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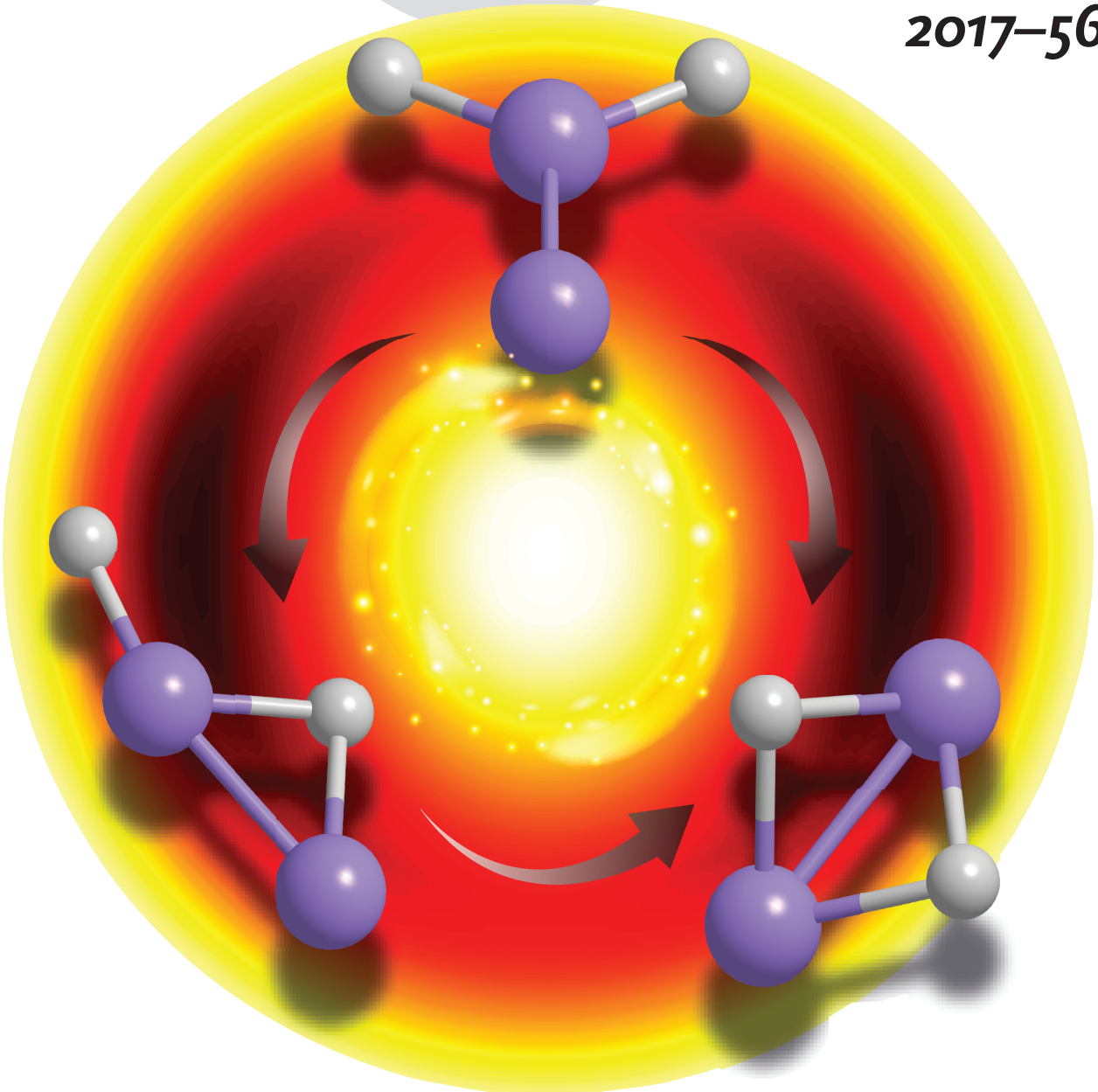

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… of the reactive differential cross section, the hitherto elusive disilavinylidene molecule (H_2SiSi) is found to be initially formed in the gas-phase reaction of ground-state atomic silicon (Si) with silane (SiH_4) and in equilibrium with the mono-bridged (Si(H)SiH) and di-bridged ($Si(H_2)Si$) isomers. As shown by R. I. Kaiser, A. H. H. Chang, J. F. Stanton et al. in their Communication on page 1264 ff., the dynamics are distinct from those of the isovalent carbon/methane system, and provide a rare glimpse of unusual silicon chemistry.

