**Formation of the 2,3-Dimethyl-1-silacycloprop-2-enylidene Molecule via the Crossed Beam Reaction of the Silyl­id­yne Radical (SiH; X2Π) with Dimethylacetylene (CH3CCCH3; X1A1g)**

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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]](#endnote-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; XXX),[[2]](#endnote-2) the boronyl radical (BO; XX),[[3]](#endnote-3) singlet and triplet dicarbon (C2; XXX, XXX),[[4]](#endnote-4) atomic carbon (C(3P)),[[5]](#endnote-5) and atomic boron (B(2B)).[[6]](#endnote-6) 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 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 were 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; X2A’’). Dicarbon exhibits a similar indirect reaction mechanisms dictated by an addition of singlet/ dicarbon to the carbon-carbon triple bond of diacetylene followed by multiple isomerization (ring closure/ring opening) to form eventually dimethyldiacetylene intermediates (CH3CCCCCH3), which then eject atomic hydrogen to synthesize the 1-methylpentatetraenyl radical (CH3CCCCCH2; X2A’’).[[7]](#endnote-7) On the other hand, atomic boron exhibits rather unique reaction dynamics. The reaction is also initiated by the interaction of the boron atom with the π electron density of the dimethylacetylene molecule forming eventually 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 of the doublet radicals (addition – elimination) differ strongly from those of carbon/dicarbon (addition - ring opening/closure – atomic hydrogen loss) and in particular from atomic boron (addition - cyclization – hydrogen migration – atomic hydrogen loss).

     The aforementioned compilation suggests that all reactions of dimethylacetylene studied so far under single collision conditions involve radicals/atoms 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; XXX) with dimethylacetylene (CH3CCCH3) and combine these investigations with electronic structure calculations. These studies will then be compared to the related silylidyne – methylacetylene (SiH – CH3CCH)[[8]](#endnote-8) and silylidyne – acetylene (SiH – HCCH)[[9]](#endnote-9) 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).[[10]](#endnote-10)

**2. EXPERIMENTAL**

The bimolecular gas phase reactions of the silylidyne (SiH; X2Π) and D1-silylidyne (SiD; X2Π) radical with dimethyl­acetylene (CH3CCCH3; X1A1g) were studied under single collision conditions in a universal crossed molecular beam machine.[[11]](#endnote-11) First, a pulsed supersonic beam of ground state silylidyne radicals (SiH; X2Π) was formed via pho­tolysis of disilane (Si2H6; 99.998 %; Voltaix) seeded in he­lium (He; 99.9999 %; Gaspro) with fraction of 0.5 %. This mixture was introduced into a pulsed piezoelectric valve ope­ra­ting at 120 Hz, pulse widths of 80 μs, and a backing pressure of 1,520 Torr. The output of an excimer laser (ArF, 193 nm, 30 mJ per pulse) was then focused to a spot size of 1 mm × 4 mm and crossed the molecular beam down­stream the nozzle. The pulsed beam of the silylidyne radicals passed 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 1730 ± 13 m s-1 and 18.9 ± 2.9, respec­tively. Second, a pulsed, supersonic beam of the D1-silylidyne radi­cal (SiD; X2Π) at fractions of about 0.5 % in deuterium gas was prepared *in situ* via laser ablation of a silicon rod with 266 nm, 10-15 mJ pulses and subsequent entrainment of the ablated silicon atoms in deuterium gas (D2, 99.7 %; Icon Isotopes).[[12]](#endnote-12) The segment of the pulsed molecular beam entraining the D1-silylidyne radicals with a well-defined peak velocity of 2555 ± 110 ms-1 and speed ratio of 3.3 ± 1.2 was chosen exploiting a four slit chopper wheel after passing through a skimmer. In the interaction region of the scattering chamber, these sections of the (D1)-silylidyne radical beams crossed the most intense part of a pulsed dimethylacetylene beam (C4H6, Sigma Aldrich) released by a second pulsed valve at a backing pressure of 550 Torr perpendicularly. In separate experiments, peak velocities (v*p*) and speed ratios (*S*) for the dimethylacetylene beam were determined to be 800 ± 10 ms-1 and 12.0 ± 0.4 resulting in nominal collision energies of 30.3 ± 0.7 kJ mol-1 (SiH) and 31.4 ± 1.0 kJ mol-1 (SiD) along with center-of-mass angles of 32.5 ± 0.6° and 34.6 ± 0.6°, respectively. The rotational temperature of the silylidyne radical (SiH; X2Π) was characterized through laser induced fluorescence (LIF) to be mainly 40 ± 10 K.[[13]](#endnote-13)

The reactively scattered products were mass 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 ions of a well-defined mass-to-charge (*m/z*) ratio were aimed 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 aluminum coated stainless steel target, an electron cascade is formed and accelerated onto an aluminum-coated organic scintillator to generate a photon pulse; the latter is amplified by a photo­multiplier tube (PMT, Burle, Model 8850) operating at -1.35 kV. The signal was filtered by a discriminator (Advanced Research Instruments, Model F-100TD) and fed into a multichannel scaler. At each angle, up to 6×105 TOF spectra were recorded. The TOF spectra were then integrated and normalized 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. To gain information on the reactive scattering dynamics, the laboratory data were then transformed into the center-of-mass reference frame using a forward-convolution routine.[[14]](#endnote-14) This iterative method exploits a para­me­terized or point-form angular flux distribution, *T(θ)*, and transla­tio­nal energy flux distribution, *P(ET)*, in the center-of-mass (CM) frame. Laboratory TOF spectra and the laboratory angular distributions are extracted from these *T(θ)* and *P(ET)* functions and averaged over a grid of Newton diagrams accounting for the apparatus functions, beam diver­gen­ces, and velocity spreads. During the analytical fitting, we considered a reactive scattering cross section with an Ec-1/3 energy dependence with Ec being the collision energy. This energy dependence is utilized for barrier-less reactions dominated by long-range attractive forces within the line-of-center model.[[15]](#endnote-15)

**3. THEORETICAL**

**4. RESULTS**

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