

Crossed Molecular Beams Study on the Formation of Vinylacetylene in Titan's Atmosphere[†]

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The reaction of ground-state ethynyl radicals, $C_2H(X^2\Sigma^+)$, with d_4 -ethylene, $C_2D_4(X^1A_g)$, was investigated at a collision energy of 20.6 ± 0.4 kJ mol⁻¹ utilizing the crossed-beams technique. Combined with electronic structure calculations, our results elucidate that this reaction follows indirect reaction dynamics via a doublet radical complex. The reaction is initiated by a barrierless addition of the ethynyl radical to a carbon atom of the d_4 -ethylene molecule to form a C_4HD_4 intermediate. The latter is long-lived compared with its rotational period and decomposes via a tight exit transition state to form the d_3 -vinylacetylene product ($HCCC_2D_3$) plus a deuterium atom while conserving the ethynyl group; the center-of-mass angular distribution suggests that the deuterium atom leaves almost perpendicularly to the rotational plane of the fragmenting C_4HD_4 complex. The overall reaction is found to be exoergic by 94 ± 20 kJ mol⁻¹; this value agrees nicely with a computational data of 103 ± 5 kJ mol⁻¹. This study indicates that the analogous vinylacetylene molecule ($HCCC_2H_3$) can be synthesized in a low-temperature environment such as Titan's atmosphere via the neutral–neutral reaction of ethynyl radicals with ubiquitous ethylene. The similarity between this reaction and that of the isoelectronic cyano radical, $CN(X^2\Sigma^+)$, with ethylene-yielding vinylcyanide (C_2H_3CN) is also discussed.

1. Introduction

The chemical dynamics of reactions of ethynyl radicals, $C_2H(X^2\Sigma^+)$, with unsaturated hydrocarbons are of paramount importance in understanding the formation of complex hydrocarbon molecules such as polycyclic aromatic hydrocarbons together with their hydrogen-deficient precursors in hydrocarbon-rich atmospheres of planets and their moons.¹ In Saturn's moon, Titan,^{2–4} molecular nitrogen and methane are the main constituents of the atmosphere, followed by hydrogen, nitrogen-bearing molecules, and hydrocarbons.^{5–13} Even though the unsaturated hydrocarbon molecules such as acetylene, ethylene, diacetylene, and benzene occur only in trace amounts,¹⁴ they are of particular importance because they are thought to be key intermediates to form Titan's organic, aerosol-particle-based haze layers. These haze layers are of basic significance to Titan's chemistry and to hydrocarbon-rich atmospheres of planets in the outer solar system in general. First, the mainly hydrocarbon-based aerosol particles absorb the destructive ultraviolet radiation to protect astrobiologically important molecules from being destroyed in the lower parts of the atmosphere.¹⁵ Second, the haze layer contains predominant "anti-greenhouse species", which prevents Titan's atmosphere from heating up (temperature inversion at the tropopause).¹⁶ Therefore, hydrocarbon molecules play a crucial role in the radiation and temperature balance.¹⁷ Third, Titan's haze makes an important contribution to the dynamics of the atmosphere.^{18,19} This leads to latitudinal and seasonal patterns of hydrocarbons in the atmosphere of Titan. The haze particles may provide nucleation sites for hydrocarbon snow and rain. Therefore, an understanding of the formation of the haze layers is also important to comprehend the meteorology on Titan.^{19–22}

