

Reaction Dynamics Study of the Molecular Hydrogen Loss Channel in the Elementary Reactions of Ground-State Silicon Atoms ($\text{Si}(^3\text{P})$) With 1- and 2-Methyl-1,3-Butadiene (C_5H_8)

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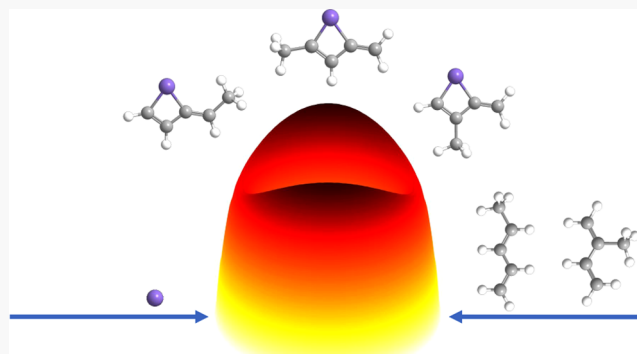


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ABSTRACT: The bimolecular gas-phase reactions involving ground-state atomic silicon ($\text{Si}; ^3\text{P}$) and 1- and 2-methyl-1,3-butadiene were studied via crossed molecular beam experiments. Our data revealed indirect scattering dynamics through long-lived SiC_5H_8 collision complex(es) along with molecular hydrogen loss pathways, leading to facile formation of SiC_5H_6 isomer(s). We propose that the reactions of silicon with 1- and 2-methyl-1,3-butadiene possess reaction dynamics in an analogy to the silicon–1,3-butadiene system. This leads to cyclic methyl-substituted 2-methylene-1-silacyclobutene isomers via nonadiabatic reaction dynamics through intersystem crossing (ISC) from the triplet to the singlet surface in overall exoergic reactions through tight exit transition states and molecular hydrogen loss. Our study also suggests that the methyl group—although a spectator from the chemical viewpoint—can influence the disposal of the angular momentum into the rotational excitation of the final product.



1. INTRODUCTION

Carbon (C) and silicon (Si) both belong to main group XIV and hence have each four valence electrons along with a $^3\text{P}_j$ electronic ground state. Despite their isovalency, carbon and silicon depict distinct chemical dynamics upon reaction with unsaturated hydrocarbons (alkynes, alkenes, aromatics).^{1–11} Reactions of $\text{C}(^3\text{P}_j)$ with unsaturated hydrocarbons are very fast close to gas kinetic limits and hold rate constants of a few $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ over temperatures from 15 to 300 K.^{12–17} These processes are barrierless and proceed via addition of the carbon atom to one and/or both carbon atoms of the unsaturated bond; the initial reaction intermediates either isomerize through ring opening/ring closure and facile hydrogen shifts eventually forming highly unsaturated, often resonantly stabilized free radicals (RSFRs) through the carbon versus hydrogen atom exchange pathways in overall exoergic reactions.^{18–22} These RSFRs are frequently substituted propargyl radicals as derived from the replacement of a hydrogen atom of propargyl (1) by methyl (CH_3), ethynyl (CCH), or vinyl (C_2H_3) groups and might act as a feedstock of (doubly) substituted benzenes in combustion flames and in deep space. With the exception of the carbon–acetylene system,^{5,8,11,23} which also reveals nonadiabatic reaction dynamics through intersystem crossing (ISC) from the triplet to the singlet surface accompanied by molecular hydrogen loss

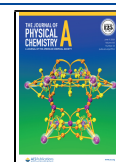
and tricarbon (C_3) formation, all carbon–hydrocarbon exchange reactions proceed likely on the triplet surface.

On the other hand, the reactivities of $\text{Si}(^3\text{P}_j)$ with hydrocarbon systems are quite distinct. Upon collisions with C1–C3 hydrocarbons, silicon does not react at all under single collision conditions through exoergic reactions. A crossed molecular beam study probed the $\text{Si}(^3\text{P})$ plus acetylene (C_2H_2) system, revealing the formation of the linear ethynylsilylydyne (SiCCH) molecule and atomic hydrogen at a collision energy of $101.6 \pm 1.6 \text{ kJ mol}^{-1}$ and a reaction endoergicity of $+84 \pm 6 \text{ kJ mol}^{-1}$.²⁴ No reactive scattering signal could be detected for experiments under single collision conditions of $\text{Si}(^3\text{P})$ with any hydrocarbon up to C3 including the C_3H_4 isomers methylacetylene (CH_3CCH) and allene (CH_2CCH_2) at collision energies up to 30 kJ mol^{-1} , indicating that endoergicities and/or reaction barriers in this reaction system are insurmountable. This lack of reactivity seems to be in contrast to early kinetics studies by Canosa et al.,²⁵ Basu and Husain,^{26,27} which suggest that the reactions of $\text{Si}(^3\text{P})$ with