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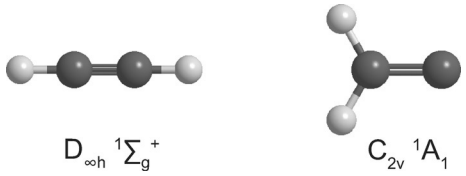
Gas-Phase Formation of the Disilavinylidene (H_2SiSi) Transient

Tao Yang[+], Beni B. Dangi[+], Ralf I. Kaiser, Kang-Heng Chao, Bing-Jian Sun, Agnes H. H. Chang,* Thanh Lam Nguyen, and John F. Stanton**

Abstract: *The hitherto elusive disilavinylidene (H_2SiSi) molecule, which is in equilibrium with the mono-bridged (Si(H)SiH) and di-bridged (Si(H_2)Si) isomers, was initially formed in the gas-phase reaction of ground-state atomic silicon (Si) with silane (SiH_4) under single-collision conditions in crossed molecular beam experiments. Combined with state-of-the-art electronic structure and statistical calculations, the reaction was found to involve an initial formation of a van der Waals complex in the entrance channel, a submerged barrier to insertion, intersystem crossing (ISC) from the triplet to the singlet manifold, and hydrogen migrations. These studies provide a rare glimpse of silicon chemistry on the molecular level and shed light on the remarkable non-adiabatic reaction dynamics of silicon, which are quite distinct from those of isovalent carbon systems, providing important insight that reveals an exotic silicon chemistry to form disilavinylidene.*

For the last century, Langmuir's concept of isoelectronicity, in which two molecular entities with the same number of valence electrons have similar chemistries,[1] has been of central importance in developing modern concepts of chemical bonding and rationalizing basic principles of molecular structure and chemical reactivity. Particular attention has been devoted to comparing the chemistries of carbon to silicon. Residing in Group 14, both carbon and silicon have four valence electrons and are hence isovalent. Nevertheless, their chemical bonding can be quite distinct as demonstrated by the quasilinear structure of the tricarbon molecule (C_3) strongly differing from the cyclic trisilicon molecule (Si_3).[2] The divergent chemical bonding of carbon versus silicon is also illustrated when comparing the acetylene (HC≡CH)/vinylidene ($H_2C{=}C{:}$) system (Scheme 1)[3,4] with the isovalent silicon analogues. Whereas vinylidene has been experimentally probed,[5–10] the isovalent disilavinylidene molecule ($H_2Si{=}Si{:}$) has eluded any identification to date[11–15] initially suggesting that silicon can hardly form silicon–silicon double bonds as a result of the covalent radius of the silicon atom that prevents neighboring atomic p orbitals from coming sufficiently close to form π molecular orbitals. The detection of the non-classical, hydrogen-bridged Si(H_2)Si[12,13] and Si(H)SiH isomers[16] demonstrates the exotic chemical bonding and unusual molecular structures in this system. Therefore, a replacement of carbon by silicon leads to novel molecules, whose isovalent carbon counterparts do not exist[13,17,18] hence classifying the Si_2H_2 system as an excellent target to provide fundamental perspectives on chemical reactivity of silicon-bearing species.



Scheme 1. Structures of energy minima on the C_2H_2 potential energy surface, acetylene (left) and vinylidene (right), along with their point groups and electronic ground-state wave functions.