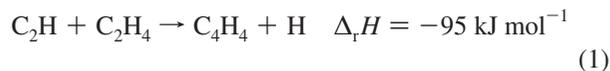
Here the ethynyl molecule is considered to be the key radical involved in the formation of unsaturated hydrocarbon molecules in Titan's atmosphere.^{23–25} Whereas the main source of the ethynyl radicals has been unambiguously identified as the photolysis of acetylene (C_2H_2),^{26–34} the dynamics of ethynyl radical reactions and their role in the build-up of complex hydrocarbons are far less clear. In this context, the C_4H_4 potential energy surface (PES), which also includes vinylacetylene ($HCCC_2H_3$)^{35–37} and its butatriene^{38,39} isomer, has received considerable attention.^{40–43} Cremer et al.⁴⁴ revealed that the singlet manifold is particularly rich in carbene and also biradical structures. This is the result of a low hydrogen-to-carbon ratio. Some of the carbenes possess surprisingly high thermodynamic stability and should be detectable in the matrix at low temperature. This has been confirmed in the case of the allenylcarbene (CH_2CCH).^{45,46} In the same study, vinylacetylene ($HCCC_2H_3$) was found to be the most stable C_4H_4 species; the isomerization has high energy barriers comparable to those typically observed in the unimolecular decomposition of closed shell hydrocarbons. Cremer et al. also investigated the photodissociation of vinylacetylene at 220 nm under temperature and pressure conditions similar to those of Titan's atmosphere. The products were found to be acetylene (C_2H_2), diacetylene (C_4H_2), and the C_4H_3 radical with branching ratios of 66:7:27. Experimentally, the C_4H_4 surface was also accessed via the crossed-beams reactions of singlet and triplet dicarbon molecules (C_2) with ethylene (C_2H_4)⁴⁷ and through the reactions of carbon atoms with two C_3H_4 isomers, that is, methylacetylene and allene.^{48,49} These studies were accompanied by electronic structure calculations.⁵⁰ However, in Titan's atmosphere, those C_4H_4 structures formed as intermediates in bimolecular reactions are relatively short-lived and cannot be stabilized via a third-body reaction.

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As such, they will decompose prior to a collision-induced stabilization.

But how could C_4H_4 molecules, such as the thermodynamically most stable vinylacetylene molecule, be formed under the conditions similar to those of Titan's atmosphere? On the basis of the energetics, one thermodynamically accessible reaction channel is the reaction of ground-state ethynyl radicals, $C_2H(X^2\Sigma^+)$, with ethylene (X^1A_g) (reaction 1)⁵¹



Here the ethynyl radical is proposed to be the major photodissociation product of acetylene in Titan's atmosphere.^{52–55} Ethylene has also been detected in Voyager I and II as well as in the Cassini–Huygens mission.^{56–62} Note that Leone's group measured the rate coefficients of this reaction from 150 to 359 K⁵¹ and at 103 and 296 K,⁶³ respectively. Their results show that this reaction of ethynyl radicals with ethylene molecules is very rapid and can be fit via the expressions $k = (7.8 \pm 0.6) \times 10^{-11} \exp[(134 \pm 44)/T]$ from $T = 150$ to 359 K; at 103 K, which is typical for Titan's atmosphere, a large rate constant of $(1.4 \pm 0.4) \times 10^{-10}$ is evident. Nevertheless, the true reaction product(s) have never been identified to date. To shed light on this open question, we report in this article our results on the cross beams study of the ethynyl radical with d_4 -ethylene under single collision conditions and combine these experimental findings with comprehensive electronic structure calculations on this system.

2. Experimental and Data Analysis

A universal crossed molecular beams machine was utilized to study the reaction of the ground-state ethynyl radical, $C_2H(X^2\Sigma^+)$, with d_4 -ethylene, $C_2D_4(X^1A_1)$, under single-collision conditions. The experimental setup has been described in detail elsewhere.^{64–67} In brief, a supersonic beam of ethynyl radicals, $C_2H(X^2\Sigma^+)$, was generated in the primary source via photodissociation of bromoacetylene (C_2HBr , 99.5+%) which was seeded in helium (99.9999%, Airgas) at a ratio of about 1%. The gas mixture was released by a Proch–Trickl pulsed valve operating at 60 Hz and 700 Torr backing pressure. A Teflon extension tube with a slit located parallel to the expansion direction of the pulsed beam was interfaced to the end of the nozzle; this allowed a 193 nm laser beam focused to 2 mm by 5 mm from a Lambda Physik Compex 110 Excimer laser operated at 30 Hz and 35–40 mJ per pulse to intercept the bromoacetylene beam perpendicularly downstream of the nozzle. Under our operation conditions, about 6% of the bromoacetylene precursor molecules were photodissociated to generate an ethynyl radical and a bromine atom. Because the lifetime of the A^2A' state of ethynyl is less than 1 μ s, any $C_2H(A^2A')$ species will relax while traveling from the photolysis center to the interaction region of the scattering chamber. A four-slot chopper wheel was installed after a skimmer to select a part of the ethynyl beam at a peak velocity (v_p) of $1490 \pm 20 \text{ ms}^{-1}$ and a speed ratio (S) of 8.5 ± 0.5 . This segment crossed a pulsed d_4 -ethylene beam (C_2D_4 , 99% deuterium, CDN; 550 Torr; $v_p = 850 \pm 20 \text{ ms}^{-1}$; $S = 13.0 \pm 0.2$) released by a second pulsed valve perpendicularly in the interaction region. Under these conditions, a collision energy of $20.6 \pm 0.4 \text{ kJ mol}^{-1}$ was obtained.

