PCCP

Cite this: *Phys. Chem. Chem. Phys.*, 2012, **14**, 477–481

www.rsc.org/pccp

COMMUNICATION

Crossed beam study of the atom-radical reaction of ground state carbon atoms ($C(^3P)$) with the vinyl radical ($C_2H_3(X^2A')$)

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Received 20th September 2011, Accepted 31st October 2011
DOI: 10.1039/c1cp22993a

The atom-radical reaction of ground state carbon atoms ($C(^3P)$) with the vinyl radical ($C_2H_3(X^2A')$) was conducted under single collision conditions at a collision energy of 32.3 ± 2.9 kJ mol^{-1}. The reaction dynamics were found to involve a complex forming reaction mechanism, which is initiated by the barrier-less addition of atomic carbon to the carbon–carbon-double bond of the vinyl radical forming a cyclic C_3H_3 radical intermediate. The latter has a lifetime of at least 1.5 times its rotational period and decomposes *via* a tight exit transition state located about 45 kJ mol^{-1} above the separated products through atomic hydrogen loss to the cyclopropenylidene isomer (c-C_3H_2) as detected toward cold molecular clouds and in star forming regions.

The reaction dynamics of atomic carbon in its ^3P electronic ground state with unsaturated hydrocarbon molecules are of major importance in interstellar chemistry,[1,2] combustion processes,[3] and in chemical vapor deposition.[4] Among the hydrocarbon-molecules detected in the interstellar medium, cyclopropenylidene (c-C_3H_2)[5–9] is ubiquitous in dark clouds (TMC-1, Oph A, Ori A), toward star forming regions (SgrB2), and in circumstellar envelopes of carbon stars (IRC + 10216). Singlet vinylidene carbene (H_2CCC) was also observed in TMC-1.[10] Computational studies, summarized by Maksyutenko *et al.*,[11] suggest that cyclopropenylidene (c-C_3H_2, X^1A_1) presents the global minimum with triplet propargylene (HCCCH, X^3B) and singlet vinylidene carbene (H_2CCC, X^1A_1) being higher in energy by 53 and 49 kJ mol^{-1}, respectively.[12] How can these isomers be formed in the interstellar medium? In cold molecular clouds and in circumstellar envelopes of carbon-rich stars, chemical reactions are driven by bimolecular collisions, among them reactions between two neutral species.[13,14] Therefore, crossed molecular beam experiments, which are conducted under collision-free conditions without the interference of wall-effects, present an ideal experimental approach to study the formation of organic molecules in extraterrestrial environments.[13–15] This approach is of particular relevance, if the chemical dynamics of reactions involving two open shell species are examined, since atoms and radicals can be prepared independently in separate side chambers under well-defined conditions.

To date, only a few atom-radical reactions have been reported in the literature under single collision conditions. In 1997, Kaiser *et al.* investigated the formation of diacetylene (HCCCCH) *via* reaction of ground state carbon atoms with propargyl radicals (C_3H_3) conducted at a collision energy of 42 kJ mol^{-1}.[16] The reaction was found to be indirect *via* complex formation and initiated by the addition of the carbon atom to the propargyl radical. The resulting C_4H_3 intermediate had lifetime of about 1.4 ± 0.6 of its rotation period and decomposed *via* a tight exit transition state through atomic hydrogen loss as the driving force. Later, Casavecchia *et al.* disseminated the results of the crossed beam reactions of ground and excited state oxygen atoms with methyl (CH_3)[17,18] and allyl radicals (C_3H_5)[19,20] at collision energies of 55.9 kJ mol^{-1} and 73.0 kJ mol^{-1}, respectively. Further, Choi *et al.* conducted a series of experiments with the main emphasis focusing on the reactions of ground state atomic oxygen atoms ($O(^3P)$) with hydrocarbon radicals allyl, *t*-butyl, ethyl, propyl, and propargyl,[21–26] Luntz *et al.* revised selected systems.[27,28] The reactions investigated by Choi *et al.* followed similar patterns, *i.e.* two reaction pathways with the first being abstraction of hydrogen by oxygen forming the hydroxyl radical (OH) and the second involving a barrier-less addition of oxygen to the hydrocarbon radical followed by isomerization and hydroxyl radical loss.

In this Communication, we expand the previous crossed beam reactions of bimolecular collisions between two reactive open shell species and investigate the chemical dynamics of the atom-radical reaction of ground state carbon atoms ($C(^3P)$) with the vinyl radical ($C_2H_3(X^2A')$) and the reaction pathway(s) leading to the formation of C_3H_2 isomers.

