

Supporting Information

Gas-Phase Formation of the Disilavinylidene (H₂SiSi) Transient

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Experimental Methods

The experiments were conducted under single collision conditions in a crossed molecular beams machine.^[1] A pulsed beam of ground state atomic silicon was generated via laser ablation of a silicon rod (Si; 99.999 %; Good Fellow Corporation) and seeding the ablated species in neon carrier gas (Ne; 99.999 %; Specialty Gases of America) in the primary source.^[2] Here, the 10 mJ per pulse output of a neodymium: yttrium aluminum garnet (Nd:YAG) laser operating at 266 nm was focused by a lens of 1.5-meter focal length onto the rotating silicon rod on an area of 1 mm^2 . As determined via laser-induced fluorescence (LIF), the silicon atoms are only in their ${}^{3}P_{1}$ electronic ground state, but not in their first excited ¹D state. The pulsed beam entraining the silicon atoms passed a skimmer and a four-slot chopper wheel, which selected segments of the pulsed atomic beam of well-defined peak velocities (v_p) and speed ratios (S) of 923 ± 13 ms⁻¹ and 6.3 ± 0.4 , respectively. This beam bisected a section of a pulsed molecular beam of silane (SiH₄; 99.9999 %; Voltaix) with v_p and S of 841 ± 10 ms⁻¹ and 10.2 ± 0.3, respectively, resulting in a collision energy of 12 ± 2 kJ mol⁻¹ and a center-of-mass (CM) angle of $46 \pm 1^{\circ}$. The reaction products were monitored exploiting a triply differentially pumped quadrupole mass spectrometer (QMS) in the time-of-flight (TOF) mode after electron-impact ionization of the neutral molecules at 80 eV. The ions were separated according to their mass-to-charge ratio (m/z) by a quadruple mass spectrometer; only ions with the desired m/z value passed through and were accelerated toward a high voltage (-22.5 kV) stainless steel target coated with an aluminum layer. The ions hit the surface and initiated an electron cascade that was accelerated by the potential until they reached an aluminum coated organic scintillator whose photon cascade was detected by a photomultiplier tube. The signal from the PMT was then fed into a multichannel scaler to record time-of-flight spectra. The TOF spectra recorded at each angle and the product angular distribution in the laboratory frame (LAB) were fit with Legendre polynomials using a forward-convolution routine.^[3] This method uses an initial choice of the product translational energy $P(E_{\rm T})$ and the angular distribution $T(\theta)$ in the center-of-mass (CM) reference frame to reproduce TOF spectra and a product angular distribution. The TOF spectra and product angular distribution obtained from the fit were then compared to the experimental data. The parameters of the $P(E_{\rm T})$ and $T(\theta)$ were iteratively optimized until the best fit was reached.

In addition to the mass spectrometric method, the silicon atomic beam was also characterized by LIF technique to probe the silicon atom quantum states. The LIF setup developed for the use in the crossed beam apparatus was described in detail previously.^[4-5] Briefly, the directions of the Si radical beam, pulsed excitation laser beam and fluorescence collection, were mutually orthogonal. Fluorescence from the Si atoms was detected by a photomultiplier tube (PMT) Hamamatsu R955. The signal from PMT was amplified in Hamamatsu C7247 socket assembly and then detected by a digital oscilloscope communicating with a computer. Silicon atoms in the ground (triplet) and excited (singlet) spin states were monitored via $3p^2 {}^{3}P \rightarrow 3p4s {}^{3}P$ and $3p^2 {}^{1}D \rightarrow 3p4s {}^{1}P$ transitions around 251 nm and 288 nm correspondingly. Tunable radiation near 251 nm was produced by a Lambda Physik Scanmate dye laser with circulating Coumarin 503 dye, frequency doubled in a BBO II nonlinear crystal in Lambda Physik Scanmate frequency conversion unit. The dye laser was pumped by the third harmonic of an integrated Nd:YAG laser operating at 10 Hz repetition rate and 10 ns pulse duration. The pulse energy was attenuated to 9 nJ by turning off the amplification stages of the dye laser and reducing iris diameter in the beam path. Tunable radiation near 288 nm was also produced by the combination of dye laser and frequency doubling. The 288 nm radiation was obtained by using Rhodamine 590 dye with frequency doubled output with energy value of 36 nJ per pulse.

The excitation LIF spectra of Si atoms in $3p^2 {}^{3}P \rightarrow 3p4s {}^{3}P$ and $3p^2 {}^{1}D \rightarrow 3p4s {}^{1}P$ bands are presented in Figure S1 (a) and (b) as measured in the ablation source. As shown in the figure, we detected several transitions corresponding to spin-orbit coupled states (*J* states) for the ground electronic state ${}^{3}P$ and none for the excited ${}^{1}D$ electronic state. As shown in Figure 1(b), corresponding to excitation transition for ${}^{1}D_{2} \rightarrow {}^{1}P_{1}$, a transition around 288.15 nm is expected. Detection of only ground ${}^{3}P$ states of silicon imply that the Si atomic beam contains only the ground electronic state and any reactivity of silicon atoms in crossed beams arises from ground state only. Note that the different *J* states detected within the ground ${}^{3}P$ state differ only by a maximum of 3 kJ mol⁻¹, which is too small to be resolved in product translational distribution resulting in our scattering experiments. Upper limits of Si({}^{1}D) of 0.01 % relative to ground state silicon atoms were determined.