The reactively scattered species were monitored using a triply differentially pumped quadrupole mass spectrometric detector

in the time-of-flight (TOF) mode after electron-impact ionization of neutral species at 80 eV electron energy. This detector can be rotated within the plane defined by the primary and the secondary reactant beams to allow taking angular resolved TOF spectra. At each angle, up to 1.5×10^6 TOF spectra (up to 14 h per angle) were accumulated. The recorded TOF spectra were then integrated and normalized to extract the product angular distribution in the laboratory frame (LAB). In this setup, both the primary and secondary pulsed valves were operated at 60 Hz, but the photodissociation laser was operated at only half the repetition rate of 30 Hz. This allows a background subtraction by taking TOF spectra in the 'laser on' mode and subtracting from the TOF spectra recorded on the 'laser off' mode. To extract information on the reaction dynamics, the experimental data must be transformed into the center-of-mass reference frame utilizing a forward-convolution routine.^{68,69} This iterative method initially assumes an angular flux distribution, $T(\theta)$, and the translational energy flux distribution, $P(E_T)$ in the center-of-mass system (CM). Laboratory TOF spectra and the laboratory angular distributions (LAB) were then calculated from the $T(\theta)$ and $P(E_T)$ functions and were averaged over a grid of Newton diagrams to account for the apparatus functions and the beam spreads. Each diagram defines, for instance, the velocity and angular spread of each beam and the detector acceptance angle. We obtained best fits by iteratively refining the adjustable parameters in the center-of-mass functions within the experimental error limits of, for instance, peak velocity, speed ratio, and error bars in the LAB distribution. The ultimate output of this procedure is a product flux contour map, $I(\theta, u) = P(u) \times T(\theta)$. This function plots the intensity of the reactively scattered products (I) as a function of the center-of-mass scattering angle (θ) and product velocity (u). The map can be seen as the image of the chemical reaction and contains all information on the scattering process.

3. Results

In the crossed-beams experiment of the ethynyl radical with d_4 -ethylene, a reactive scattering signal was observed at mass-to-charge ratios of $m/z = 55$ ($C_4HD_3^+$), 54 ($C_4D_3^+$), 53 ($C_4HD_2^+$), 52 ($C_4D_2^+$), 51 (C_4HD^+), 50 (C_4D^+), 49 (C_4H^+), and 48 (C_4^+). No reactive scattering signal was detected at $m/z = 30$ ($C_2D_3^+$) and 27 (C_2HD^+). All TOF spectra between $m/z = 55$ ($C_4HD_3^+$) and 48 (C_4^+) were superimposable after scaling. Therefore, in this system, the only open channel, at least at a collision energy of 20.6 kJ mol^{-1} , is the formation of a product of the gross formula C_4HD_3 together with a light deuterium atom. No atomic hydrogen loss is observable at $m/z = 56$ ($C_4D_4^+$). The signal at lower mass-to-charge ratios originated within our detection limit solely from a dissociative ionization of the C_4HD_3 parent molecule in the ionizer of the detector. Because of the strongest reactive scattering signal at $m/z = 55$, TOF spectra and the laboratory angular distribution were extracted from the corresponding $C_4HD_3^+$ ions. These data are shown in Figures 1 and 2. As evident, the LAB distribution is relatively broad and spreads over 60° within the scattering plane defined by the ethynyl and the d_4 -ethylene beams. Furthermore, the LAB distribution peaks close to the corresponding center-of-mass angle of $36.2 \pm 0.5^\circ$. We also conducted a study on the ethynyl–ethylene (C_2H_4) reaction; at the center-of-mass, we recorded TOF spectra at $m/z = 52$ ($C_4H_4^+$) (Figure 3). However, at angles closer to the primary beam, the background interference from the doubly charged $C_2H^{79} Br^{2+}$ ion ($m/z = 52$) was too strong to record reliable TOF spectra and a laboratory angular distribution. Therefore, the experiments were conducted with d_4 -ethylene to eliminate this background problem.