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unsaturated hydrocarbons are close to gas kinetics values with rate constants of a few $10^{-10} \text{ cm}^3 \text{ s}^{-1}$. However, only the decay kinetics of the silicon atom were probed in these studies, without the identification of the reaction products. In fact, these reaction products are of critical importance since they can help unraveling fundamental constraints on the exotic chemical bonding and reaction mechanism(s) (bimolecular versus three-body reactions) of organosilicon molecules. This discrepancy might be explained through the formation of collision complexes between silicon and the hydrocarbons followed by rapid collisional stabilization. The results of calculations by Talbi also suggested that the rapid rate constants for the silicon plus acetylene and silicon plus ethylene reactions were due to the intervention of a third body. Within the hypotheses of efficient intersystem crossing to the singlet surface, the barrierless formation of some singlet and triplet SiC_2H_2 and SiC_2H_4 isomers should be inhibited.²⁸ Bimolecular reactions of ground-state oxygen atoms $\text{O}(^3\text{P})$ with unsaturated hydrocarbons like acetylene,²⁹ ethylene,³⁰ propene,³¹ allene,³² and 1-butene³³ have been studied previously. These multichannel reactions involve important nonadiabatic effects, and products can be formed through exoergic reactions even in reactions with C1–C3 hydrocarbons; this finding is quite different from the silicon reactions. Very recently, crossed beam experiments revealed that $\text{Si}(^3\text{P})$ reacts exoergically with four C_4H_6 isomers, i.e., 2-butyne (CH_3CCCH_3),³⁴ 1,3-butadiene ($\text{H}_2\text{CCHCHCH}_2$), 1,2-butadiene ($\text{CH}_2\text{CCHCH}_3$), and 1-butyne ($\text{CH}_3\text{CH}_2\text{CCH}$), producing multiple singlet SiC_4H_4 isomers such as 2-methylene-1-silacyclobutene ($\text{SiC}_2\text{H}_2\text{CCH}_2$; X^1A) along with molecular hydrogen (H_2) through nonadiabatic reaction dynamics.³⁵ Considering the lack of rapid reaction of C1 to C3 hydrocarbons with ground-state atomic silicon, but the facile nonadiabatic dynamics of atomic silicon with the four C_4H_6 isomers, the chemical dynamics of $\text{Si}(^3\text{P}_i)$ with hydrocarbons still remain poorly understood, and a more systematic investigation is required.

Here, the experimental results of the $\text{Si}(^3\text{P})$ reactions with two C_5H_8 isomers, 1-methyl-1,3-butadiene and 2-methyl-1,3-butadiene, are reported to expand our knowledge of the fundamental reaction mechanisms of the silicon–carbon chemistry in the gas phase. The formal linkage of these hydrocarbons to 1,3-butadiene can be explored by replacing one of the hydrogen atoms at the C1/C4 and C2/C3, respectively, by a methyl group. An understanding of the inherent (nonadiabatic) reaction dynamics will explore to what extent the methyl group simply acts as a spectator, induces steric effects, and/or is actively engaged in the gas-phase chemistry such as via methane (CH_4) elimination accompanied by formation of SiC_4H_4 isomers.

2. EXPERIMENTAL METHODS

The reactions of atomic silicon (Si ; ^3P) with 1-methyl-1,3-butadiene ($\geq 97\%$; TCI America) and 2-methyl-1,3-butadiene (isoprene; $\geq 99\%$; TCI America) were carried out in a crossed molecular beams machine.^{36–38} Briefly, a supersonic atomic beam of ground-state silicon atoms was prepared in the primary source chamber in situ through ablation of a rotating silicon rod exploiting the 266 nm pulse (4th harmonic of a Nd:YAG; $5 \pm 1 \text{ mJ}$ per pulse; 30 Hz)^{39–42} and entraining the ablated atoms in a pulsed neon (Ne ; 99.999%; Airgas; 60 Hz; 4 atm) beam. The laser-induced fluorescence (LIF) spectra measured in the ablation source are presented in Figure 1; at

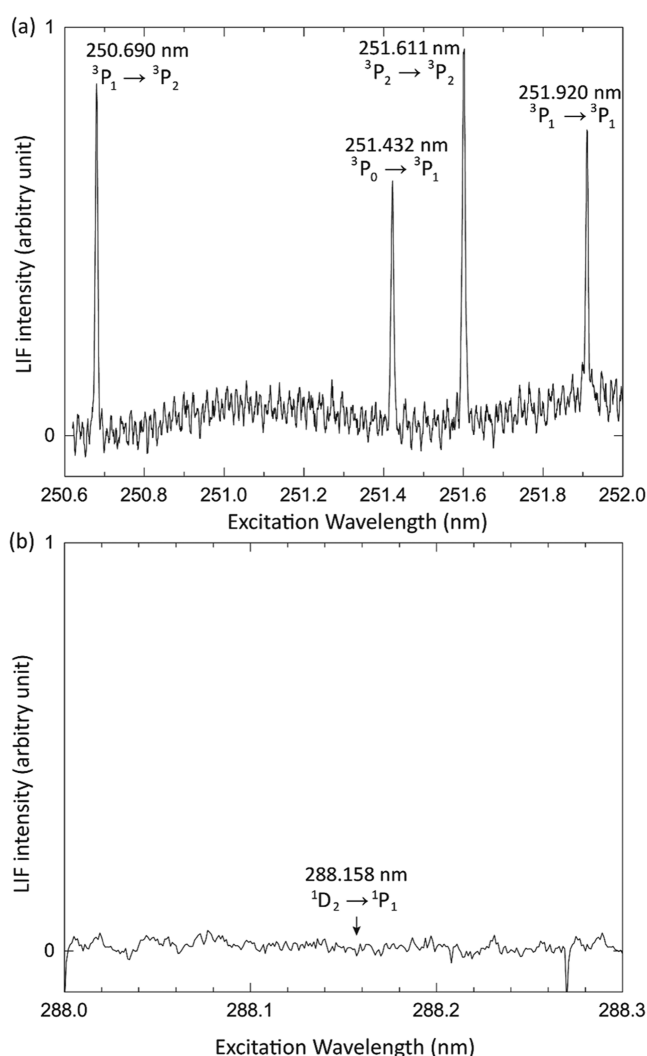


Figure 1. Laser-induced fluorescence (LIF) spectra of the (a) ground (^3P) and (b) excited (^1D) states of atomic silicon. The arrow in panel (b) indicates the expected position for the noted transition.

