**Formation of the 2,3-Dimethyl-1-silacycloprop-2-enylidene Molecule via the Crossed Beam Reaction of the Silyl­id­yne Radical (SiH; *X*2Π) with Dimethylacetylene (CH3CCCH3; *X*1A1g)**

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1. **Introduction**

During the last years, the dimethylacetylene molecule (2-butyne; CH3CCCH3) has received considerable attention in the reaction dynamics community to investigate the sterical effects[1](#_ENREF_1) of replacing one and/or two hydrogen atoms by bulky methyl groups (CH3) in the acetylene (C2H2) molecule upon undergoing bimolecular reactions with the cyano radical (CN; *X*2Σ+),[2](#_ENREF_2), [3](#_ENREF_3) the boronyl radical (BO; *X*2Σ+),[4](#_ENREF_4) atomic carbon (C; *3P*),[5-7](#_ENREF_5) singlet and triplet dicarbon (C2; *X*1Σg+, *a*3Πu),[8](#_ENREF_8) and atomic boron (B; *2P*) (Scheme 1).[9](#_ENREF_9), [10](#_ENREF_10) Considering the reactions with the diatomic cyano and boronyl radicals, the reaction dynamics were dictated by the addition of the doublet radicals with their radical center located at the carbon and boron atom, respectively, to one of the central carbons of the carbon-carbon triple bond followed by loss of atomic hydrogen and/or the methyl group. On the other hand, the reaction dynamics with dicarbon, atomic carbon, and boron atoms are more complex. In case of ground state atomic carbon, the carbon atom adds to either one or both carbon atoms yielding triplet collision complexes, which eventually isomerize via ring closure/ring opening to yield the acyclic triplet dimethylpropargylene intermediate (CH3CCCCH3); the latter ejects a hydrogen atom from the methyl group forming the 1-methylbutatrienyl radical (CH3CCCCH2). In the singlet surface, dicarbon follows indirect reaction mechanism dictated by an addition of dicarbon to the central acetyl carbons of dimethylacetylene followed by multiple isomerization (ring closure/ring opening) to form eventually 2,4-hexadiyne intermediate (CH3CCCCCH3), which then eject atomic hydrogen from the methyl group to synthesize the 1-methylpentatetraenyl radical (CH3CCCCCH2). In the triplet surface, dicarbon can add barrierlessly to both carbons concurrently or one central carbon of dimethylacetylene leading to an intermediate CH3C(CC)CCH3 which can follow methyl group loss directly to CCCCCH3 or further isomerize prior to atomic hydrogen loss to CH3C(CCH)CCH. Atomic boron also exhibits rather unique reaction dynamics. The reaction is initiated by the interaction of the boron atom with the π electron density of the dimethylacetylene molecule which later forms a 2,3-dimethyl-1-bora-cyclopropenylidenyl radical intermediate (c-BC2(CH3)2). However, rather than undergoing ring opening, this intermediate isomerizes via a hydrogen shift from the carbon to the boron atom, followed by atomic hydrogen loss from the remaining methyl group. This process forms the cyclic 1,2-dimethylene-3-bora-cyclopropane product. These considerations suggest that the reaction dynamics involving dimethylacetylene with the doublet radicals (addition – elimination) differ strongly from those with carbon/dicarbon (addition – ring closure/opening – atomic hydrogen/methyl group loss) and in particular with atomic boron (addition – cyclization – hydrogen migration – atomic hydrogen loss).

     The aforementioned compilation suggests that all reactions with dimethylacetylene studied so far under single collision conditions involve atoms/radicals of the second row of the periodic table of the elements: boron, carbon, nitrogen, and oxygen. To expand these investigations to radicals carrying third row elements, we present here data on the crossed beam reaction of the silylidyne radical (SiH; *X*2Π) with dimethylacetylene (CH3CCCH3; *X*1A1g) and combine these investigations with electronic structure calculations. These studies will then be compared to the related silylidyne – methylacetylene (SiH – CH3CCH)[11](#_ENREF_11) and silylidyne – acetylene (SiH – HCCH)[12](#_ENREF_12) systems studied previously in our group. Finally we contemplate the reaction dynamics of the silylidyne reaction plus dimethylacetylene reactants with its low energy isomer: the 1,3-butadiene molecule (H2CCHCHCH2).[13](#_ENREF_13)