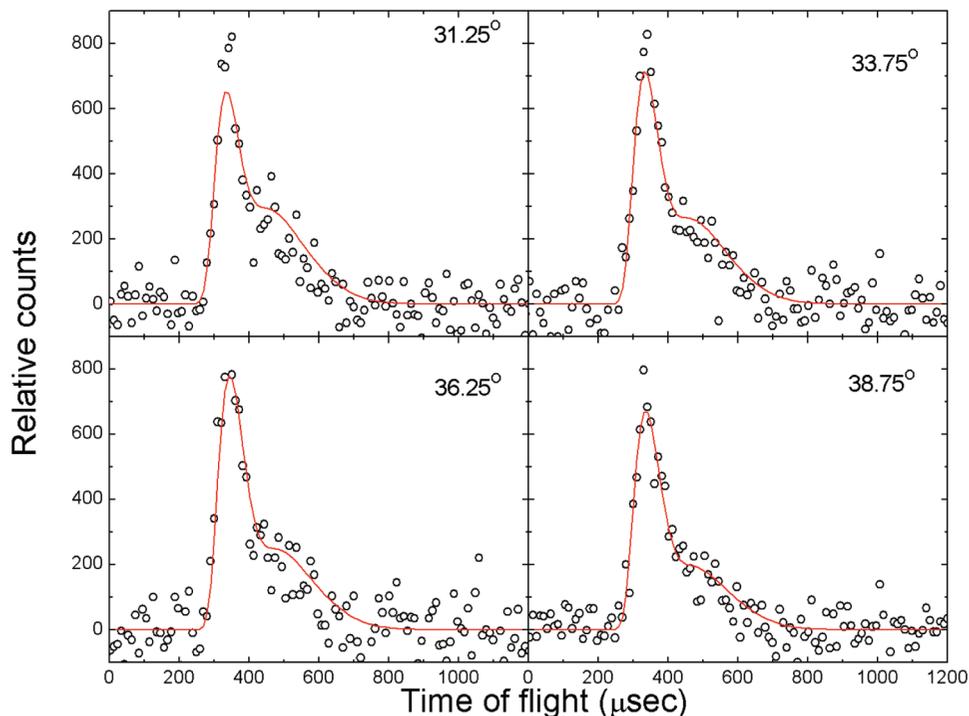


Figure 1. Selected time-of-flight (TOF) spectra recorded at $m/z = 55$ ($C_4HD_3^+$) at various laboratory angles for the reaction of the ethynyl radical with d_4 -ethylene at a collision energy of 20.6 kJ mol^{-1} . The circles indicate the experimental data, the solid lines represent the calculated fits.

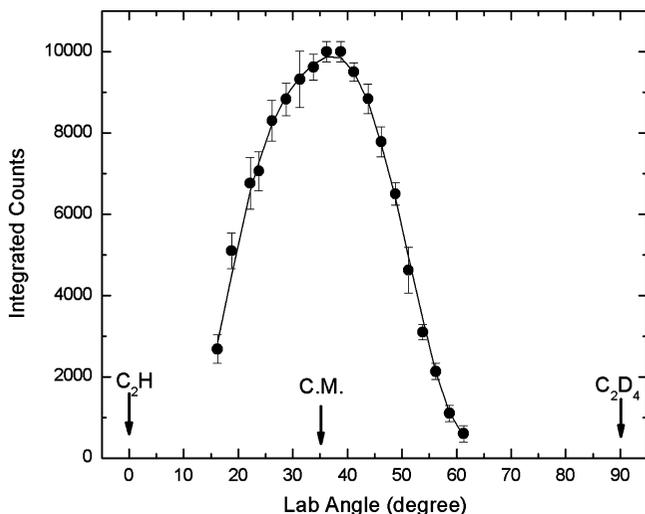


Figure 2. Laboratory angular distribution (LAB) of the C_4HD_3 product recorded at $m/z = 55$ ($C_4HD_3^+$) at a collision energy of 20.6 kJ mol^{-1} for the reaction of the ethynyl radical with d_4 -ethylene. Circles and error bars indicate experimental data, and the solid line represents the calculated distribution with the best-fit center-of-mass functions.

