Research paper

Untangling the reaction dynamics of the silylidyne radical (SiH; $X^2\Pi$) with acetylene (C_2H_2; $X^1\Sigma_g^+$)

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A R T I C L E   I N F O

A B S T R A C T

The chemical reaction dynamics of silylidyne (SiH; $X^2\Pi$) with acetylene (C_2H_2; $X^1\Sigma_g^+$) were studied exploiting the crossed molecular beam approach, and compared with previous studies on D1-silylidyne with acetylene. The reaction is initiated by a barrierless addition of silylidyne to one or both carbons of acetylene leading to 1-sila-1-propene-1,3-diylidene and/or the cyclic 1-silacyclopropenyl with the former isomerizing to the latter. 1-Silacyclopropenyl eventually loses atomic hydrogen yielding sila-cyclopropenylidene (c-SiC₂H₂) in an overall exoergic reaction (experiment: -14.7 ± 8.5 kJ mol^{-1}; theory: -13 ± 3 kJ mol^{-1}). The enthalpy of formation for silacyclopropenylidene is determined to be 421.4 ± 9.3 kJ mol^{-1}.

1. Introduction

The elucidation of the energetics and dynamics of elementary reactions of the simplest silicon-bearing radical, silylidyne (SiH; $X^2\Pi$), with prototype hydrocarbon molecules under single collision conditions and the inherent formation of small organosilicon molecules is of core significance spanning astrochemistry, physical organic chemistry, and fundamental reaction dynamics. Considering astrochemical implications, an understanding of the chemical dynamics of silylidyne radical reactions with small hydrocarbon molecules is crucial to reveal the underlying molecular processes involved in the formation of organosilicon molecules in the interstellar medium [1–4]. These molecules are thought to play a key role in the formation of silicon carbide dust grains in the outflow of circumstellar envelopes of carbon rich Asymptotic Giant Branch (AGB) stars such as IRC+10216 holding temperatures up to a few 1000 K close to the photosphere of the central star [5–8]. Nevertheless, the basic molecular processes that link the circumstellar silicon and carbon chemistries to dust formation are far from being understood as contemporary astrochemical models show inconsistent growth mechanisms for the principal routes to the build-up of organosilicon molecules. This disagreement is based on insufficient laboratory data such as products, branching ratios, and an elusive thermochemistry of the neutral – neutral reactions of the silylidyne radical with hydrocarbon molecules [9,10].
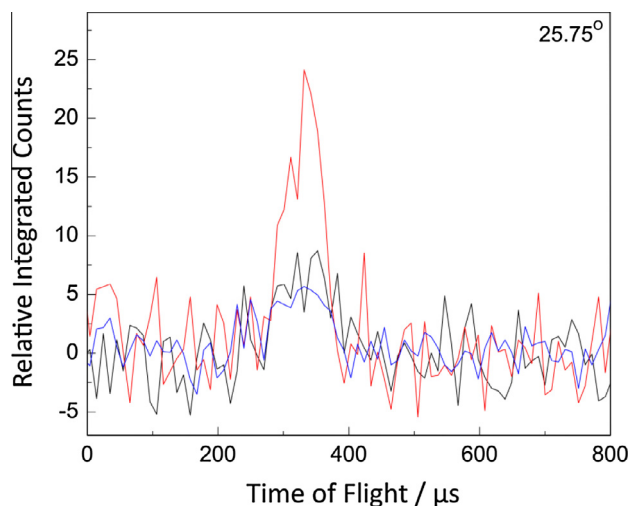
Furthermore, Langmuir's concept of isoelectronicity has fascinated physical organic chemists to explore the fundamental properties of molecular structures in the carbon versus silicon chemistry [11]. This is well reflected in the difference in chemical bonding of the c-SiC₂ molecule, which exhibits a cyclic C_{2v} symmetric structure, while the tricarbon (C_3) molecule is (quasi)linear at its ground state molecular geometry. Similarly, the isovalent cyano (CN) and silicon nitride (SiN) radicals revealed significant discrepancies in reactivity with unsaturated hydrocarbons such as acetylene (C_2H_2) and ethylene (C_2H_4), by bonding the carbon in the cyano (CN) and nitrogen in the silicon nitride (SiN) to the unsaturated hydrocarbons [12–17]. Considering the title reaction, the diverse chemical bonding of silicon analogous species is also evident, when comparing the silylidyne-acetylene (SiH–C₂H₂) and methylidyne–acetylene (CH–C₂H₂) potential energy surfaces (PESs) [18,19] as well as the cyclopropenylidene (c-CC₂H₂) and silacyclopropenylidene (c-SiC₂H₂) isomers in particular [20,21]. Here, cyclopropenylidene presents as a transition state, while sila-cyclopropenylidene has been found to be a global minimum. Therefore, a replacement of a carbon by an isovalent silicon atom may even lead to novel molecules, whose carbon-analog counterparts may not exist. So far, these aspects of the organosilicon chemistry and the formation of chemical bonds involving silicon are not well understood. Hence, the elucidation of reaction mechanisms involving organosilicon molecules and a comparison with the carbon-analog systems under single collision conditions can help to shed light not only on the distinct reactivity of silylidyne versus methylidyne, but also on the molecular structures and chemical bonding of hitherto elusive silicon-bearing molecules.