Theoretical Methods

The channels of the reaction of ground state silicon atoms (Si; ³P) with silane (SiH₄; X^1A_1) were investigated on the triplet and singlet Si₂H₄ potential energy surfaces (PESs). Probable collision

complexes were identified; the subsequent isomerization and dissociation paths were characterized. The geometries of the collision complex, intermediates, transition states, atomic along with molecular hydrogen dissociation products are optimized with calculations of harmonic frequencies by employing coupled cluster^[6-7] CCSD/cc-pVTZ calculations. The CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVTZ and CCSD(T)/cc-PVQZ energies were then computed and extrapolated to complete basis set limits,^[8] CCSD(T)/CBS, with CCSD/cc-pVTZ zero-point energy corrections. These energies are accurate to within 8 kJ mol⁻¹.^[9] The barrierless potential energy curve of the entrance channel was mapped out by constrained optimization at the B3LYP^[10]/cc-pVTZ level of theory along the breaking silicon-silicon bond of [³i0]. The minimum energy crossing point between ³[i1] and ¹[i1] were located with CPMCSCF^[11]/TZVPP method with energy refined via CCSD(T)/CBS. GAUSSIAN09 programs^[12] were used for the coupled cluster calculations, and MOLPRO^[11] was exploited for the surface-crossing computations. Selected energy-dependent RRKM rate constants^[13-14] were computed at collision energies between 0 and 50 kJ mol⁻¹ utilizing CCSD/cc-pVTZ harmonic frequencies and CCSD(T)/CBS energies. The barrierless transition state to disilavinylidene (H₂SiSi) was located by applying variational RRKM^[15-16] with CCSD(T, FULL)/cc-pCVTZ frequencies and CCSD(T)/CBS energies. The Runge-Kutta method was used to solve rate equations of the reaction mechanism at 0-50 kJ mol⁻¹. The solutions provided the concentrations as a function of time, of which the asymptotic values yielded the branching ratios. To estimate the lifetime of disilavinylidene (H₂SiSi), microcanonical rate constants k(E, J = 0) for the isomerization step of disilavinylidene to the mono-bridged isomer HSi(H)Si were computed using Miller's semiclassical transition state theory (SCTST).^[17-18] The barrier height was obtained with the HEAT-345Q method.^[19-20] Rovibrational parameters and anharmonic constants were computed using second-order perturbation theory (VPT2),^[21] in which the harmonic and anharmonic force fields were respectively constructed using CCSD(T,FULL)/cc-pCVQZ and CCSD(T,FULL)/ccpCVTZ levels of theory. These latter calculations were done with the CFOUR program package.^[22]



Figure S1: Laser-induced fluorescence (LIF) spectra of ground $({}^{3}P)$ (**a**), and excited $({}^{1}D)$ (**b**) states of atomic silicon recorded in a laser ablation source. Arrow in the panel (**b**) indicates the expected position for noted transition.





Figure S2: (a) Potential energy surface for $Si({}^{3}P) + SiH_{4}(X^{1}A_{1})$ reaction with CCSD(T)/CBS relative energies in kJ mol⁻¹. Triplet surface is shown in black color while the single surface is shown in red. Intermediates are labeled as 'i', transition states as 'ts' and products as 'p'. Triplet and singlet states are noted by superscripts '³' and '¹', respectively. Dotted pathway lines are not actual calculated paths but only guides to the eyes. Only hydrogen atom and hydrogen molecule loss products have been calculated. (b) Relative energies of singlet products and transition states connecting various products (geometry optimized by MP2/cc-pVTZ).





Figure S3: Bond lengths (in Ångstöm), bond angles (in degree), electronic states and point groups of the reactants, intermediates, transition states and products. ^a: variational transition states with the corresponding collision energies in the parentheses obtained by CCSD(T,FULL)/cc-pCVTZ; ^b: geometry optimized by MP2/cc-pVTZ.



Figure S4: Kinetic scheme used to calculate the branching ratio of singlet products at the collision energy of 12 kJ mol^{-1} .

Table S1: The RRKM rate constants (s⁻¹) computed with CCSD/cc-pVTZ zero-point energy corrected CCSD(T)/CBS energies and CCSD/cc-pVTZ harmonic frequencies at the collision energy of 12 kJ mol^{-1} .

k ₁	5.56×10 ¹²
k.1	1.14×10^{13}
k ₂	8.66×10 ⁹
k.2	5.36×10 ¹¹
k ₃	5.73×10 ¹²
k-3	2.14×10^{12}
k_4	2.71×10 ⁹
k5	2.50×10^{10}
k ₆	8.31×10 ⁶
k ₇	1.39×10 ⁸
k ₈	1.69×10 ⁹
k9	2.86×10 ¹⁰

E _c (kJ mol ⁻¹)	0	10	12	14	20	30	40	50
¹ p1	3.01 ×10 ⁻⁴	1.54 ×10 ⁻³	2.00 ×10 ⁻³	2.50 ×10 ⁻³	4.16 ×10 ⁻³	6.12 ×10 ⁻³	6.26 ×10 ⁻³	5.67 ×10 ⁻³
¹ p2	0.00	3.86 ×10 ⁻⁵	8.51 ×10 ⁻⁵	1.72 ×10 ⁻⁴	7.58 ×10 ⁻⁴	2.75 ×10 ⁻³	4.71 ×10 ⁻³	5.98 ×10 ⁻³
¹ p3	1.00	0.98	0.97	0.95	0.84	0.55	0.31	0.17
¹ p4	0.00	0.02	0.03	0.05	0.15	0.44	0.68	0.82

Table S2: Calculated branching ratio of Si_2H_2 products on the singlet PES at various collision energies (E_c).

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