these experimental conditions, there are no electronically excited silicon atoms $\text{Si}(^1\text{D})$ in the molecular beam. Thirty Hertz of ablation laser versus 60 Hz of the gas will allow a “laser on” minus “laser off” background subtraction. The neon-seeded primary silicon beam was skimmed and then velocity-selected by a 120 Hz high-precision four-slit chopper wheel (2057S024B, MC 5005 S RS, Faulhaber), which resulted in well-defined speed ratios (S) of 6.2 ± 0.4 and 6.1 ± 0.4 along with peak velocities (v_p) of 975 ± 30 and $982 \pm 30 \text{ m s}^{-1}$ (Table 1). As verified by the laser-induced fluorescence spectra, all silicon atoms of our neon-seeded silicon beam are in their electronic ground state (^3P).⁴³ As for the secondary source, the hydrocarbon reactant 1-methyl-1,3-butadiene or 2-methyl-1,3-butadiene was kept in a stainless-steel reservoir at 293 K under backing pressure of 400 or 430 Torr. The corresponding peak velocities and speed ratios of $v_p = 711 \pm 20 \text{ m s}^{-1}$ with $S = 8.5 \pm 0.7$ and $v_p = 721 \pm 20$ with $S = 8.5 \pm 0.6$ were derived, respectively. The hydrocarbon beams crossed perpendicularly with the primary $\text{Si}(^3\text{P})$ beam in the interaction region yielding center-of-mass (CM) angles of 60.5 ± 0.6 and $60.7 \pm 0.5^\circ$ and collision energies of 14.4 ± 0.4 and $14.7 \pm 0.4 \text{ kJ mol}^{-1}$ (Table 1).

Table 1. Peak Velocity (v_p) and Speed Ratios (S) of the Silicon (Si), 1,3-Pentadiene ($\text{CH}_2\text{CHCHCHCH}_3$), and Isoprene ($\text{CH}_2\text{CHCCH}_3\text{CH}_2$) Beams along With the Corresponding Collision Energy (E_c), Spread Ratio of Collision Energy (S), and Center-of-Mass Angle (Θ_{CM}) for Each Reactive Scattering Experiment

beam	v_p (m s $^{-1}$)	S	E_c (kJ mol $^{-1}$)	S	Θ_{CM} (°)
Si (^3P)	975 $\pm$ 30	6.2 $\pm$ 0.4			
$\text{CH}_2\text{CHCHCHCH}_3$ ($\text{X}^1\text{A}'$)	711 $\pm$ 20	8.5 $\pm$ 0.7	14.4 $\pm$ 0.4	4.0 $\pm$ 0.3	60.5 $\pm$ 0.6
Si (^3P)	982 $\pm$ 30	6.1 $\pm$ 0.4			
$\text{CH}_2\text{CHCCH}_3\text{CH}_2$ ($\text{X}^1\text{A}'$)	721 $\pm$ 20	8.5 $\pm$ 0.6	14.7 $\pm$ 0.4	4.0 $\pm$ 0.3	60.7 $\pm$ 0.5

In our experiment, a quadrupole mass filter was exploited to mass filter the ionized (80 eV, 2 mA) reactive scattering products, a 1.2 MHz oscillator, and a Daly-type time-of-flight (TOF) detector, which is installed in a ultrahigh vacuum ($<10^{-11}$ Torr) chamber, were also used. The recorded TOF spectra eventually provide the product angular distribution in the laboratory frame and provide the basis for the transformation of the laboratory data into the center-of-mass (CM) frame through the use of a forward-convolution routine. This results in the extraction of the CM angular flux distribution $T(\theta)$ and translational energy flux distribution $P(E_T)$. Finally, the best fits of the lab angular distribution and TOF spectra are derived by optimizing the $T(\theta)$ and $P(E_T)$ functions. The reactive differential cross section can be displayed via the flux contour map with the CM velocity u and scattering angle θ , i.e., $I(u, \theta) \sim P(u) \times T(\theta)$.