Previously, Parker et al. investigated the reaction of laser-ablation generated D1-silylidyne radicals (SiD) with acetylene exploiting the crossed beam approach [19]. However, various

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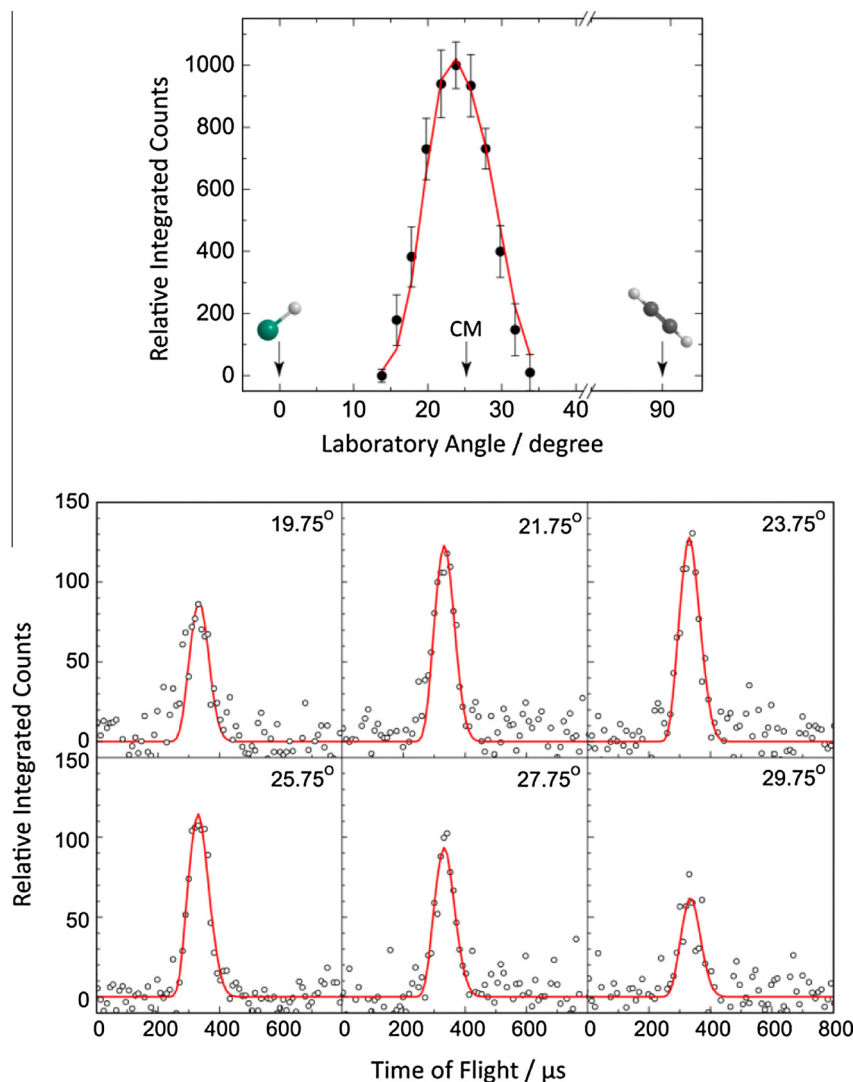
Fig. 1. Comparison of the time-of-flight (TOF) spectra at mass-to-charge ratios (m/z) of 54 ($SiC_2H_2^+$, black), 53 (SiC_2H^+, red) and 52 (SiC_2^+, blue) at the center-of-mass angle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
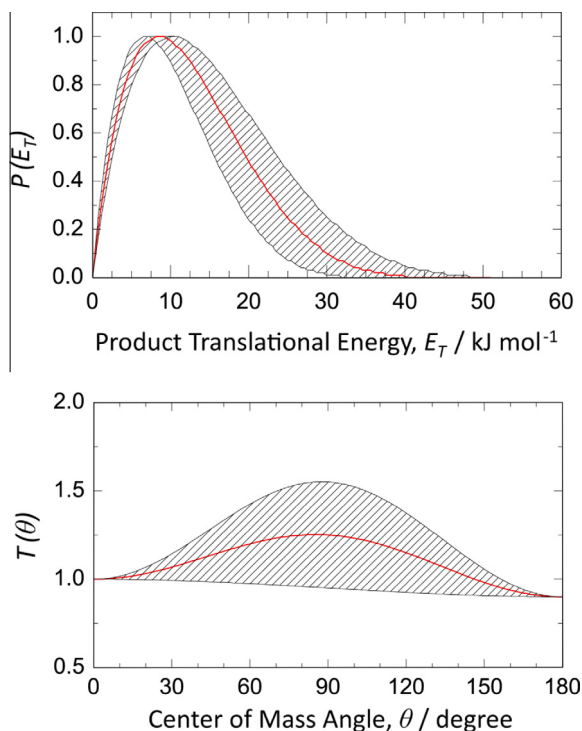
aspects of this reaction have remained unanswered so far. Here, due to the enhanced signal-to-noise ratio in the present experimental setup and the incorporation of a photolytic silylidyne radical source, we can investigate if only the atomic hydrogen or also the molecular hydrogen elimination channel is open. Furthermore, the low collision energy of 25.3 ± 0.5 kJ mol^{-1} compared to 41.2 ± 4.0 kJ mol^{-1} in the previous study enables us to record a full laboratory angular distribution, which in turn provides considerable constraints on the center-of-mass (CM) angular and translational energy distributions. These data along with the enhanced signal-to-noise ratio complete the investigation of the SiC_2H_3 potential energy surface and will also result in significantly reduced error bars on the overall reaction energies thus providing accurate enthalpies of formation of the organosilicon reaction product(s).