Herein, we access the Si_2H_2 system via the crossed molecular beam reaction of ground-state silicon atoms (Si; ^3P_j) with silane (SiH_4; X^1A_1) under single-collision conditions. This reaction acts as a benchmark to probe the outcome of the elementary reaction of the simplest silicon-bearing open-shell species (atomic silicon) with the prototype closed-shell silicon-carrying molecule (silane) to form Si_2H_2 isomers via Si_2H_4 intermediates. By merging the experimental data with electronic structure and statistical calculations, we find a barrierless formation route to the elusive disilavinylidene ($H_2SiSi{:}$; X^1A_1) molecule. The chemical dynamics of the reaction involve a van der Waals complex and submerged barrier in the entrance channel, non-adiabatic dynamics, and surface hopping from the triplet to the singlet manifold, isomerization of the initial insertion product, and the formation of disilavinylidene ($H_2SiSi{:}$ (hereafter: H_2SiSi), X^1A_1), which can isomerize to the mono-bridged Si(H)SiH isomer. These findings shed light on an exotic silicon chemistry and unusual chemical dynamics of silicon, which are distinct from those of the isovalent carbon system.

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The bimolecular gas-phase reaction of ground-state silicon atoms with silane was explored under single-collision conditions exploiting a crossed molecular beam machine by intersecting supersonic beams of atomic silicon and silane perpendicularly at a collision energy of 12 ± 2 kJ mol^{-1} (Supporting Information). The neutral reaction products were ionized by electron impact at 80 eV within a triply differentially pumped quadrupole mass spectrometric detector, which is rotatable within the scattering plane, and then mass- and velocity-analyzed to record angular resolved time-of-flight (TOF) spectra. Reactive scattering signal was collected from mass-to-charge (m/z) 60 to 56 with signal at m/z 58 ($^{28}Si_2H_2^+$/$^{29}Si^{28}SiH^+$/$^{29}Si_2^+$/$^{30}Si^{28}Si^+$) and m/z 56 ($^{28}Si_2^+$) showing similar intensity. The count rates at m/z 57 ($^{28}Si_2H^+$/$^{29}Si^{28}Si^+$) and 59 ($^{28}Si_2H_3^+$/$^{29}Si^{28}SiH_2^+$/$^{29}Si_2H^+$/$^{30}Si^{28}SiH^+$/$^{30}Si^{29}Si^+$) were significantly lower with only 15% to 20% of the count rates at m/z 56 and 58. No definite signal of the adduct could be observed at m/z 60. Accounting for the natural isotope abundances of silicon of ^{30}Si (3.1%), ^{29}Si (4.67%), and ^{28}Si (92.23%) and considering that the TOF spectra recorded from m/z 59 to 56 reveal identical patterns after scaling, we conclude that signal at m/z from 58 to 56 originates from $^{28}Si_2H_2^+$, $^{28}Si_2H^+$, and $^{28}Si_2^+$ with $^{28}Si_2H_2^+$ generated upon electron impact ionization of the neutral $^{28}Si_2H_2$ product formed as the heavy product in the reaction of atomic silicon with silane via molecular-hydrogen elimination; the $^{28}Si_2H^+$ and $^{28}Si_2^+$ ions origin from dissociative electron impact ionization of the primary $^{28}Si_2H_2$ product. Consequently, signal at m/z 59 is based on $^{29}Si^{28}SiH_2^+$, $^{29}Si_2H^+$, $^{30}Si^{28}SiH^+$, and/or $^{30}Si^{29}Si^+$, but not from an atomic-hydrogen-loss channel leading to $^{28}Si_2H_3^+$ after ionization of the neutral product. Based on the aforementioned consideration, the angular resolved TOF spectra were taken at m/z 58 ($^{28}Si_2H_2^+$; Figure 1). The laboratory angular distribution of m/z 58 ($^{28}Si_2H_2^+$; Figure 1) spans over 45° within the scattering plane defined by the reactant beams; the forward-backward symmetry with respect to the center-of-mass (CM) angle suggests that the reaction of ground state silicon atoms with silane involves indirect reaction dynamics through a $^{28}Si_2H_4$ complex leading through molecular hydrogen elimination to a molecule with the formula $^{28}Si_2H_2$ (hereafter: Si_2H_2) via a single collision event.