The experiments were conducted using the crossed molecular beam machine at the University of Hawai'i.[29] Briefly, a supersonic beam of ground state carbon atoms was generated *via* laser ablation of a rotating graphite rod in the primary chamber.[30] A Spectra-Physics Quanta-Ray Pro 270 Nd : YAG laser was focused onto the rotating graphite rod with an energy of 30 mJ at 266 nm. The laser ablated carbon atoms were then seeded into helium gas (Airgas; 99.9999%) with a backing pressure of 4 atm. A four slot chopper wheel located between the skimmer of the primary source and the interaction region allowed segments of the pulsed carbon beam to be selected with velocities of $v_p = 2750 \pm 115$ ms^{-1} and speed ratios of 2.6 ± 0.3. Under these conditions, no electronically excited carbon atoms were present in the primary beam. Vinyl radicals were produced in the secondary source region *via* photodissociation of a 1% vinylbromide (Aldrich)—99% helium

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(Airgas) mixture at a total pressure of 900 Torr at 30 mJ and 193 nm utilizing a Lambda Physik Compex 110 excimer laser. This yielded a vinyl radical beam with a velocity of $v_p = 1528 \pm 30$ ms^{-1} and a speed ratio, $S = 10.5 \pm 0.5$; this photolytic source has a similar design as the propargyl radical (C_3H_3) source utilized in the crossed beams reaction of ground state carbon atoms with the propargyl radical.[16]

The products were monitored using a triply differentially pumped quadrupole mass spectrometer in the time-of-flight (TOF) mode. An electron-impact ionizer, operated with 80 eV electrons at a current of 2 mA ionized the neutral molecules. A total of 2×10^7 TOFs had to be accumulated in batches of 10^6 TOFs at distinct angles; to account for fluctuating beam intensities, the TOFs recorded at the center-of-mass angle were taken as a reference point. To analyze the data and obtain information on the underlying reaction dynamics, the TOF spectra and the laboratory angular distribution (LAB) were fit using a forward-convolution routine.[31,32] This method uses the initial choice of the product translational energy $P(E_T)$ and the angular distribution $T(\theta)$ in the center-of-mass frame (CM) to reproduce TOF spectra and a product angular distribution. The TOF spectra and product angular distribution were then compared to the experimental data. The parameters of the $P(E_T)$ and $T(\theta)$ were optimized until the best fit was achieved.

We detected scattering signal at $m/z = 38$ and 37; the laboratory data (time-of-flight spectra; laboratory angular distribution) are shown in Fig. 1 and 2, respectively. Signal at $m/z = 38$ had to be fit with two components. The fast component originated from non-reactively scattered $^{13}C_2C$ (38 amu). Recall that besides carbon atoms, the laser ablation source also generates dicarbon (C_2; 24 amu) and tricarbon molecules (C_3; 36 amu)[30] with ^{13}C showing a natural abundance of 1.1%. Doubly ^{13}C substituted tricarbon molecules (38 amu) are expected to be produced at fractions of 3.3×10^{-4} compared to C_3 (36 amu). The second channel contributing to signal at $m/z = 38$ originated from reactive scattering of ground state carbon atoms with the vinyl radical forming products of the mass combination 38 amu (C_3H_2) plus 1 amu (H). Note that carbon atoms and dicarbon molecules can also react with the non-photolyzed vinyl bromide precursor. However, the center of mass angles of these systems of ~79° and ~68° are much closer to the secondary beam. Fits to reproduce any component of signal at $m/z = 38$ based on the C/C_2H_3Br and C_2/C_2H_3Br were not successful. The corresponding LAB distribution of $m/z = 38$ is depicted in Fig. 2. For the reactive scattering signal, the LAB distribution is spread over at least 40° in the scattering plane defined by the primary and secondary beam. This distribution peaks at 50°, *i.e.* slightly forward scattered with respect to the center-of-mass angle of 55.3°.

