\text{C}(^3\text{P})$ – 2-butyne system [68]. Nonetheless, it is clear that the reactivity of carbon is dictated by its preference to form carbon-carbon multiple bonds whereas silicon is recognized to form exotic cyclic products or silene-type structures – which are analogous to carbenes in the carbon chemistry – as revealed in our $\text{Si}(^3\text{P})$ plus 1,3-butadiene-(d_2/d_4) studies.

Finally, it is worth noting the recent series of reactions of atomic oxygen ($\text{O}(^3\text{P})$) with the unsaturated hydrocarbons acetylene (C_2H_2) [69,70], ethylene (C_2H_4) [71–74], allene (CH_2CCH_2) [75,76], propyne (CH_3CCH) [76–79], propylene (CH_3CHCH_2) [80,81], and 1-butene ($\text{CH}_2\text{CHCH}_2\text{CH}_3$) [82] that were conducted under single-collision conditions using the crossed molecular beams method equipped with soft electron impact ionization by tunable low-energy electrons [69].

Although these reactions originate on the triplet PES, the incorporation of the heavy $\text{O}(^3\text{P})$ atom increases spin-orbit coupling thereby granting access to distinct product channels born of activity on both the triplet and singlet surfaces [83,84]. The extrema of this series are the $\text{O}(^3\text{P})$ + acetylene reaction that proceeded exclusively on the triplet surface within the detection limits of the experiment [69,70], and the $\text{O}(^3\text{P})$ + allene system where over 90% of detected products were formed via an ISC-mediated reaction mechanism [75,76]. The extent of ISC in each $\text{O}(^3\text{P})$ -hydrocarbon system is dictated by the topology of the PES with an emphasis on the stability of the initially formed triplet intermediate which directly influences its tendency to either proceed to products along the triplet surface or to undergo ISC and dissociate on singlet surface [84]. In strong contrast to this observation, $\text{Si}(^3\text{P})$ collisions with hydrocarbons in the gas-phase under single-collision conditions either do not react (C1/C3 hydrocarbons), or react adiabatically as was observed for the endoergic reaction $\text{Si}(^3\text{P}) + \text{C}_2\text{H}_2(\text{X}^1\Sigma_g^+) \rightarrow \text{SiCCH}(\text{X}^2\Pi) + \text{H}(\text{S}_{1/2})$ [36]. Intersystem crossing does not appear to play a role until the $\text{Si}(^3\text{P})$ - C_4H_6 system at which point, as supported by our theory, it is the only viable path to product formation. It will be interesting to probe the reactivity of $\text{Si}(^3\text{P})$ with the butene (C_4H_8) isomers, along with other unsaturated C4 hydrocarbons such as vinylacetylene ($\text{C}_2\text{H}_3\text{CCH}$) and diacetylene (C_4H_2), to determine to what extent, if any, ISC is involved in the reaction dynamics and to determine whether product formation can occur on both the singlet and triplet potential energy surfaces as was observed in most of the $\text{O}(^3\text{P})$ -hydrocarbon catalogue.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemphys.2019.01.001>.

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