Having discussed the laboratory data, we are now turning our attention to the center-of-mass angular ($T(\theta)$) and translational energy distributions ($P(E_T)$) (Figure 4). Most importantly, the laboratory data (Figures 1 and 2) could be fit with only a single channel of the mass combination 55 amu (C_4HD_3) plus 2 amu (D). Important information on the dynamics were extracted from these functions. First, the center-of-mass translational energy distribution peaks away from zero translational energy and depicts a relatively broad distribution maximum located at about $35\text{--}50 \text{ kJ mol}^{-1}$. This finding indicates that for this system at least one exit channel leading to the formation of the C_4HD_3 isomer is rather tight. According to the principle of microscopic reversibility of a chemical reaction, the reversed addition of a deuterium atom to the C_4HD_3 product is therefore

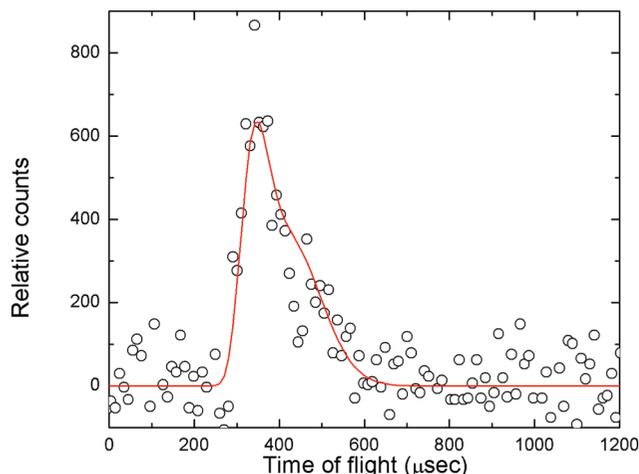


Figure 3. Time-of-flight (TOF) spectrum of $m/z = 52$ ($C_4H_4^+$) recorded at a collision energy of 20.6 kJ mol^{-1} at center-of-mass angle of 36.25° for the reaction of ethynyl radical with ethylene. The circles indicate the experimental data, and the solid line represents the calculated fit using the same center-of-mass functions as those of the ethynyl- d_4 -ethylene system. As dictated by momentum conservation, because of the lighter hydrogen coproduct, the C_4H_4 product has a smaller recoil sphere compared with the C_4HD_3 molecule. This translates into broader TOF spectra of the C_4HD_3 versus the C_4H_4 product, for instance of 450 versus $350 \mu\text{s}$ at the center-of-mass angle. Also, the bimodal structure is clearly pronounced in the TOF spectra of the C_4HD_3 product.

expected to have an entrance barrier; the order of magnitude indicates that the deuterium atom likely adds to a closed shell molecule holding a double or triple bond.⁷⁰ Second, for the best-fit functions, the maximum translational energy cutoff, E_{max} , is found to be about 115 kJ mol^{-1} . Our error analysis indicates that the tail of the $P(E_T)$ can be either extended or cut by up to 20 kJ mol^{-1} without significantly changing the results of the fit. Recall that the maximum translational energy resembles the sum of the collision energy and the absolute of the exoergicity of the reaction. Therefore, by subtracting the collision energy,