We shift our attention now to the identification of the Si_2H_2 product isomer(s). This requires the elucidation of the underlying chemical dynamics of the silicon/silane system by transforming the experimental data from the laboratory to the CM reference frame.[19] The laboratory data can be fit with a single channel of a mass combination of the products of 58 amu (Si_2H_2) and 2 amu (H_2). The best fit CM translational energy distribution ($P(E_T)$) and angular distribution ($T(\theta)$) are presented in Figure 2. For those molecules formed without internal excitation, the high energy cutoff of the $P(E_T)$ of 40 ± 10 kJ mol^{-1} represents the sum of the reaction exoergicity and the collision energy. A subtraction of the collision energy suggests that the reaction is exoergic by 28 ± 12 kJ mol^{-1}. This value agrees with the computed data revealing an exoergicity of 38 ± 8 kJ mol^{-1} to form disilavinylidene (H_2SiSi) in its $^1A_1$ electronic ground state via molecular-hydrogen elimination (Figure 3). The *trans*-disilaa-

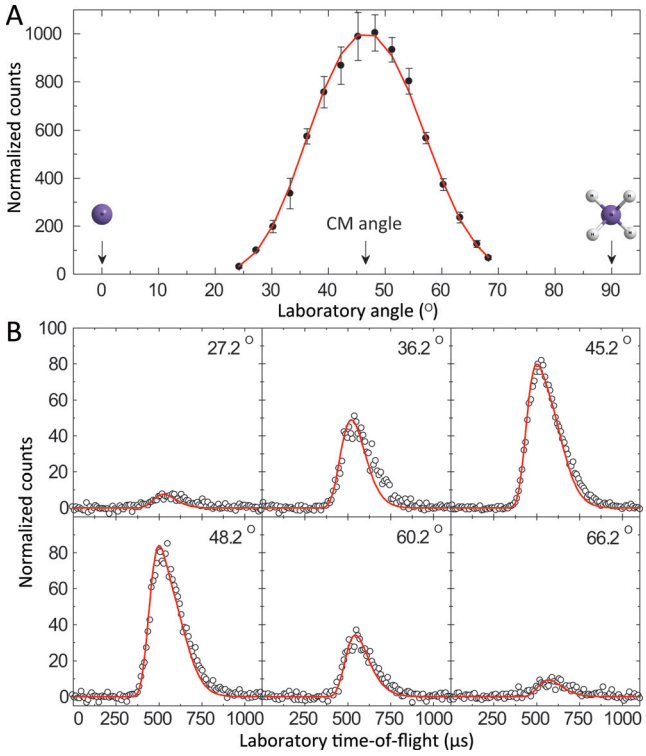

Figure 1. Laboratory angular distribution (A) and time-of-flight spectra (B) recorded at m/z 58 ($Si_2H_2^+$) in the reaction of ground-state atomic silicon with silane. The circles are the experimental data and the red lines are the calculated distribution with the best-fit center-of-mass functions as depicted in Figure 2. The laboratory angular distribution exhibits a $\pm 1\sigma$ uncertainty.

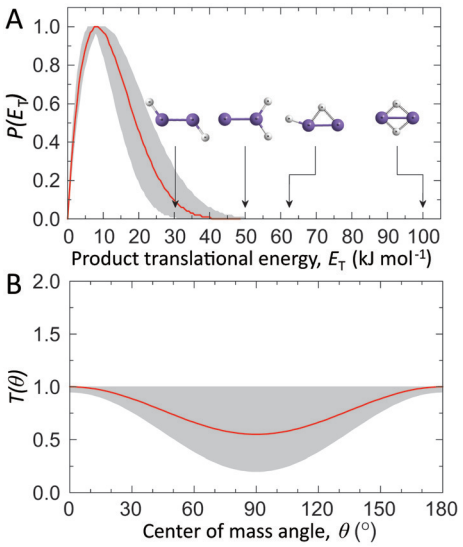

Figure 2. CM translational energy (A) and angular (B) distributions leading to the formation of the disilavinylidene (H_2SiSi) in the reaction of ground-state atomic silicon with silane. The red lines are the best fit functions while the shadow areas indicate the acceptable upper and lower error limits of the fits. Calculated high-energy cut-offs corresponding to different isomeric products are indicated by arrows.