3. RESULTS

3.1. Laboratory Frame. Our scattering experiments explored signal at mass-to-charge ratios (m/z) 98 to 94 and 82 to 80 to investigate the presence of molecular (H_2) and atomic (H) hydrogen loss channels, methylene (CH_2), methyl (CH_3), and methane (CH_4) elimination pathways along with adducts. Accounting for the natural abundances of three silicon isotopes (^{30}Si (3.1%), ^{29}Si (4.7%), and ^{28}Si (92.2%)) as well as carbon (^{13}C (1.1%), ^{12}C (98.9%)), we were not able to detect signal at m/z 98 and 97. Signal was observed at m/z 96 ($^{30}\text{SiC}_5\text{H}_6^+$, $^{30}\text{Si}^{13}\text{CC}_4\text{H}_5^+$, $^{29}\text{SiC}_5\text{H}_7^+$, $^{29}\text{Si}^{13}\text{CC}_4\text{H}_6^+$, $^{28}\text{Si}^{13}\text{CC}_4\text{H}_7^+$, $^{28}\text{SiC}_5\text{H}_8^+$), 95 ($^{30}\text{SiC}_5\text{H}_5^+$, $^{30}\text{Si}^{13}\text{CC}_4\text{H}_4^+$, $^{29}\text{SiC}_5\text{H}_6^+$, $^{29}\text{Si}^{13}\text{CC}_4\text{H}_5^+$, $^{28}\text{Si}^{13}\text{CC}_4\text{H}_6^+$, $^{28}\text{SiC}_5\text{H}_7^+$), and 94 ($^{30}\text{SiC}_5\text{H}_4^+$, $^{30}\text{Si}^{13}\text{CC}_4\text{H}_3^+$, $^{29}\text{SiC}_5\text{H}_5^+$, $^{29}\text{Si}^{13}\text{CC}_4\text{H}_4^+$, $^{28}\text{Si}^{13}\text{CC}_4\text{H}_5^+$, and $^{28}\text{SiC}_5\text{H}_6^+$). Since after scaling, the TOFs at m/z = 96, 95, and 94 reveal identical patterns and hence do overlap, a single reaction channel is likely. These findings propose the absence of adducts ($^{30}\text{SiC}_5\text{H}_8^+ / ^{29}\text{SiC}_5\text{H}_8^+ / ^{28}\text{SiC}_5\text{H}_8^+$) and the nonexistence of the atomic hydrogen loss channel ($^{30}\text{SiC}_5\text{H}_7^+ / ^{29}\text{SiC}_5\text{H}_7^+ / ^{28}\text{SiC}_5\text{H}_7^+$). Quantitatively spoken, signal at m/z 96 to 95 was observed at levels of close to 4% ($4 \pm 1\%$ for 1,3-pentadiene, $3 \pm 1\%$ for isoprene), 10% ($12 \pm 3\%$ for 1,3-pentadiene, $11 \pm 2\%$ for isoprene) compared to m/z = 94, which is close to the calculated isotopic ratios. Signal at m/z 96, 95, and 94 can be attributed to $^{30}\text{SiC}_5\text{H}_6^+$, $^{29}\text{SiC}_5\text{H}_6^+$, $^{28}\text{Si}^{13}\text{CC}_4\text{H}_6^+$, and $^{28}\text{SiC}_5\text{H}_6^+$ (hereafter: SiC_5H_6), respectively, along with their fragment ions ($^{30}\text{SiC}_5\text{H}_5^+ / ^{30}\text{SiC}_5\text{H}_4^+ / ^{29}\text{SiC}_5\text{H}_5^+ / ^{28}\text{Si}^{13}\text{CC}_4\text{H}_5^+$) (Figures 2a and 2b). Therefore, according to the laboratory data, there is strong evidence of the molecular hydrogen loss pathway, leading to the formation of SiC_5H_6 isomers in the reaction of $\text{Si}(^3\text{P})$ with both C_5H_8 isomers, 1,3-pentadiene and isoprene. For both systems, TOF spectra for the molecular hydrogen loss channel were collected at m/z = 94, i.e., the dominant ion, in steps of 2.5° . The TOF spectra are very broad from at least

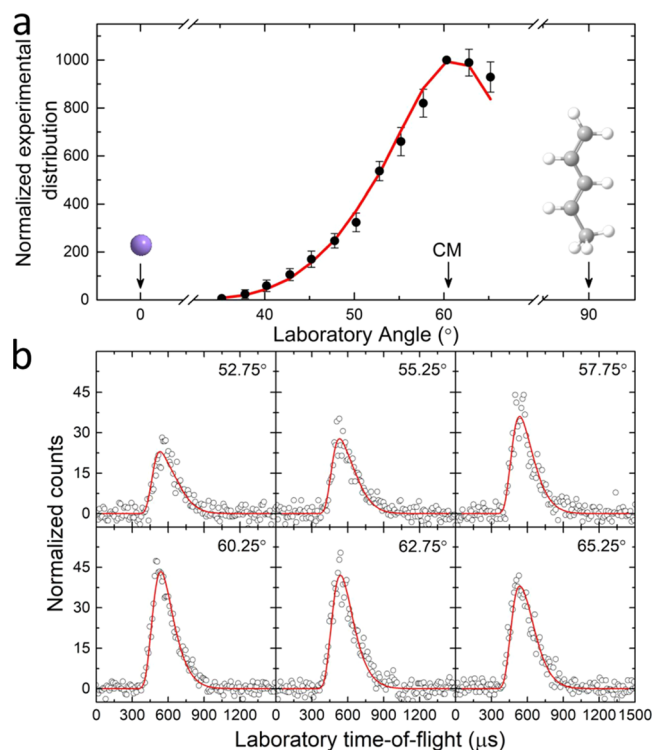


Figure 2a. Laboratory angular distribution (a) and time-of-flight spectra (b) recorded in the reaction of the ground-state atomic silicon with 1,3-pentadiene at a mass-to-charge ratio of m/z = 94. The normalized experimental distribution is represented by the solid circles with $\pm 1\sigma$ error bars and the experimental time-of-flight spectra data points are indicated by the open circles. The best fits represented by the red lines are derived from the optimized center-of-mass (CM) functions, as depicted in Figure 3a. Silicon, carbon, and hydrogen are color-coded in purple, gray, and white, respectively.