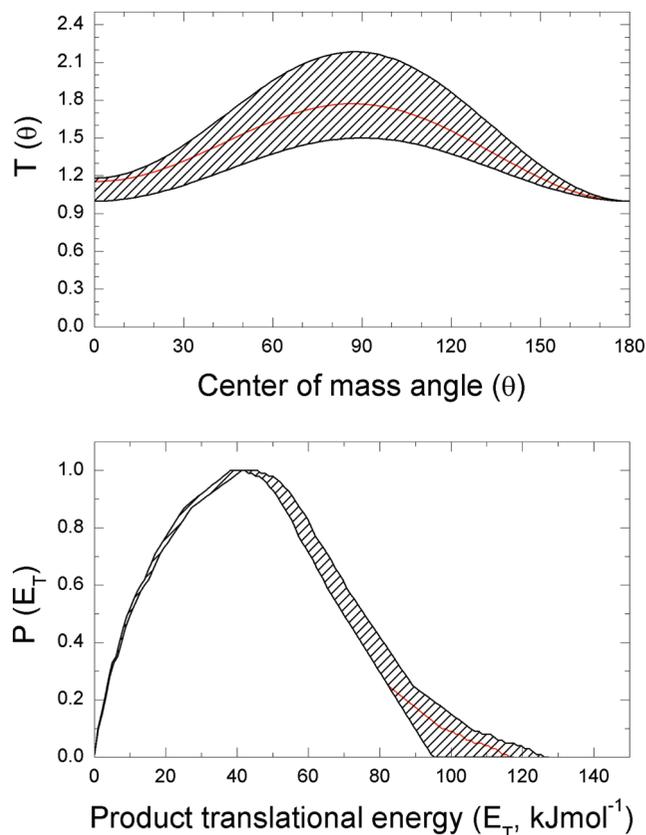


Figure 4. Center-of-mass angular (top) and translational energy flux distributions (bottom) of the C_4HD_3 plus atomic deuterium channel of the reaction of ethynyl radical with d_4 -ethylene. Hatched areas indicate the acceptable upper and lower error limits of the fits. The red line defines the best fit functions.

we determine that the formation of the C_4HD_3 product plus a deuterium atom is exoergic by $94 \pm 20 \text{ kJ mol}^{-1}$. From this center-of-mass translational energy distribution, we can also compute the fraction of the energy channeling into the translational modes of the products, that is, $\langle E_T \rangle / E_{\text{max}}$ with $\langle E_T \rangle$ being the averaged translational energy of the products. This suggests fractions of about $38 \pm 2\%$ for the ethynyl- d_4 -ethylene system. This order of magnitude is consistent with indirect scattering dynamics.⁷¹

The derived center-of-mass angular distribution for the ethynyl- d_4 -ethylene system is also shown in Figure 4. Mostly evidently, it is forward-backward symmetric and depicts flux over the whole scattering range from 0 to 180°. This finding indicates that the ethynyl- d_4 -ethylene reaction involves indirect scattering dynamics via the formation of C_4HD_4 intermediate(s), whose lifetime is longer than its rotational period.^{72,73} Most important, the center-of-mass angular distribution has a substantial maximum at 90°. Here the ratio of the flux intensities at 0 versus 90° was determined to be 0.51 ± 0.05 . The polarization and maximum at 90° strongly suggest geometrical constraints of the decomposing complex, here a preferential deuterium atom ejection perpendicular to the molecular plane of the rotating C_4HD_4 moiety and almost parallel to the total angular momentum vector.⁷² This is also visualized in the flux contour map (Figure 5). Note that within the error limits, a slightly forward favored peaking of the center-of-mass angular distribution can also fit the experimental data.

4. Discussions

The results indicate that the product of the ethynyl- d_4 -ethylene reaction holds a general formula of C_4HD_3 (C_4H_4 for

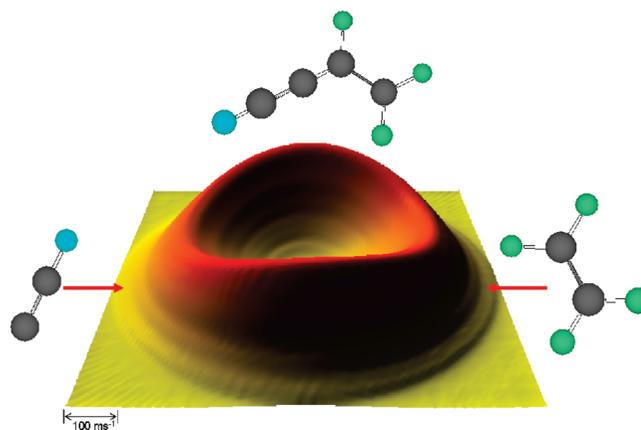


Figure 5. Flux contour map of the C_4HD_3 product (d_3 -vinylacetylene) formed in the reaction of ethynyl radical with d_4 -ethylene, as derived from the best-fit functions (Figure 4).