2. Experimental

The crossed molecular beam reaction of the silylidyne radical (SiH; $X^2\Pi$) with acetylene (C_2H_2; $X^1\Sigma_g^+$) was carried out under single collision conditions exploiting a crossed molecular beams

Fig. 2. Laboratory angular distribution at m/z = 53 extracted in the reaction of silylidyne with acetylene (top) along with the corresponding TOF spectra (bottom). The circles represent the data points, while the solid lines represent the best fits obtained from the forward-convolution routine.

Fig. 3. Center-of-mass (CM) translation translational energy flux distribution ($P(E_T)$, top) and angular flux distribution ($T(\theta)$, bottom) fitted with the product mass combination of 54 amu (SiC_2H_2) plus 1 amu (hydrogen). The red solid lines represent the best fits, while the hatched areas indicate the error limits. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
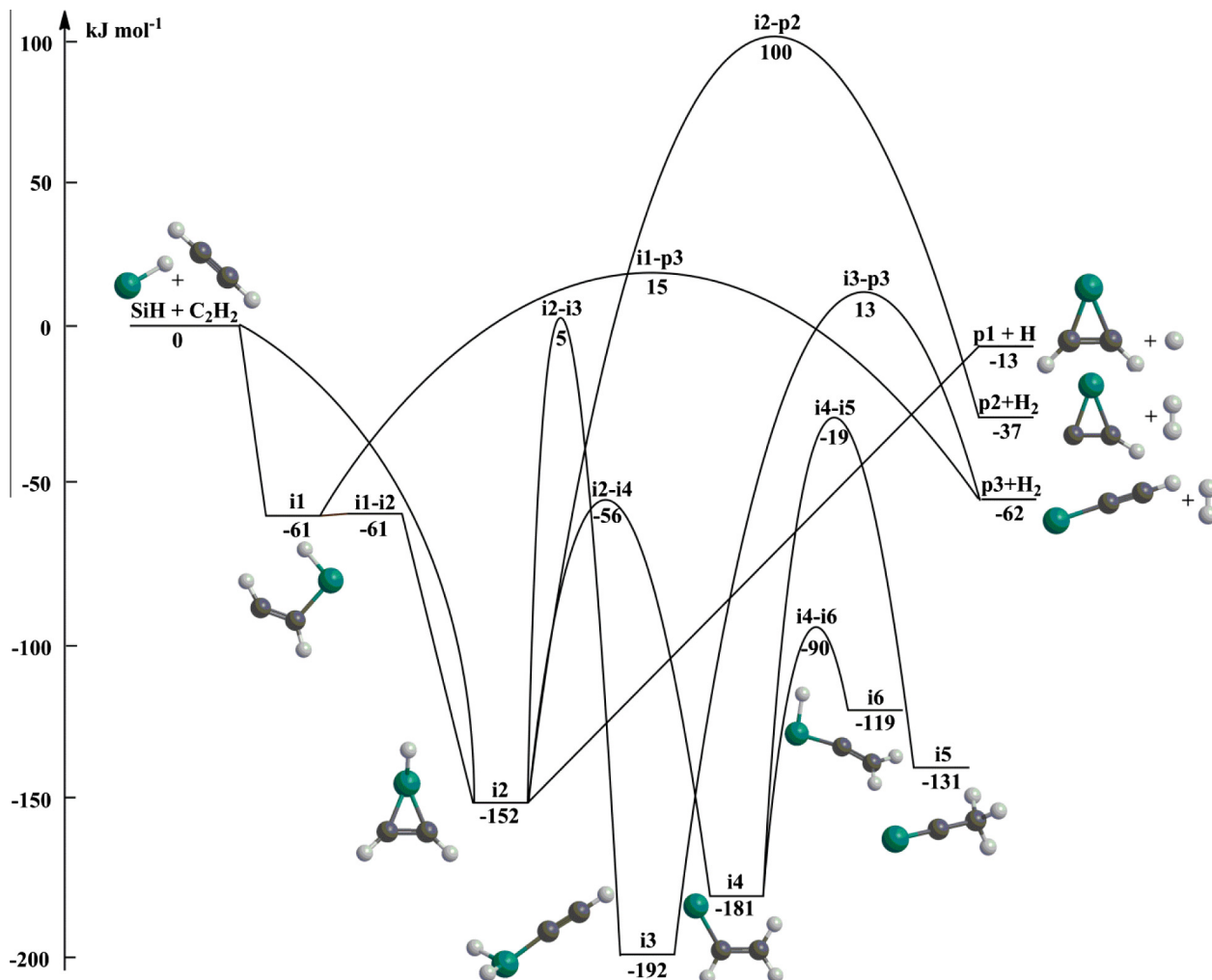
machine [22–25]. Briefly, disilane (Si_2H_6) seeded in helium at a fraction of 0.5% was fed into a piezoelectric valve (Physik Instrumente) operating at 120 Hz, −300 V peak voltage, and 2 atm backing pressure; the supersonic beam was intercepted by the 193 nm ArF output of an excimer laser (Coherent, Inc.) which was focused to a 1 mm × 4 mm spot with a pulse energy of 30 mJ at a repetition rate of 60 Hz. The photodissociation products were probed via an on axis quadrupole mass spectrometer in the time-of-flight (TOF) mode and by laser-induced fluorescence (LIF) technique [26–28]. The rotational temperature