350 to 900 μs and peak between 400 and 500 μs . The normalized laboratory angular distributions span at least 35° and reveal maxima close to their respective CM angles (Figures 2a and 2b). Their symmetries around the CM angles propose indirect reaction mechanisms with at least one SiC_5H_8 reaction intermediate and molecular hydrogen (H_2) loss to form the SiC_5H_6 isomer(s).

3.2. Center-of-Mass Frame. An $E_c^{-1/3}$ dependence reaction cross section for a dipole-induced dipole interaction and a single reaction channel fit with the mass combination Si (28 amu) + C_5H_8 (68 amu) $\rightarrow$ SiC_5H_6 (94 amu) + H_2 (2 amu) were utilized for both systems.⁴⁴ The best-fitting CM functions are compiled in red lines in Figures 3a and 3b and 1σ error limits of the scattering experiment are represented by the hatched areas of the $P(E_T)$ and $T(\theta)$ functions. First, let us consider the center-of-mass translational energy distributions. The maximum energy E_{max} available to the translation degrees of freedom of the nascent SiC_5H_6 plus molecular hydrogen

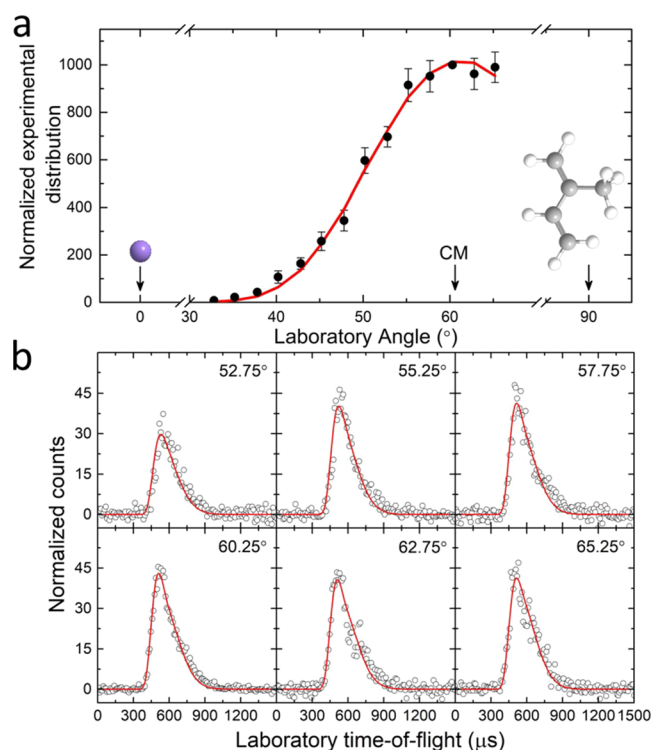


Figure 2b. Laboratory angular distribution (a) and time-of-flight spectra (b) recorded in the reaction of the ground-state atomic silicon with isoprene at a mass-to-charge ratio of $m/z = 94$. The normalized experimental distribution is represented by the solid circles with $\pm 1\sigma$ error bars and the experimental time-of-flight spectra data points are indicated by the open circles. The best fits represented by the red lines are derived from the optimized center-of-mass (CM) functions, as depicted in Figure 3b. Silicon, carbon, and hydrogen are color-coded in purple, gray, and white, respectively.

products is determined as $E_{\max} = E_C - \Delta_r G$ through energy conservation by summing the reaction energy and the collision energy. Accordingly, by subtracting the collision energy from the maximum translational energy (Figures 3a and 3b), the reactions of $\text{Si}(^3\text{P})$ with 1-methyl-1,3-butadiene and 2-methyl-1,3-butadiene to form SiC_5H_6 plus molecular hydrogen are exoergic by 113 ± 19 and 101 ± 21 kJ mol^{-1} , respectively. The $P(E_T)$ s of the two systems peaked at translational energies of 20 ± 4 and 30 ± 5 kJ mol^{-1} . These relatively high energies provide evidence of the existence of tight exit transition states in the molecular hydrogen elimination. Overall, both $P(E_T)$ s are very similar in shape, albeit the silicon–1-methyl-1,3-butadiene system revealing a slightly higher translational energy release. Comparable $T(\theta)$ functions are also evident for both systems with best-fitting $T(\theta)$ achieved for a product flux over the entire angular range. The forward–backward symmetries and sideways scattering (maximum at 90°) suggest the presence of a decomposing SiC_5H_8 intermediate (indirect scattering dynamics) with a lifetime comparable to or exceeding its rotational period;^{45,46} the sideways scattering reveals significant geometrical constraints and suggests that molecular hydrogen elimination occurs nearly parallel to the total angular momentum vector and hence perpendicularly to the rotational plane of the decomposing intermediate.^{45,46} However, the more pronounced peaking in the silicon–1-methyl-1,3-butadiene system is evident (Figure 3a).