the homologous C_2H_4 reactant). To determine which isomer is this product(s), we need to compare our experimentally derived reaction energy with theoretical values and with those from literature data. A previous study suggested that the reaction to form vinylacetylene molecule ($HCCC_2H_3$) (**p1**) plus atomic hydrogen is exoergic by 95 kJ mol^{-1} .¹⁹ This value correlates well with our experimental result (for deuterated reactants and products, the energy difference is only a few kilojoules per mole), and thus d_3 -vinylacetylene must be the most likely product of this reaction. However, we also have to consider the possibility that other C_4HD_3 isomers might have been formed. On the basis of the energetics, the formation of the second and third most stable isomers, butatriene (H_2CCCCH_2) and methylenecyclopropane ($c-C_4H_4$), are exoergic by 47 and 2 kJ mol^{-1} , respectively.¹² On the basis of the energetics alone, we can say with confidence that d_3 -vinylacetylene is the major heavy product in the ethynyl- d_4 -ethylene reaction (vinylacetylene in the homologous ethynyl plus ethylene reaction).

To extract the chemical dynamics leading to the formation of the d_3 -vinylacetylene ($HCCC_2D_3$), we are now comparing the structures of the ethynyl and d_4 -ethylene reactants with the three possible products. Our detailed analysis of the C_4H_5 PES obtained by ab initio CCSD(T)/cc-pVQZ//B3LYP/6-311G** calculations combined with RRKM calculations of rate constants and branching ratios is given in the accompanying theoretical paper in this special issue. Here we consider only the most important channels of relevance to the experimental findings. (See Figure 6.) First, let us focus on the major product, d_3 -vinylacetylene: effectively, the ethynyl group replaces one deuterium atom of the d_4 -ethylene molecule in the process. Therefore, we can propose the following reaction dynamics: the ethynyl with its radical center adds to the π -electron of one of the carbon atoms of d_4 -ethylene, without an entrance barrier, to form an acyclic C_4HD_4 intermediate, CD_2CD_2CCH (**i1** d_4 -3-butyn-1-yl). Then, one of the deuterium atoms at the α -carbon departs from the complex via a tight exit barrier of 20 kJ mol^{-1} to form the d_3 -vinylacetylene product. According to our present calculations, the overall reaction exothermicity to form this product is 103 kJ mol^{-1} . An alternative pathway to d_3 -vinylacetylene involves a 1,2-D shift to the terminal CD_2 group to form CD_3CDCCH (**i2** d_4 -3-butyn-2-yl), followed by a deuterium atom emission from the CD_3 group. Note that our B3LYP/6-311G** calculations failed to locate a deuterium elimination transition state from **i2** and converged to the separated products, indicating that this channel occurs without an exit barrier. However, because the reverse reaction, a