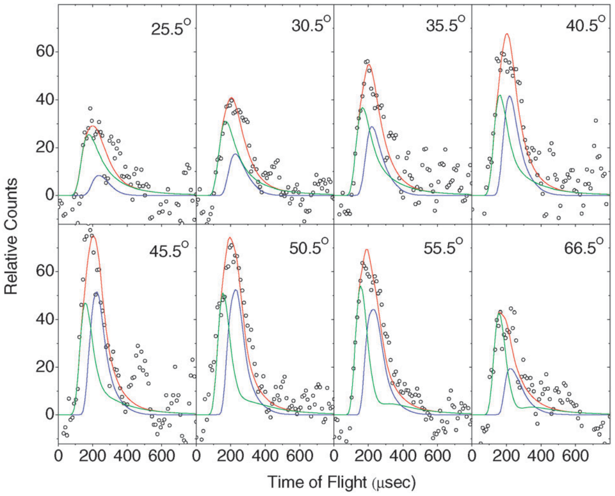

Fig. 1 Time-of-flight data recorded at mass-to-charge, m/z, of 38. The experimental data had to be fit with two contributions: (i) reactive scattering of ground state carbon atoms, $C(^3P)$, with the vinyl radical, $C_2H_3(X^2A')$, leading to products with a mass combination of 38 amu (C_3H_2) and 1 amu (H) (blue) and (ii) non-reactively scattered $^{13}C_2C$ (38 amu) (green). The red lines present the sum of both channels and the open circles the experimental data.

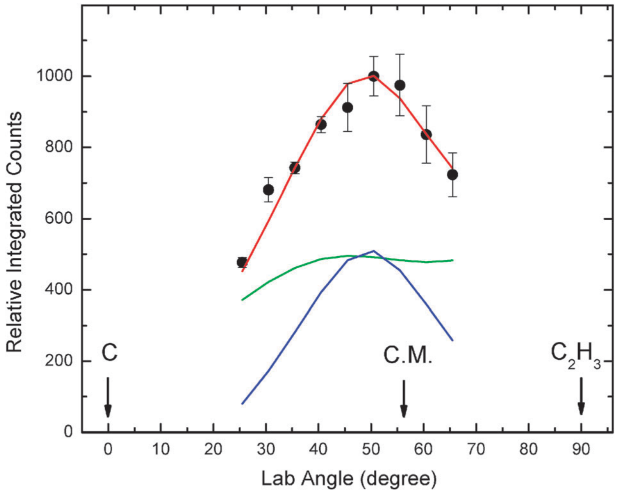

Fig. 2 Laboratory angular distribution recorded at $m/z = 38$ (filled circles) and the corresponding fit to the data for the reactive (blue) and non-reactive (green) scattering channel. The red line presents the sum. C.M. designates the center-of-mass angle.

The center-of-mass functions utilized for the best fits of our data of the reactive scattering channel leading to the formation of C_3H_2 isomer(s) plus atomic hydrogen are shown in Fig. 3. The center-of-mass translational energy distribution extends to a maximum translational energy of 330 ± 30 kJ mol^{-1}. Further, the $P(E_T)$ depicts a broad maximum about 90 kJ mol^{-1} wide. The average amount of available energy channeling into the translational degrees of freedom was calculated to be $43 \pm 4\%$. On the other hand, the best fit center-of-mass angular distribution depicts intensity over the whole scattering range indicating that the reaction dynamics are indirect and initiated *via* complex formation. Further, the fits are slightly forward scattered with respect to the carbon atom beam with intensity ratios at the poles, I(0°)/I(180°), between 1.30 and 1.04. Considering the osculating complex model,[33,34] we can suggest life times of the C_3H_3 reaction intermediate(s) of at least 1.5 times their rotational period. Finally, we shall point out the relatively weak polarization of the $T(\theta)$. This likely results from an insufficient and hence poor coupling between the initial (**L**) and final orbital angular momentum (**L**′) of the system, with $\mathbf{L}' \sim 0.2 \pm 0.1\ \mathbf{L}$ for a reaction without an entrance barrier and within orbiting limits.[34] This is the direct consequence of the light hydrogen atom departing from the decomposing C_3H_3 complex; most of the total angular momentum