of the silylidyne radical (SiH; $X^2\Pi$) was determined to be 40 ± 10 K. The pulsed beam then passed through a stainless steel skimmer, a four-slot chopper wheel rotating at a speed of 120 Hz, which selected a portion of the beam with a well-defined peak velocity (v_p) and speed ratio (S) of 1714 ± 13 m s^{-1} and 13.1 ± 1.9 for silylidyne and 1730 ± 15 m s^{-1} and 15.4 ± 1.7 for atomic silicon. A pulsed beam of neat acetylene (C_2H_2; $X^1\Sigma_g^+$) was generated by a second piezoelectric valve in the secondary source chamber operating at 120 Hz, −300 V peak voltage and 550 torr backing pressure and crossed the primary beam with a peak velocity of 900 ± 10 m s^{-1} and speed ratio of 9.0 ± 0.2, leading to the CM angles and collision energies of 25.1 ± 0.5° and 25.3 ± 0.5 kJ mol^{-1} (SiH–C_2H_2), and of 25.6 ± 0.5° and 25.3 ± 0.5 kJ mol^{-1} (Si–C_2H_2), respectively. The triggers of the pulsed valves and laser were initiated by the time zero of the infrared diode located on top of the chopper wheel, and the optimized trigger values were selected for the best reactive scattering signal. We monitored the reactive products using a Daly type detector consisting of an electron impact ionizer operating at 34 eV (1.2 mA emission current), a quadrupole mass spectrometer, a stainless steel target floated at −22.5 kV, an aluminum-coated organic scintillator and a photomultiplier tube. The product velocity distributions were recorded utilizing the angular-resolved TOF approach, i.e. collecting the arrival time of the ionized products