1. **Experimental**

The bimolecular gas phase reactions of the silylidyne (SiH; *X*2Π) and D1-silylidyne (SiD; *X*2Π) radical with dimethyl­acetylene (CH3CCCH3; *X*1A1g) were studied under single collision conditions in a universal crossed molecular beam machine.[14-17](#_ENREF_14) The pulsed supersonic beam of the silylidyne radicals was prepared by pho­tolysis of disilane (Si2H6; 99.998 %; Voltaix) seeded in he­lium (He; 99.9999 %; Gaspro) with fraction of 0.5 % and backing pressure of 2 atm.[18](#_ENREF_18) This mixture was initially introduced into a pulsed piezoelectric valve ope­ra­ting at 120 Hz, -400 V amplitude and pulse width of 80 µs, and the released pulsed beam will overlap with a 1 mm × 4 mm laser spot from an excimer laser (ArF, 193 nm, 30 mJ per pulse, 60 Hz) right after the nozzle. The D1-silylidyne radical beam with a seeded ratio of 0.5 % in deuterium was produced *in situ* by ablating a rotating silicon rod with the output of a Spectra-Physics Quanta-Ray Pro 270 Nd:YAG laser operating at 30 Hz and 266 nm with pulse energies of 10-15 mJ, and seeding the ablated species in 4 atm backing pressure of deuterium gas (D2, 99.7 %; Icon Isotopes) released by the piezoelectric valve ope­ra­ting at 60 Hz, -400 V amplitude and pulse width of 80 µs.[12](#_ENREF_12) Prior to arriving at the center of interaction region, the pulsed beam of the silylidyne/D1-silydyne radicals will pass through a skimmer, and a four-slit chopper wheel operating at 120 Hz; the latter selected a section of the pulsed beam with a well-defined peak velocity (v*p*) and speed ratio (*S*) of 1715 ± 13 m s-1 and 13.1 ± 1.9 for silylidyne, and of 1981 ± 38 m s-1 and 5.2 ± 1.0 for D1-silylidyne, individually. In the interaction region of the scattering chamber, the individual primary radical beam will cross perpendicularly with the most intense part of a pulsed dimethylacetylene beam (C4H6, Sigma Aldrich) released by a second pulsed valve operating at -400 V amplitude, pulse width of 80 µs and the same repetition rate of the primary pusle at a backing pressure of 550 Torr. In separate experiments, peak velocities and speed ratios for the dimethylacetylene beam were determined to be 780 ± 10 m s-1 and 8.2 ± 0.4, resulting in nominal collision energies of 33.0 ± 0.7 kJ mol-1 (SiH with C4H6) and 41.2 ± 2.2 kJ mol-1 (SiD with C4H6) along with center-of-mass angles of 40 ± 0.7° and 35.8 ± 1.1°, respectively.

The reactively scattered products were filtered by a quadrupole mass spectro­meter (QMS; Extrel QC 150) operated in the time-of-flight (TOF) mode after electron-impact ionization at an electron energy of 80 eV and an emission current of 2 mA. The product ions with a well-defined mass-to-charge (*m/z*) ratio were directed toward a stainless steel target coated with a thin aluminum layer floated at -22.5 kV. Triggered by the impact of the cations on the target, an electron cascade was initiated and accelerated onto an aluminum-coated organic scintillator to generate a photon pulse; the latter was amplified by a photo­multiplier tube (PMT, Burle, Model 8850) operating at -1.35 kV, prior to being filtered by a discriminator (Advanced Research Instruments, Model F-100TD) and fed into a multichannel scaler. The TOF spectra were then integrated and normalized according to the number of scans, to yield the product angular distribution in the laboratory frame. The detector is rotatable within the plane defined by both beams to record angular resolved TOF spectra. The laboratory data will also be converted into the center-of-mass (CM) reference frame using a forward-convolution routine.[19](#_ENREF_19), [20](#_ENREF_20) This iterative method exploits a para­me­terized set or point-form transla­tio­nal energy flux distribution (*P(ET)*) and angular flux distribution (*T(θ)*) in the CM frame, to optimize the laboratory TOF spectra and the laboratory angular distribution over a grid of Newton diagrams accounting for the apparatus functions, beam diver­gen­ces, and velocity spreads, as well as the reactive scattering cross section with an Ec-1/3 energy dependence with Ec being the collision energy. This energy dependence is utilized for barrierless reactions dominated by long-range attractive forces within the line-of-center model. [1](#_ENREF_1)