4. DISCUSSION

Our experimental results reveal that atomic silicon reacts exoergically with 1-methyl- and 2-methyl-1,3-butadiene to SiC_5H_6 organosilicon product(s) together with molecular hydrogen (H_2) through tight exit transition states and long-lived SiC_5H_8 reaction intermediate(s). The molecular formula of these newly synthesized organosilicon reaction products has

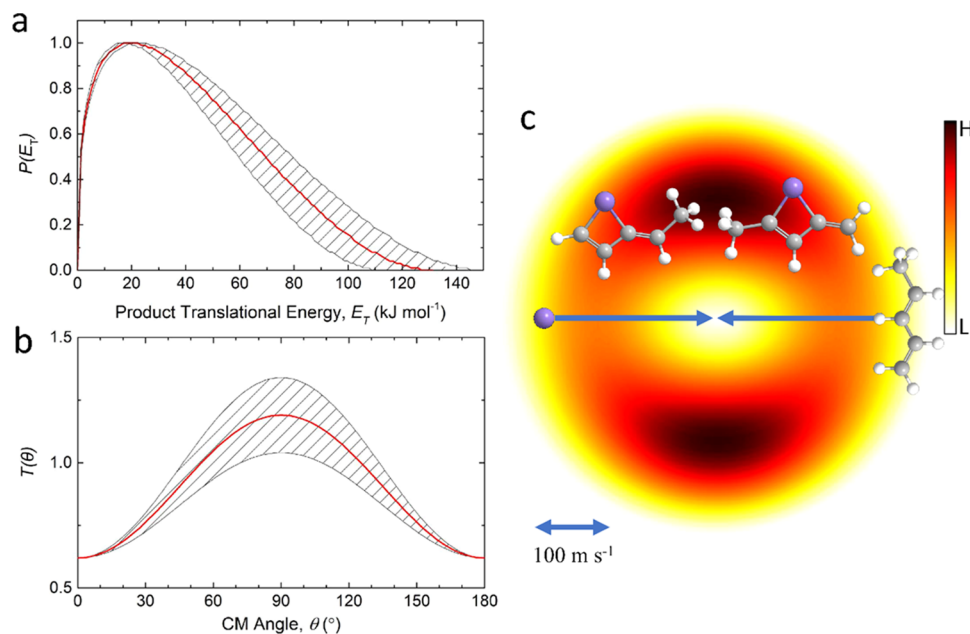


Figure 3a. Center-of-mass (CM) translational energy flux distribution (a), angular distribution (b), and the corresponding flux contour map (c) for the reaction of ground-state atomic silicon with 1,3-pentadiene. The 1σ error limits of the scattering experiment are represented by the shaded areas and the best-fit functions are defined by the red solid lines. The flux contour map symbolizes the reactive scattering products as a function of the CM scattering angle (θ) and product velocity (u). The flux gradient from high (H) intensity to low (L) intensity is indicated by the color bar. Silicon, carbon, and hydrogen are color-coded in purple, gray, and white, respectively.

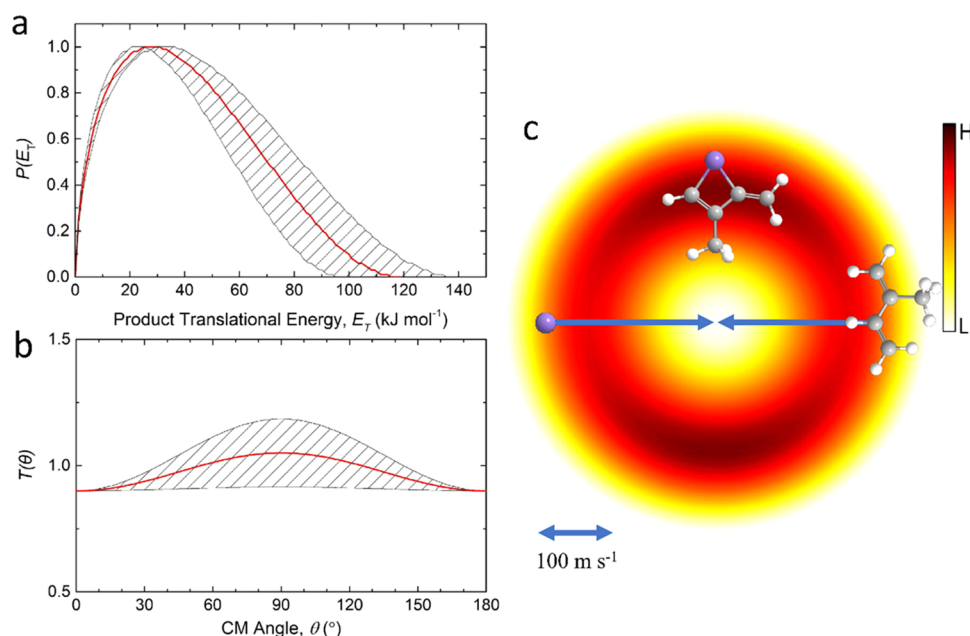


Figure 3b. Center-of-Mass (CM) translational energy flux distribution (a), angular distribution (b) and the corresponding flux contour map (c) for the reaction of ground-state atomic silicon with isoprene. The 1 σ error limits of the scattering experiment are represented by the shaded areas and the best-fit functions are defined by red solid lines. The flux contour map symbolizes the reactive scattering products as a function of the CM scattering angle (θ) and product velocity (u). The flux gradient from high (H) intensity to low (L) intensity is indicated by the color bar. Silicon, carbon, and hydrogen are color-coded in purple, gray, and white, respectively.