for distinct mass-to-charge ratios (m/z) at different scattering angles in the laboratory reference frame. The TOF spectra and the laboratory angular distribution were further analysed using a forward-convolution fitting routine [29,30]. This routine starts with a parameterized set of translational energy flux distribution ($P(E_T)$) and angular flux distribution ($T(\theta)$) in the center-of mass (CM) frame; these functions are then iteratively modified until the best fits of the TOF spectra and angular distribution are reached. The optimized $P(E_T)$ and $T(\theta)$ can be used to explore the reaction dynamics and yield a product flux contour map $I(\theta,u) = P(u) \times T(\theta)$ that depicts the reactive scattering product intensity (I) as a function of the product velocity (u) and CM angle (θ) [31].

3. Results & discussion

We probed the reactive scattering signal at mass-to-charge ratios (m/z) of 55 ($SiC_2H_3^+$), 54 ($SiC_2H_2^+$), 53 (SiC_2H^+) and 52 (SiC_2^+). No signal was detected at $m/z = 55$ indicating that no SiC_2H_3 adduct survives the flight time from the interaction region to the ionizer. A comparison of the TOF spectra taken for the same numbers of scans at $m/z = 54$, 53 and 52 is illustrated in Fig. 1. After scaling, the profiles of the TOF spectra at $m/z = 54$, 53 and 52 are overlapped suggesting that ion counts at $m/z = 53$ and 52 originate from dissociative ionization of the SiC_2H_2 (54 amu) in the electron impact ionizer of the detector. Accounting for the natural isotope abundances of silicon of ^{30}Si(3.10%), ^{29}Si (4.67%) and ^{28}Si(92.23%), no detection of signal at m/z of 55 and considering that after scaling, the TOF spectra recorded from $m/z = 54$ to 52 depict identical pattern, we can conclude that signal at $m/z = 54$ ($SiC_2H_2^+$) originates from the *atomic hydrogen decomposition channel* forming a molecule of the formula SiC_2H_2 in the reaction of silylidyne with acetylene. Further, these data suggest the absence of a molecular hydrogen loss in the SiH–C_2H_2 system and the lack of any reactive scattering signal from atomic and/or molecular hydrogen loss in the Si–C_2H_2 system. The lack of the molecular hydrogen loss in the reaction of silylidyne with acetylene also gains support from a previous examination of this system [19]. Likewise, the absence of any reactive scattering signal from ground state silicon atoms with acetylene can be attributed to the highly endoergic (84 kJ mol^{-1}) formation of the silapropenylidyne molecule (HCCSi) via atomic hydrogen loss and/or inability of the SiC_2H_2 intermediate to undergo intersystem crossing followed by molecular hydrogen loss [32]. Considering the best signal-to-noise, we collected a full angular scan of the TOF spectra at $m/z = 53$ from 13.75° to 33.75°, and the TOF spectra along with the laboratory angular distribution are presented in Fig. 2.