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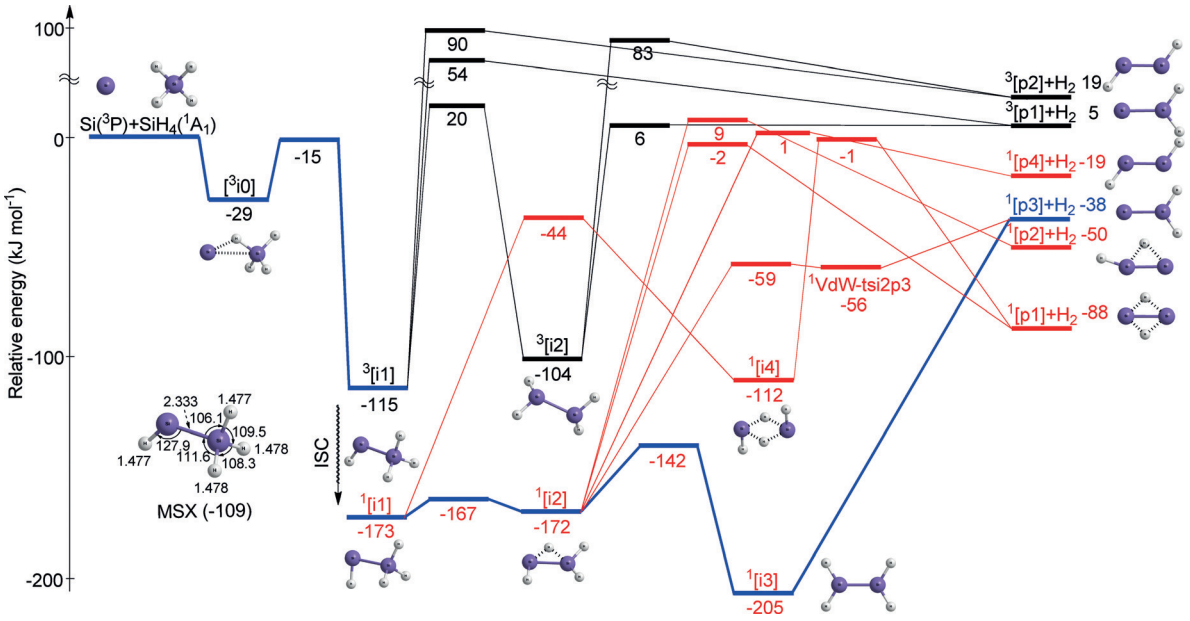

Figure 3. Potential energy surface for the reaction of ground-state atomic silicon with silane. CCSD(T)/CBS relative energies are given in units of kJ mol^{-1}. The barrierless reaction pathway followed by intersystem crossing (ISC) as highlighted in blue dominates the disilavinylidene (H_2SiSi) formation. The optimized geometry of the minimal energy crossing point (MSX) between the lowest triplet and singlet electronic states is also shown.

cetylene molecule (HSiSiH) is less stable by 19 kJ mol^{-1}; its formation is associated with an exoergicity of 19 ± 8 kJ mol^{-1}. Based on the energetics alone, the formation of this isomer cannot be excluded at the present stage. The formation of the more stable mono- and di-bridged structures Si(H)SiH and Si(H_2)Si would result in reaction energies of -50 ± 8 kJ mol^{-1} and -88 ± 8 kJ mol^{-1} and hence high energy cut-offs of the $P(E_T)$ of 62 ± 10 kJ mol^{-1} and 100 ± 10 kJ mol^{-1}; these isomers can be accounted for by accepting that a significant fraction of the Si(H)SiH and Si(H_2)Si product isomers are rovibrationally excited. Therefore, based on $P(E_T)$ we believe that at least the disilavinylidene isomer (H_2SiSi; X^1A_1) is formed; if the Si(H)SiH and Si(H_2)Si isomers are formed as well, they have to be rovibrationally excited to account for the energetics derived from the $P(E_T)$. Finally, $P(E_T)$ peaks close to zero translational energy with a maximum around 5–10 kJ mol^{-1}. This pattern suggests a rather loose exit transition state to form Si_2H_2 and H_2 from a decomposing Si_2H_4 complex. The CM angular distribution $T(\theta)$ has intensity over the complete angular range from 0° to 180°, suggesting indirect scattering dynamics through the formation of Si_2H_4 complex(es) with lifetimes longer than rotational periods.[20] Best fits reveal that the $T(\theta)$ shows a distribution minimum at 90°, implying geometrical constraints of the exit transition state(s) and that the hydrogen molecule is emitted within the plane of the decomposing complex and almost perpendicular to the total angular momentum vector.[20]