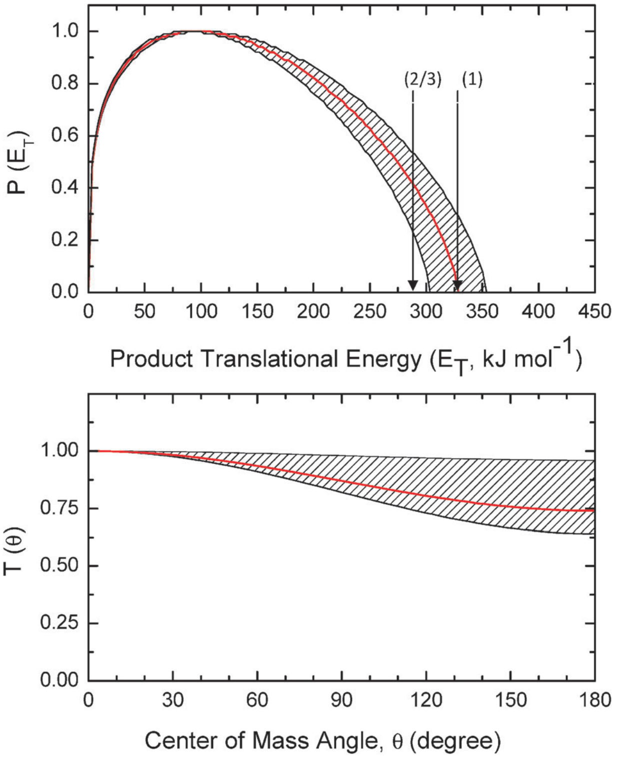

Fig. 3 Center-of-mass translational energy flux distribution (upper) and angular distribution (lower) for the hydrogen atom loss pathway(s) in the atomic carbon–vinyl radical reaction. Hatched areas indicate the acceptable upper and lower error limits to the fits; the solid red line defines the best-fit function. (1) and (2/3) depict the theoretical limits if the cyclopropenylidene (c-C_3H_2) and vinylidene carbene/propargylene (H_2CCC/HCCCH) isomers are formed.

of the system channels into rotational excitation of the product C_3H_2 isomer(s).

It is worth commenting on the signal at m/z = 37. The related system of methylidyne (CH) with acetylene (C_2H_2) studied earlier in our group[11] also accessed the C_3H_3 potential energy surface. Here, competing atomic and molecular hydrogen elimination pathways with fractions of about 91 ± 10% and 9 ± 2% were monitored. Therefore, we also attempted to elucidate the formation of molecular hydrogen with the tricarbon hydride (C_3H) as a counter fragment. This turned out to be very complicated. First, non-reactively scattered $^{13}CC_2$ (37 amu) present in the primary beams with 3.3% compared to tricarbon (36 amu) lead to a strong non-reactive scattering signal. Secondly, the reaction of ground state carbon atoms with acetylene, which was also produced in the photodissociation of vinyl bromide, forms C_3H (37 amu) plus atomic hydrogen.[35] Therefore, the dominance of these channels to produce a signal at m/z = 37 prohibited an objective assessment, if the reactive scattering channel $C_3H + H_2$ is open in the reaction of ground state carbon atoms with vinyl radicals or not.

First, we will attempt to elucidate which isomer(s) is (are) being formed in the reaction of ground state carbon atoms with the vinyl radical. First, recall that center-of-mass translational energy distribution extends to a maximum translational energy of 330 ± 30 kJ mol^{-1}. For polyatomic products formed without internal energy, a subtraction of the collision energy of 32.3 ± 2.9 kJ mol^{-1} suggests that the reaction to form C_3H_2 plus atomic hydrogen is exoergic by 298 ± 33 kJ mol^{-1}. A comparison of this data with the computed reaction energies for three C_3H_2 isomers indicates that at least the thermodynamically most stable cyclopropenylidene isomer (c-C_3H_2) is formed; the computed value suggests a reaction exoergicity of 291 ± 8 kJ mol^{-1}. Both the vinylidene carbene (H_2CCC) and the propargylene (HCCCH) isomers are associated with reaction energies of −234 and −238 kJ mol^{-1}, respectively. However, based on the energetics alone, we cannot dismiss their formation at the present stage.