The analysis of the laboratory data depicted convincing evidence that in the reaction of silylidyne radical (SiH; $X^2\Pi$) with acetylene (C_2H_2; $X^1\Sigma_g^+$), a molecule with the formula SiC_2H_2 is formed via atomic hydrogen loss. In order to elucidate the product isomer(s) formed and the underlying reaction mechanisms, now we are converting the data from the laboratory to the CM reference system. The laboratory data could be fit with a single channel in a product mass combination of 54 amu (SiC_2H_2) and 1 amu (H). The best fitted CM translational flux distribution $P(E_T)$ and angular distribution $T(\theta)$ are shown in Fig. 3. The CM translational energy distribution, $P(E_T)$, depicts a maximum energy cutoff at 40.0 ± 8.0 kJ mol^{-1}, which represents the sum of the collision energy plus the absolute value of the reaction exoergicity for products born without internal excitation. Considering the collision energy of 25.3 ± 0.5 kJ mol^{-1}, we can therefore derive the reaction to be exoergic by −14.7 ± 8.5 kJ mol^{-1}. We also noticed that $P(E_T)$ depicts a distribution maximum around 9.0 ± 3.0 kJ mol^{-1} indicating a loose exit transition state upon decomposition of the SiC_2H_3 complex to the final products [33]; this is consistent with an earlier

Fig. 4. Potential energy surface for the reaction of silylidyne (SiH; $X^2\Pi$) with acetylene (C_2H_2; $X^1\Sigma_g^+$) compiled from Ref. [19]. The numbers are the relative energies with respect to the separated reactants, and are given in kJ mol^{-1}.

study of the D1-silylidyne – acetylene reaction [19]. Considering the CM angular distribution, $T(\theta)$, intensity is found to span over the complete angular range from 0° to 180°; this finding is indicative of indirect scattering dynamics involving the unimolecular decomposition of SiC$_2$H$_3$ complex(es) [33]. We also observe that the distribution exhibits a slight forward scattering with an intensity ratio of 1 : 0.9 at the poles, $I(0°)/I((180°)$; this result indicates that the decomposing complex possesses a lifetime comparable to its rotational period [34]. In addition, $T(\theta)$ depicts a pronounced distribution maximum near 90° proposing that the hydrogen loss is connected with geometric constraints [31]. In other words, the hydrogen emission takes place at an angle at about 90° with respect to rotational plane of the decomposing complex and almost parallel to its total angular momentum (sideways scattering).

We are now comparing our experimental results with previous studies of the SiD($X^2\Pi$)–C_2H_2($X^1\Sigma_g^+$) [19], based on which we reproduce the PES of SiH ($X^2\Pi$)–C_2H_2($X^1\Sigma_g^+$) in Fig. 4. First, the experimentally determined reaction exoergicity -14.7 ± 8.5 kJ mol^{-1} correlates very well with the theoretically predicted reaction energy of -13 ± 3 kJ mol^{-1} associated with the formation of the silacyclopropenylidene isomer (c-SiC$_2$H$_2$) plus atomic hydrogen (H). Here, reaction of the silylidyne radical with acetylene proceeds via indirect scattering dynamics and is – as contemplated by electronic structure calculations – initiated by the barrierless addition of silylidyne radical to one or two carbon atoms of the acetylene molecule forming the collision complexes **i1** (1-sila-1-

propene-1,3-diylidene) and **i2** (1-silacyclopropenyl), respectively. The intermediate **i1** is only metastable and undergoes rapid ring closure to **i2** via the state **i1–i2** which is iso-energetic to **i1**. Eventually, the cyclic intermediate **i2** undergoes unimolecular decomposition de-facto barrierlessly through atomic hydrogen loss from the silicon atom yielding the silacyclopropenylidene molecule (c-SiC$_2$H$_2$; **p1**). The non-existence of the exit transition state leading to **p1** was also predicted by the near-zero peaking of the CM translational energy distribution. On the contrary, the PES and the inherent barriers involved in the molecular hydrogen loss pathways also rationalize the failed detection of the **p2** and **p3**, whose exoergicities were found to be accessible under current experiment. Although **i1** can decompose via molecular hydrogen elimination, the exit barriers are located 15 kJ above the energies of the separated products **p3** and H_2, which cannot compete with the interconversion of **i1** into **i2** and facile decomposition to **p1** and H. Similar arguments eliminate the possibility of intermediates **i2** and **i3** leading to molecular hydrogen loss products, considering that the exit barriers are 100 kJ mol^{-1} and 13 kJ mol^{-1} above the energies of **p2** plus H_2 and **p3** plus H_2. Consequently, the experiments and computations agree well and propose the overall barrierless formation of the silacyclopropenylidene (c-SiC$_2$H$_2$) molecule via indirect scattering dynamics. Note that in the related reaction of the D1-silylidyne radical with acetylene, isotopic scrambling could not be detected; this process would require a hydrogen shift from the carbon to the silicon and hence an isomerization of **i2–i3**

(plus back reaction via deuterium migration from the silicon to the carbon atom). This pathway involves a barrier of 157 kJ mol^{-1}, which is not competitive compared to the unimolecular decomposition of **i2** to **p1** + H.