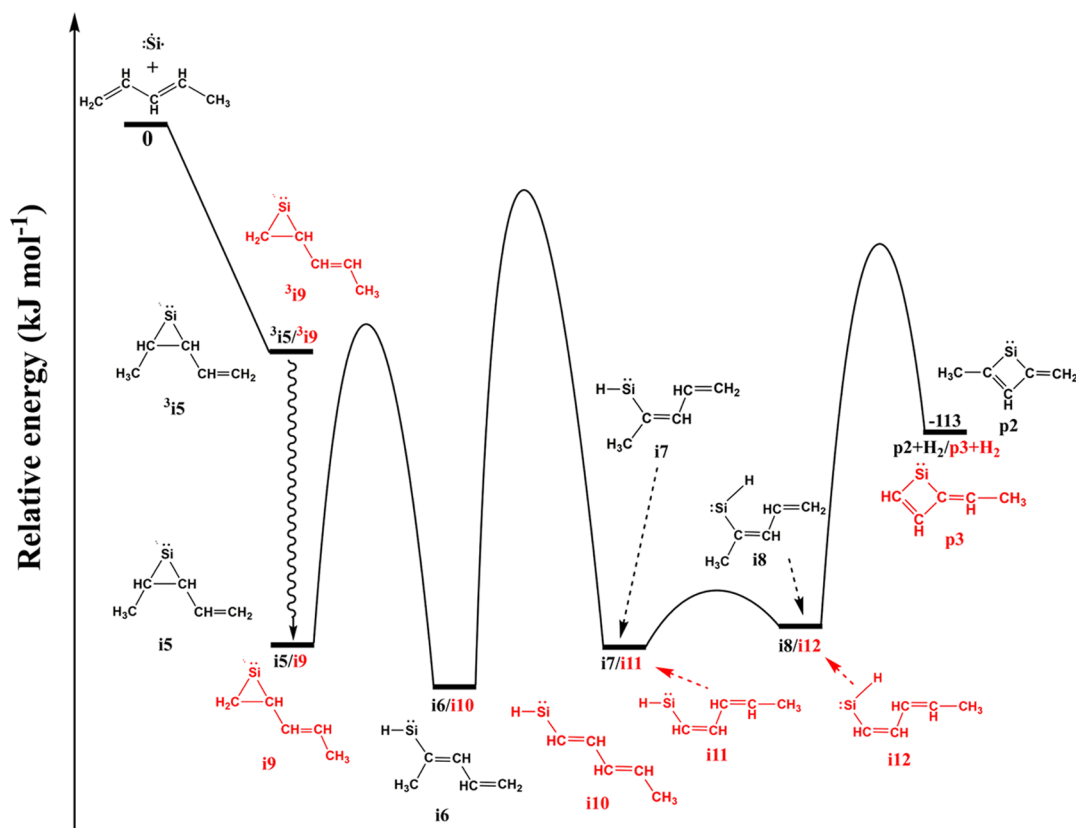


Figure 4a. Inferred reaction pathway of ground-state silicon atom ($\text{Si}(^3\text{P})$) with 1,3-pentadiene ($\text{CH}_2\text{CHCHCHCH}_3$) by analogy with the 1,3-butadiene case (Figure 8 in ref 35), leading via molecular hydrogen loss to methyl-substituted c-SiCHCHCHCH_2 products. Two proposed pathways accounting for the barrierless addition of the silicon atom to the different carbon–carbon double bond of the 1,3-pentadiene are color-coded in black and red, respectively.

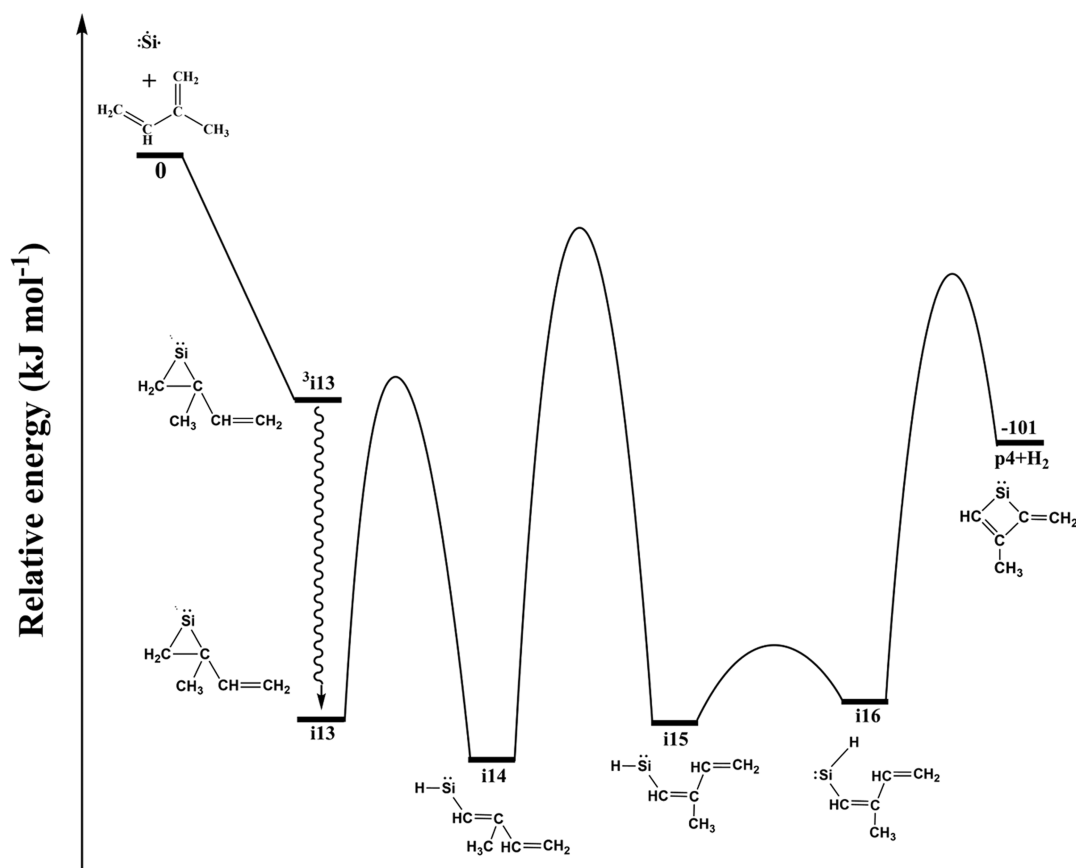


Figure 4b. Inferred reaction pathway of ground-state silicon atom ($\text{Si}(^3\text{P})$) with isoprene ($\text{CH}_2\text{CHCCH}_3\text{CH}_2$) by analogy with the 1,3-butadiene case (Figure 8 in ref 35) leading via molecular hydrogen loss to methyl-substituted $c\text{-SiCHCHCCH}_2$ products.