How can the cyclopropenylidene isomer (c-C_3H_2) be formed under single collision conditions? The computed potential energy surface (Fig. 4) indicates two possible reaction pathways originating from intermediate (2) and (4). Here, (2) can be formed *via* barrier-less addition of the carbon atom to both carbon atoms of the vinyl radical or—after adding to one carbon atom of the vinyl radical to form intermediate (1)—*via* isomerization of the latter by ring closure. Note that the best fits suggest a slightly forward-scattering of the c-C_3H_2 with respect to the carbon atom beam. The preferential forward-scattering also suggests that the incorporated carbon atom and the departing hydrogen atom must be located on opposite sides of the rotation axis of the decomposing intermediate. This can be fulfilled if intermediate (2), rotating around the *A*-axis, decomposes to cyclopropenylidene plus atomic hydrogen. Further, this process is linked to a tight exit transition state located about 45 kJ mol^{-1} above the separated products. Note that the broad plateau of the center-of-mass translational energy distribution also proposes a tight exit transition state for at least one channel. On the other hand, intermediate (2) might also undergo a hydrogen shift leading to intermediate (4). The hydrogen loss from this cyclopropenyl intermediate has a very loose exit transition state resembling a simple bond rupture process; this would be reflected in a center-of-mass translational energy distribution peaking at or very close to zero translational energy. Clearly, this contradicts our experimental findings. Therefore, an exclusive decomposition of (4) cannot account for the experimental data, and we can conclude that the cyclopropenylidene isomer (c-C_3H_2) is at least formed *via* decomposition of intermediate (2). Considering the pathways leading to (4), an isomerization from (1) can be likely ruled out, since based on the isomerization barriers, (1)—if formed—is expected to undergo a facile hydrogen shift to the propargyl radical intermediate (3), which presents the global minimum of the C_3H_3 potential energy surface. Recent crossed beam experiments of the methylidyne radical with acetylene[11] suggested that the propargyl radical can undergo a preferential hydrogen atom loss yielding vinylidene carbene (H_2CCC) and/or the propargylene (HCCCH). To a minor amount, a molecular hydrogen loss was found as a competing channel leading to c-C_3H at the level of about 10%. A previous prediction of the branching ratios for this reaction indicated that the propargylene isomer (HCCCH) was formed with about 78.3–81.8%; both other isomers were holding fractions of 6.1–7.3% (c-C_3H_2) and 4.4–8.1% (H_2CCC).[36] Therefore, the theoretically predicted formation of cyclopropenylidene (c-C_3H_2) can be confirmed in our experiments.

Considering the center-of-mass angular distribution, the intensity ratio at the poles, I(0°)/I(180°), allows us to estimate

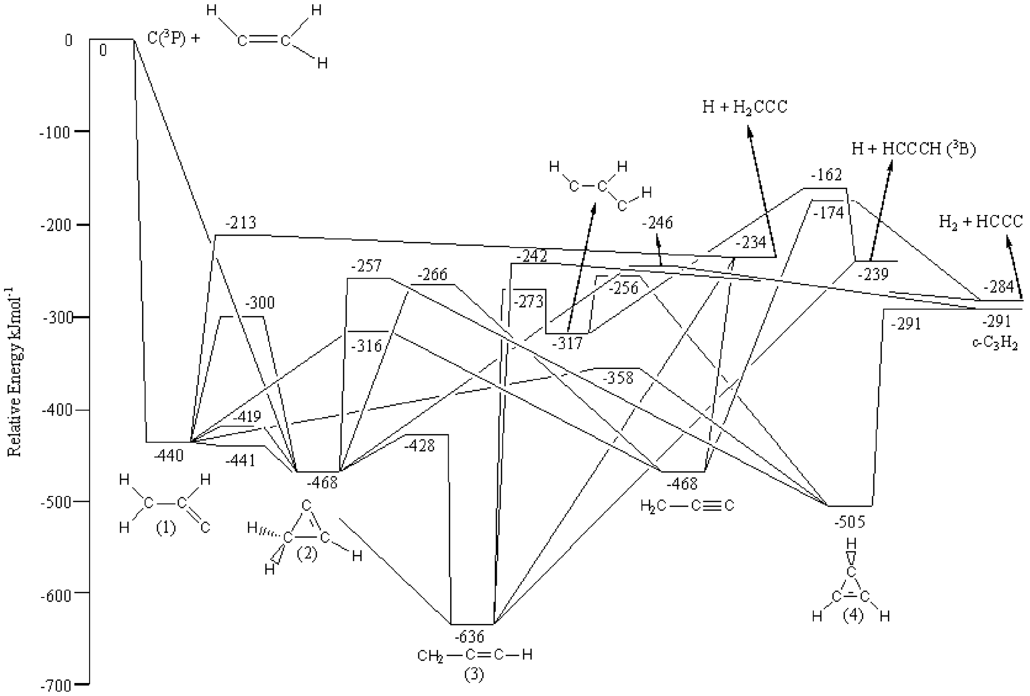

Fig. 4 Schematic potential energy surface of the reaction of ground state carbon atoms with the vinyl radical calculated at the RCCSD(T)/6-311 + G(3df,2p)//B3LYP/6-311G(d,p) + ZPE[B3LYP/6-311G(d,p)] level of theory giving chemical accuracy of ±5 kJ mol^{-1}.[39]

Table 1 Calculated values for the moment of inertia, and lifetime of the complex from both experimental results and previous computational results.[36] The computational calculations only quote the lifetime around the *A*-axis, the *B*-axis and *C*-axis lifetime were calculated using the same method as used for the experimental results for comparison