Finally, it is interesting to compare the SiH–C$_2$H$_2$ system with the methylidyne–acetylene system (CH–C$_2$H$_2$), and unveil the reactivity and reaction mechanism of these isovalent systems [35]. The CH radical can also add barrierlessly to one or both carbons atoms in acetylene to form HCCHCH/c-C$_3$H$_3$ collision complexes, both of which are connected by a relatively shallow barrier of about 29 kJ mol^{-1} above HCCHCH. The resulting products are insensitive to the initial branching ratios of the HCCHCH and c-C$_3$H$_3$ collision complexes with atomic hydrogen loss contributing about 98% of the total amounts of the products. Strikingly different from the analogues silicon system, the linear product propargylene (HCCCH) constitutes up to 85–87% of the overall products, while the cyclic molecule cyclopropenylidene (c-CC$_2$H$_2$) only accounts for 13–10%. The insensitivity of the branching ratios with respect to the initial concentrations of the collision complexes is mainly driven by the preferential isomerization to the acyclic HCCHCH intermediate and to the propargyl radical (H$_2$CCCH), which in turn can lead to the formation of propargylene (HCCCH). On the contrary, the silapropargyl radical (H$_2$SiCCH) can only be formed via ring opening of the c-SiC$_2$H$_3$ (intermediate **i2**) by overcoming a barrier higher than the energy of the separated reactants; these unfavorable energetics rather prefer the decomposition of **i2** to silacyclopropenylidene (c-SiC$_2$H$_2$) via an atomic hydrogen loss.

4. Conclusion

Crossed molecular beam experiments were exploited to probe the chemical dynamics in the reaction of the silylidyne radical (SiH; X$^2\Pi$) with acetylene (C$_2$H$_2$; X$^1\Sigma_g^+$). The reaction was found to follow indirect dynamics and is initiated by the barrierless addition of silylidyne to one or both carbon atoms of acetylene leading to an open chain 1-sila-1-propene-1,3-diylidene intermediate and/or to a cyclic collision complex 1-silacyclopropenyl with the former intermediate isomerizing to the cyclic structure. 1-Silacyclopropenyl then ejects atomic hydrogen from the silicon atom via a loose exit transition state yielding the silacyclopropenylidene molecule (c-SiC$_2$H$_2$) in an overall weakly exoergic reaction (−14.7 ± 8.5 kJ mol^{-1}), which agrees well with the theoretical exoergicity of −13 ± 3 kJ mol^{-1}. The experimental enthalpy of formation for the silacyclopropenylidene molecule is then determined to be 421.4 ± 9.3 kJ mol^{-1}. This study addresses the possible formation route of the hitherto astronomically unobserved silacyclopropenylidene molecule in circumstellar envelopes of carbon-rich AGB stars, thus providing important implications to astrochemical models on how organosilicon molecules can form and evolve in those interstellar environments.