We now merge our experimental data with computational results to untangle the underlying reaction mechanism(s) (Figure 3; Supporting Information) and to elucidate the Si_2H_2 isomers formed. Since the feasible product isomers along with molecular hydrogen have singlet ground states, but the reaction is initiated on a triplet surface, both triplet and singlet Si_2H_4 potential energy surfaces (PESs) along with intersystem crossing (ISC) are explored to account for the non-adiabatic reaction dynamics. Our calculations reveal that the reaction of ground state atomic silicon with silane can lead to five doublet Si_2H_3 and four triplet/singlet Si_2H_2 isomers via atomic-hydrogen and molecular-hydrogen loss, respectively (Supporting Information). Three Si_2H_3 isomers ($SiSiH_3$, $HSiSiH_2$, Si(H)SiH_2) are nearly isoenergetic with the fourth and fifth isomers HSi(H)SiH and Si(H_2)SiH being far less stable (by 46 and 64 kJ mol^{-1}, respectively). The overall formation of all the Si_2H_3 isomers is endoergic by at least 137 kJ mol^{-1}. Therefore, considering the collision energy of 12 ± 2 kJ mol^{-1}, the atomic hydrogen loss channel to any Si_2H_3 isomer is closed in our experiments. With respect to molecular-hydrogen loss, our electronic structure calculations reveal the existence of four Si_2H_2 isomers on the singlet (^{1}[p1]–^{1}[p4]) and triplet (^{3}[p1]–^{3}[p4]) surface being overall exoergic (singlet surface; −88 to −19 kJ mol^{-1}) and endoergic reactions (triplet surface; 5 to 108 kJ mol^{-1}). The energy differences between the most stable di-bridged isomer Si(H_2)Si and the less stable mono-bridged isomer Si(H)SiH, disilavinylidene (H_2SiSi) as well as disilaacetylene (HSiSiH) are 38, 50, and 69 kJ mol^{-1}, respectively. These data agree well with previous theoretical work.[21]

Our calculations also revealed multiple pathways involving three triplet and four singlet Si_2H_4 intermediates to form Si_2H_2 isomers via molecular hydrogen loss. The reaction is initiated on the triplet surface via a barrierless insertion in the entrance channel. When the silicon atom approaches silane, the potential energy surface is attractive leading to a van der Waals complex ^{3}[i0], which is bound by 29 kJ mol^{-1} with respect to the separated reactants. This complex can isomerize via insertion of the silicon atom into the silicon-hydrogen

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bond of silane via a barrier of 14 kJ mol^{-1}, leading to the formation of a covalently bound reaction intermediate ^{3}[i1] (disilamethylcarbene). The transition state separating the van der Waals complex ^{3}[i0] and intermediate ^{3}[i1] is lower in energy than the separated reactants. Consequently, a barrier to insertion exists, but it is located below the energy of the separated reactants and is hence a submerged barrier.[22] Therefore, the overall reaction from atomic silicon with silane to intermediate ^{3}[i1] is barrierless. The existence of the van der Waals complex ^{3}[i0] and of the submerged barrier was validated by a careful scan of the potential energy surface in the entrance channel. Our computational finding of a barrierless reaction of ground state atomic silicon with silane is also supported by previous kinetics measurements proposing rapid reaction rates of a few 10^{-10} cm^3 s^{-1} essentially invariant over the temperature range of 298 to 1000 K.[23,24] The barrierless nature of insertion was further verified in matrix studies of the silicon/silane system at 10 K.[12] After isomerization to intermediate ^{3}[i1], the latter can undergo a hydrogen shift to ^{3}[i2] (disilaethylene) followed by molecular hydrogen loss to triplet disilavinylidene ^{3}[p1] or triplet disilacetylene ^{3}[p2]. Alternatively, ^{3}[i1] could undergo unimolecular decomposition to triplet disilavinylidene ^{3}[p1] or triplet disilacetylene ^{3}[p2]. However, the transition states connecting ^{3}[i1] to ^{3}[i2] and to the products ^{3}[p1] and ^{3}[p2] are much higher in energy (20 to 90 kJ mol^{-1}) than the collision energy in our experiments of 12 ± 2 kJ mol^{-1}. Therefore, under our experimental conditions, it seems that none of the processes are feasible.