	A-axis	*B*-axis	*C*-axis
Moment of inertia ($\times 10^{-47}$ kg m^2)	22.01374	39.93352	56.30205
Lifetime (τ) range from experimental ($\times 10^{-12}$ s)	0.12–1.38	0.23–2.50	0.32–3.52

the lifetime of the decomposing intermediate (2) using the osculating model.[37,38] This model relates the intensity ratio at both poles to the lifetime of the intermediate, τ, *via* eqn (1):

$$\frac{I(180^\circ)}{I(0^\circ)} = \exp\left(-\frac{t_{\rm rot}}{2\tau}\right) \tag{1}$$

with the rotational period $t_{\rm rot}$ represented by eqn (2),

$$t_{\rm rot} = 2\pi I_i / L_{\rm max} \tag{2}$$

the moment of inertia, I_i shown in Table 1, rotating around the *i*-axis, and $L_{\rm max}$ the maximum angular momentum (eqn (3)),

$$L_{\rm max} = \mu b_{\rm max} \nu_{\rm r} \tag{3}$$

Here, μ is the reduced mass of the reactants, $b_{\rm max}$ is the maximum impact parameter, and $\nu_{\rm r}$ is the average relative velocity of the reactants. Within orbiting limits, under our experimental conditions, the value of $b_{\rm max}$ at 33.2 kJ mol^{-1} was about 3.2 Å, and the relative velocity of the reactants was determined to be 2789 ms^{-1}; this results in a $L_{\rm max}$ value of 167 $\hbar$ when the *A*-axis is considered. According to eqn (1) and (3), life times can be estimated to range between 0.13–1.38 ps, 0.23–2.50 ps, and between 0.32–3.52 ps for complexes rotating around their *A*, *B*, and *C*-axis, respectively (Table 1). Such large ranges are due to the use of the natural logarithm in the rearrangement of eqn (1), and the fact that as I(0°)/I(180°) approaches unity, small changes in the ratio have large effects on the lifetime. Previous electronic structure and statistical calculations suggested that the lifetime of intermediate (2) was 1.49 ps when rotating around the *A*-axis.[36] This lifetime is close to our upper limit for a decomposing complex rotating around its *A*-axis.

To summarize, we conducted the atom-radical reaction of ground state carbon atoms ($C(^3P)$) with the vinyl radical ($C_2H_3(X^2A')$) under single collision conditions at a collision energy of 32.3 ± 2.9 kJ mol^{-1}. The reaction dynamics involve a complex forming reaction mechanism which is initiated at least by the barrier-less addition of ground state carbon atoms to the carbon–carbon double bond of the vinyl radical forming a cyclic C_3H_3 radical intermediate (2). The latter has a lifetime of at least 1.5 times its rotational period and decomposed *via* a tight exit transition state located 45 kJ mol^{-1} above the separated products to the cyclopropenylidene isomer (c-C_3H_2) plus atomic hydrogen. Based on our experimental data, the formation of cyclopropenylidene from the cyclopropenyl intermediate (4) possibly formed *via* hydrogen shift from intermediate (2) cannot be ruled out, as the involvement of any propargyl radical intermediates (3) decomposing to vinylidene carbene (H_2CCC) and/or the propargylene (HCCCH). Recall that previous calculations suggested that propargylene (HCCCH) should be preferentially formed in this reaction.[36]

The bimolecular reaction of carbon atoms with the vinyl radical holds some similarities to the related atom-radical reaction of ground state carbon atoms with the propargyl radical conducted at a collision energy of 42 kJ mol^{-1}.[16] Both systems were initiated by a barrier-less addition of the carbon atom to the π-electron system of the hydrocarbon radical reactant thus proceeding *via* indirect scattering dynamics and depicting slightly forward-peaked center-of-mass angular distributions with intensities at the poles, I(0°)/I(180°), of about 1.35 ± 0.40 for the reaction of ground state carbon atoms with propargyl radicals. Note that a possible reason for the non-detection of interstellar propargylene (HCCCH) might be due to its low dipole moment of 0.51 Debye in comparison to the two other isomers, *i.e.* 3.35 Debye for c-C_3H_2 and 4.24 Debye for vinylidene carbene (H_2CCC).[35,36]

This work was supported by the US Department of Energy, Basic Energy Sciences (DE-FG02-03ER15411) and the US National Science Foundation (NSF-0948258). The author thanks Professor Mebel (Florida International University) for discussions.

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