1. **Theoretical**
2. **Results**

The reactive scattering products for the silylidyne radical (SiH; *X*2Π) with dimethyl­acetylene (CH3CCCH3; *X*1A1g) were monitored at *m/z* of 83 (SiC4H7+), 82 (SiC4H6+), 81 (SiC4H5+) and 68 (SiC3H4+) near the CM angle. First of all, the TOF signal at m/z of 82 depicts the best signal-to-noise ratio. The TOF spectra at m/z of 83 is much weaker, indicating that the poor signal may originate from the contribution of 29SiC4H6+ and Si13CC3H6+ and in principle the formation channel of an adduct with the molecular formula SiC4H7 is closed. The TOF spectra at *m/z* of 82, 81 and 68 are actually comparable after scaling, with signal at *m/z* of 81 is much weaker than that of 82 and 68. This feature proposes that the molecular hydrogen loss (SiC4H5) and the methyl group loss (SiC3H4) channels are both closed under current experimental setup, and only the atomic hydrogen loss channel is accessible. We then proceeded to the whole laboratory angular scan spanning from 25.75° to 55.75° and illustrate the corresponding laboratory angular distribution and the selected TOFs in Figure 1. Since the atomic hydrogen loss can originate from either reactant, we further collected the TOF spectra at m/z of 83 and 82 for the reaction of D1-silylidyne with dimethylacetylene (Figure 2). We observed that the TOF signal at m/z of 82 is much stronger than that of 83 after the same number of scans, proposing that the reaction of D1-silylidyne with dimethylacetylene proceeds via an atomic deuterium loss channel dominantly. In conclusion, the reaction of silylidyne with dimethylacetylene involves the formation a SiC4H7 complex, which eventually decomposes via an atomic hydrogen loss from the silylidyne radical leading preferentially to the SiC4H6 product isomer(s).

We are able to reveal more underlying reaction dynamics by converting the laboratory data to the transla­tio­nal energy flux distribution (*P(ET)*) and angular flux distribution (*T(θ)*) in the CM frame, considering a product mass combination of 82 amu (SiC4H6) and 1 amu (H). First of all, the *P(ET)* extends up to a maximum energy of 62.3 ± 19.6 kJ mol-1, which is constituted by the sum of the collision energy and the absolute valve of the reaction exoergicity for the reaction without internal excitation. We therefore obtain the reaction exoergicity of 29.3 ± 20.3 kJ mol-1 for the title reaction. In addition, the *P(ET)* shows broad distribution maximum from 9.0 to 18.0 kJ mol-1, indicating the existence of a loose exit transition state residing at an energy of that order of magnitude above the final product system. Considering the concept of the microscopic reversibility, we expect a rather low entrance barrier for the hydrogen addition to this product.[12](#_ENREF_12) We also estimated the fraction of the total energy available to the translational degrees of the freedom to be 45 ± 14%. For *T(θ)*, it shows angular distribution spanning from 0° to 180°, indicating the formation of the SiC4H7 complex in the title reaction via indirect reaction dynamics.[21](#_ENREF_21) We also notice that forward-backward scattering pattern, with the pronounced intensity maximum at 90°. This feature reflects that the decomposing complex SiC4H7 not only possesses a lifetime that is longer than its rotational period,[22](#_ENREF_22) but also depicts geometric constraints in the atomic hydrogen decomposition, in which hydrogen atom leaves almost parallel to the total angular momen­tum vector **J** and perpendicularly to the molecular plane.[23](#_ENREF_23)

1. **Discussions**

We incorporate the theoretical calculations into our experimental findings to explore the underlying reaction mechanism. The highly reactive silylidyne radical (SiH; *X*2Π) can add barrierlessly to cis-dimethylacetylene, trans-dimethylacetylene, or both concurrently to form initial collision complexes i1, i2 and i3. The intermediate i1 and i2 can convert to each other

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