What is the fate of the disilamethylcarbene intermediate ^{3}[i1] then? The computations suggest the possibility that intermediate ^{3}[i1] can undergo rapid intersystem crossing (ISC) to intermediate ^{1}[i1]. The spin-orbit coupling and seam of crossing (MSX) between the triplet biradical and the singlet state of the silacarbene with triplet silacarbene were characterized by the CPMCSCF/TZVPP method with energy refined by CCSD(T)/CBS (Supporting Information). These investigations located a minimal energy crossing point (MSX) between the lowest triplet and singlet electronic states of intermediate [i1] in the close geometric vicinity of ^{3}[i1] with both the energy of MSX (−109 kJ mol^{-1}) and the geometry being similar to those to ^{3}[i1]. After surface hopping, disilamethylcarbene ^{1}[i1] can isomerize either to the di-bridged structure ^{1}[i4] or to the mono-bridged intermediate ^{1}[i2] followed by a hydrogen migration to ^{1}[i3]. Considering the barriers to isomerization of 6 kJ mol^{-1} (^{1}[i1]→^{1}[i2]) versus 129 kJ mol^{-1} (^{1}[i1]→^{1}[i4]), the formation of the mono-bridged isomer ^{1}[i2] (HSi(H)SiH) is clearly preferred. Likewise, a close look at the barriers to isomerization (^{1}[i2]→^{1}[i3]) versus molecular hydrogen elimination from ^{1}[i2] forming ^{1}[p1], ^{1}[p2], ^{1}[p3] or ^{1}[p4] reveals that the isomerization of ^{1}[i2] to ^{1}[i3] followed by molecular hydrogen loss via a loose exit transition state leading to disilavinylidene (H_2SiSi; X^1A_1) ^{1}[p3] is favored. This loose exit transition state warrants discussion. For hydrocarbon systems of comparable size such as ethylene (H_2CCH_2) and allene (H_2CCCH_2), molecular hydrogen loss has a tight exit transition state.[25,26] However, in case of allene, 36% of the molecular hydrogen loss proceeds via a loose exit transition state with an exit barrier of less than 5 kJ mol^{-1}.[27,28] Therefore, the computational finding of a barrierless fragmentation of ^{1}[i3], which can be considered as a silicon analogue of ethylene, highlights the differences in the chemistry of isovalent molecules. To shed further light on the nature of the product isomers, statistical rates (RRKM; Rice-Ramsperger-Kassel-Marcus) and branching ratios leading to the Si_2H_2 isomers (^{1}[p1]-^{1}[p4]) were also computed exploiting a kinetic Scheme which includes the relevant species (Supporting Information). The branching ratios suggest that at zero pressure and our collision energy of 12 ± 2 kJ mol^{-1}, the disilavinylidene molecule (H_2SiSi; X^1A_1) ^{1}[p3] is formed almost exclusively at a level of 97%. Finally, the energy dependent rate constants calculated via semi-classical transition state theory[29,30] suggest that the lifetime of disilavinylidene (H_2SiSi) is very short (Figure 4). With an internal energy of 3 and 6 kJ mol^{-1} toward the end of the translational energy distribution, the lifetime is predicted to be about 15 μs and 1 ns, respectively; this is reduced to about 1 ps for an internal energy of 40 kJ mol^{-1}, which corresponds to the distribution maximum of the translational energy distribution (Supporting Information). Therefore, in multi-collision environments, disilavinylidene (H_2SiSi) formed with sufficient internal energy might not only overcome the barrier to isomerization of 9 kJ mol^{-1} via hydrogen shift to the mono-bridged isomer Si(H)SiH ^{1}[p2], but ^{1}[p2] can also transfer (parts of) their internal energy to a three-body collider thus stabilizing ^{1}[p2] and making it available for spectroscopic detection. Alternatively, once formed in multi-collision environments, the mono-bridged isomer Si(H)SiH ^{1}[p2] may even isomerize prior to its stabilization to the di-bridged isomer $Si(H_2)Si$ ^{1}[p1]; both isomers are separated by an isomerization barrier of 14 kJ mol^{-1} (Supporting Information). However, single collision conditions provide an ideal setting to "make" initially novel, exotic molecules such as the disilavinylidene molecule (H_2SiSi; X^1A_1), which resist synthesis by conventional chemical approaches.