References

[1] S. Kwok, Organic matter in the universe, John Wiley & Sons, 2011.
[2] T. Millar, E. Herbst, R. Bettens, Mon. Not. R. Astron. Soc. 316 (2000) 195–203.
[3] L.M. Ziurys, Proc. Natl. Acad. Sci. U.S.A. 103 (2006) 12274–12279.
[4] M. Agúndez, J. Cernicharo, J. Pardo, J.F. Expósito, M. Guélin, E. Tenenbaum, L. Ziurys, A. Apponi, Astrophys. Space Sci. 313 (2008) 229–233.
[5] A. Van Orden, R. Provencal, T. Giesen, R. Saykally, Chem. Phys. Lett. 237 (1995) 77–80.
[6] D. Kokkin, S. Brünken, K. Young, N. Patel, C. Gottlieb, P. Thaddeus, M. McCarthy, Astrophys. J. Suppl. Ser. 196 (2011) 17.
[7] J.F. Stanton, J. Dudek, P. Theulé, H. Gupta, M. McCarthy, P. Thaddeus, J. Chem. Phys. 122 (2005) 124314.
[8] M. McCarthy, C. Gottlieb, P. Thaddeus, Mol. Phys. 101 (2003) 697–704.
[9] R. Bettens, H.-H. Lee, E. Herbst, Astrophys. J. 443 (1995) 664–674.
[10] T. Millar, E. Herbst, Astron. Astrophys. 288 (1994) 561–571.
[11] I. Langmuir, J. Am. Chem. Soc. 41 (1919) 868–934.
[12] L. Huang, O. Asvany, A. Chang, N. Balucani, S. Lin, Y. Lee, R. Kaiser, Y. Osamura, J. Chem. Phys. 113 (2000) 8656–8666.
[13] N. Balucani, O. Asvany, A. Chang, S. Lin, Y. Lee, R. Kaiser, Y. Osamura, J. Chem. Phys. 113 (2000) 8643–8655.
[14] L. Huang, Y. Lee, R. Kaiser, J. Chem. Phys. 110 (1999) 7119–7122.
[15] D. Parker, A. Mebel, R. Kaiser, Chem. Soc. Rev. 43 (2014) 2701–2713.
[16] D.S. Parker, A.V. Wilson, R.I. Kaiser, T. Labrador, A.M. Mebel, J. Am. Chem. Soc. 134 (2012) 13896–13901.
[17] D. Parker, A. Wilson, R. Kaiser, T. Labrador, A. Mebel, J. Org. Chem. 77 (2012) 8574–8580.
[18] P. Maksyutenko, F. Zhang, X. Gu, R.I. Kaiser, Phys. Chem. Chem. Phys. 13 (2011) 240–252.
[19] D.S. Parker, A.V. Wilson, R.I. Kaiser, N.J. Mayhall, M. Head-Gordon, A.G. Tielens, Astrophys. J. 770 (2013) 33.
[20] V. Lavallo, Y. Canac, B. Donnadieu, W.W. Schoeller, G. Bertrand, Science 312 (2006) 722–724.
[21] Q. Wu, Q. Hao, J.J. Wilke, A.C. Simmonett, Y. Yamaguchi, Q. Li, D.-C. Fang, H.F. Schaefer III, Mol. Phys. 110 (2012) 783–800.
[22] X. Gu, R.I. Kaiser, Acc. Chem. Res. 42 (2008) 290–302.
[23] Y. Guo, X.B. Gu, E. Kawamura, R.I. Kaiser, Rev. Sci. Instrum. 77 (2006).
[24] X.B. Gu, Y. Guo, F.T. Zhang, A.M. Mebel, R.I. Kaiser, Faraday Discuss. 133 (2006) 245–275.
[25] R.I. Kaiser, P. Maksyutenko, C. Ennis, F.T. Zhang, X.B. Gu, S.P. Krishtal, A.M. Mebel, O. Kostko, M. Ahmed, Faraday Discuss. 147 (2010) 429–478.
[26] T. Yang, B.B. Dangi, P. Maksyutenko, R.I. Kaiser, L.W. Bertels, M. Head-Gordon, J. Phys. Chem. A 119 (2015) 12562–12578.
[27] T. Yang, B.B. Dangi, R.I. Kaiser, L.W. Bertels, M. Head-Gordon, J. Phys. Chem. A (2016).
[28] P. Maksyutenko, D.S.N. Parker, F. Zhang, R.I. Kaiser, Rev. Sci. Instrum. 82 (2011). 083107/1–7.
[29] M.F. Vernon, Molecular beam scattering, in: Chemistry, University of California, Berkeley, 1983.
[30] P.S. Weiss, The reaction dynamics of electronically excited alkali atoms with simple molecules, in: Chemistry, University of California, Berkeley, 1986.
[31] R. Kaiser, D. Parker, F. Zhang, A. Landera, V. Kislov, A. Mebel, J. Phys. Chem. A 116 (2012) 4248–4258.
[32] R. Kaiser, X. Gu, J. Chem. Phys. 131 (2009) 104311.
[33] R.D. Levine, Molecular reaction dynamics, Cambridge University Press, 2005.
[34] D.R. Herschbach, Discuss. Faraday Soc. 33 (1962) 149–161.
[35] T.L. Nguyen, A.M. Mebel, S.H. Lin, R.I. Kaiser, J. Phys. Chem. A 105 (2001) 11549–11559.