been determined (SiC_5H_6); our study will also propose the molecular structure, inherent formation mechanism(s), and reaction dynamics of the product isomer(s). Traditionally, feasible reaction products are determined by comparing the experimentally derived reaction energies for each system (-113 ± 19 and $-101 \pm 21 \text{ kJ mol}^{-1}$) with reaction energies obtained from electronic structure calculations.^{34,35} However, a full theoretical analysis of the SiC_5H_8 potential energy surface (PES) and conical intersections along with a statistical Rice–Ramsperger–Kassel–Marcus (RRKM) treatment is well beyond the scope of this dissemination considering the complexity of both systems. Considering the fact that we only observed molecular hydrogen loss, but neither atomic hydrogen, methyl, nor methane loss pathways, we are attempting an elucidation of the reaction dynamics by comparing the reaction dynamics of the Si–1,3-butadiene reaction with the methyl-substituted systems obtained here. Briefly, the reaction of ground-state silicon atoms with 1,3-butadiene is initiated by a barrierless addition of the silicon atom to one of the carbon–carbon double bonds, forming a triplet reaction intermediate $^3\text{i1}$ stabilized by 91 kJ mol^{-1} (Figure 8 in ref 35). For the energetically most favorable channel, the latter can undergo facile intersystem crossing to the singlet manifold, which leads to an i1 intermediate, which resides in a 190 kJ mol^{-1} potential energy well. An atomic hydrogen migration from the H_2C moiety within the three-membered ring is accompanied by ring opening to i2 followed by two trans–cis isomerization (i3 , i4). The latter eventually emits molecular hydrogen followed by cyclization to 2-methylene-1-silacyclobutene ($c\text{-SiCHCHCCH}_2$); this mecha-

nism reveals that the hydrogen atoms in molecular hydrogen originate from the C1 and C3 carbon atoms each in an overall exoergic reaction ($-120 \pm 5 \text{ kJ mol}^{-1}$). These dynamics correlate with the results from the reaction of ground-state silicon with 1,1,4,4- D_4 - and 2,3- D_2 -1,3-butadiene and the identification of the HD channel. Let us evaluate what happens if this mechanism is exported to the 1-methyl- and 2-methyl-1,3-butadiene reactants (Figures 4a and 4b). Note that due to the methyl group, the carbon–carbon double bonds are not chemically equivalent as they are in 1,3-butadiene. These pathways could lead to three triplet collision complexes ($^3\text{i5}$, $^3\text{i9}$, and $^3\text{i13}$), which could undergo intersystem crossing to singlet i5 , i9 , and i13 . Successive hydrogen shifts accompanied by ring openings (i6 , i10 , and i14) followed by trans/cis isomerization eventually led to i8 , i12 , and i16 , which could emit molecular hydrogen to yield methyl-substituted analog structures of 2-methylene-1-silacyclobutene ($c\text{-SiCHCHCCH}_2$). From the chemical viewpoint, the methyl group may act as a spectator in both reactions. However, considering the distinct structures and moment of inertia of the decomposing complexes i8 , i12 , and i16 , from the dynamical viewpoint, the methyl group influences the chemical dynamics, leading to a more pronounced sideways scattering in the silicon–1-methyl-1,3-butadiene system compared to the reaction with 2-methyl-1,3-butadiene (isoprene). It shall be noted that the proposed dynamics represent one of possible multiple (less exoergic) additional reaction pathways, which remain to be explored.

5. CONCLUSIONS

In conclusion, bimolecular gas-phase reactions of ground-state atomic silicon (Si; ^3P) with 1- and 2-methyl-1,3-butadiene were studied; the reactions revealed indirect scattering dynamics through long-lived SiC_5H_8 collision complex(es) together with a facile formation of SiC_5H_6 isomer(s) along with molecular hydrogen. We propose—in an analogy of the derived center-of-mass functions of the silicon–1,3-butadiene system—that the reaction proceeds via nonadiabatic reaction dynamics through intersystem crossing (ISC) from the triplet to the singlet surface, yielding eventually to methyl-substituted 2-methylene-1-silacyclobutene isomers in overall exoergic reactions (-113 ± 19 and -101 ± 21 kJ mol $^{-1}$) through tight exit transition states. Therefore, we may conclude that at least singly, alkyl-substituted 1,3-butadiene molecules react with atomic silicon to form eventually alkyl-substituted, cyclic 2-methylene-1-silacyclobutene products. Although the methyl group acts as a spectator from the chemical viewpoint, it does influence the disposal of angular momentum into the rotational excitation of the final products, as evident from distinct center-of-mass angular distributions of both systems explored here.

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Notes

The authors declare no competing financial interest.

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