In conclusion, our combined experimental and computational investigation of the gas-phase reaction of ground-state silicon atoms with silane reveal an exoergic and barrierless route to initially form the elusive disilavinylidene molecule

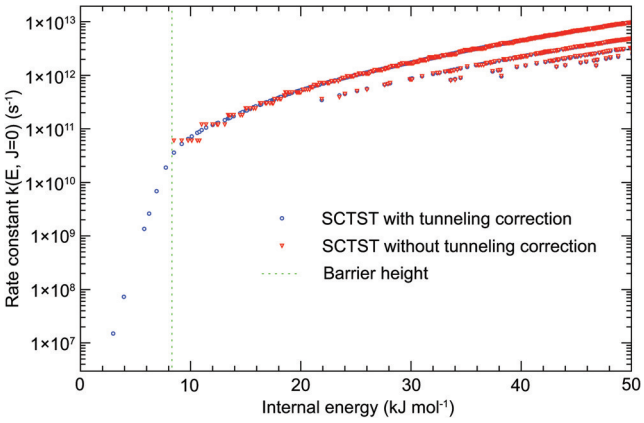

Figure 4. Rate constants for the isomerization of disilavinylidene (H_2SiSi) to the mono-bridged isomer (Si(H)SiH) and their dependence on the internal energy of the disilavinylidene product. SCTST stands for semi-classical transition state theory.

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(H_2SiSi) under single-collision conditions, which is in equilibrium with the mono-bridged (Si(H)SiH) and di-bridged ($Si(H_2)Si$) isomers. The reaction is initiated by the barrierless formation of a van der Waals complex followed by its isomerization via insertion of the silicon atom into a silicon–hydrogen bond forming the disilamethylcarbene intermediate through a submerged barrier. This intermediate likely undergoes intersystem crossing (ISC) to singlet disilamethylcarbene ($HSiSiH_3$), which isomerizes via two successive hydrogen shifts leading eventually to a long-lived disilaethylene intermediate (Si_2H_4). From there, a barrierless path involving unimolecular decomposition through molecular-hydrogen loss to form initially the disilavinylidene molecule (H_2SiSi) ^{1}[p3] is strongly favored. Considering the energy-dependent rate constants and the inherent lifetime of disilavinylidene (H_2SiSi), the disilavinylidene is in equilibrium with the mono-bridged ^{1}[p2] and di-bridged isomers ^{1}[p1]. These dynamics are distinct from the isovalent carbon–methane reaction, which shows no reaction under analogous experimental conditions owing to an inherent barrier of insertion of ground-state atomic carbon into the carbon–hydrogen bond of methane of about 51 kJ mol^{-1}.[31] Therefore, the isovalency of the silicon atom gives a misleading prediction of reactivity in this example. This influences how we rationalize not only the chemical reactivity, but also the mechanism, thermochemistry, and chemical-bonding classifying the silicon/silane system as a benchmark toward a detailed understanding of the formation of small organosilicon molecules. Considering that the hydrogen atoms in the silane reactant can be substituted by side groups, such as silyl or alkyl groups, the reaction of atomic silicon with silane represents the parent system for a previously disregarded reaction class potentially revealing an elegant path to synthesize the largely obscure group of substituted disilavinylidene molecules. This comparison of the chemical behavior of silicon relative to carbon is fundamental to our understanding of chemistry and will affect how we explain chemical bonding involving silicon atoms and how we think about chemical structure in the future.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: gas-phase chemistry · mass spectrometry · reaction dynamics · silicon · single-collision conditions

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