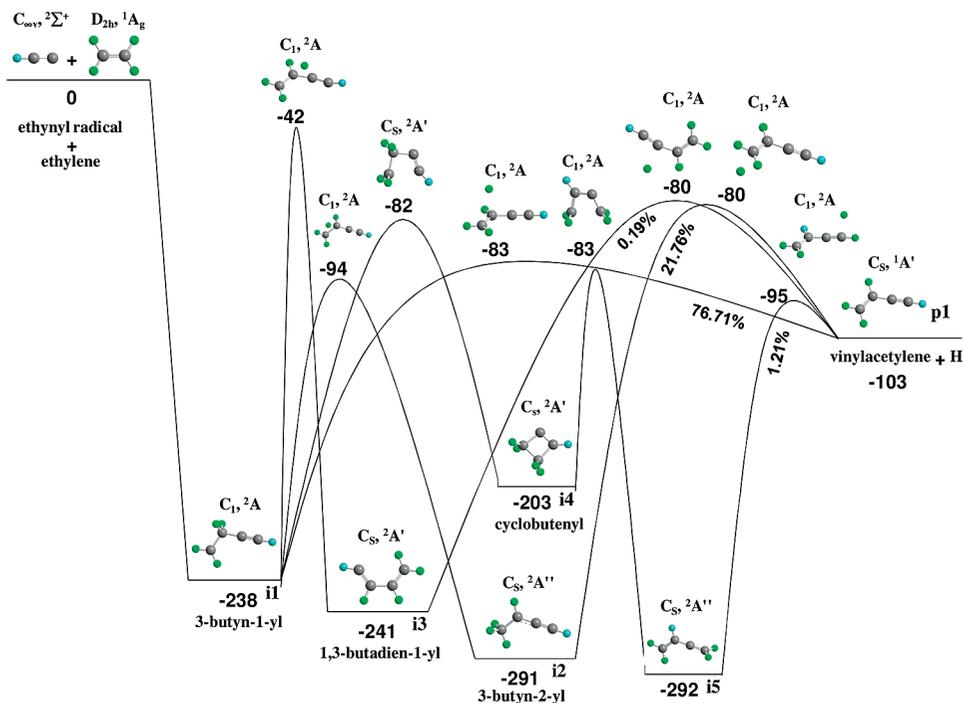


Figure 6. Potential energy surface of the reaction of ethynyl radicals with d_4 -ethylene to form D_3 -vinylacetylene plus atomic deuterium. Energies are given in kilojoules per mole. Also shown are the symmetries of the electronic wave functions and the point groups.

deuterium atom addition to the closed-shell d_3 -vinylacetylene molecule, should be expected to exhibit a barrier, we repeated the transition-state search using the second-order Møller–Plesset perturbation theory MP2/6-311G** method. In this case, a barrier was located, and its existence was verified by single-point CCSD(T)/cc-pVQZ calculations, which gave the energy of the transition state about 23 kJ mol^{-1} higher than the energy of d_3 -vinylacetylene plus deuterium. Therefore, we conclude that the deuterium emission from the CD_3 group in **i2** also occurs via a tight transition state with an exit barrier of about 23 kJ mol^{-1} .

A third pathway to the same products starts from a 1,2-deuterium migration from CD_2 to the neighboring bare carbon atom to produce CD_2CDCDCD (**i3** d_4 -1,3-butadien-1-yl) and completes by deuterium loss from the CD group formed in the previous step via a tight exit barrier of 23 kJ mol^{-1} . Another isotopomer of d_3 -vinylacetylene, CD_2CHCCD , can be formed through a three-step route involving four-member ring closure of **i1** to d_4 -cyclobutenyl **i4**, followed by ring-opening to $\text{CD}_2\text{CHCCD}_2$ (**i5** d_4 -1,3-butadien-3-yl/2,3-butadien-1-yl), and finalized by deuterium elimination from CCD_2 via an exit barrier of 8 kJ mol^{-1} . Our statistical RRKM calculations show that at the experimental collision energy of 20.6 kJ mol^{-1} , 76.7% of the d_3 -vinylacetylene CD_2CDCCH is formed from **i1**, whereas 21.8% is produced via **i2**; both channels proceed via tight transition states with exit barriers differing by only 3 kJ mol^{-1} . The contribution of the other channels to the total product yield is insignificant. Also note that none of the most important reaction channels proceeds via a hydrogen loss to produce d_4 -vinylacetylene. The formation of the d_4 -butatriene product can occur by hydrogen loss from **i5**; however, the RRKM calculated branching ratio for this channel is very small. For the d_4 -methylenecyclopropene pathway, the ethynyl group needs to add to the π -electron of both carbon atoms of d_4 -ethylene to form a cyclic C_4HD_4 intermediate (d_3 -cyclopropylidene-methyl). Then, a deuterium atom at one of the carbon atoms of d_4 -ethylene molecule shifts to the terminal carbon of the ethynyl unit via a 1,3-deuterium migration. Lastly, a deuterium atom at

the other carbon atom of ethylene molecule detaches from the complex to form the **p3** product. However, if the reaction is to occur statistically, then the branching ratio of the methylenecyclopropene route is immaterial. Evidently, the d_3 -vinylacetylene pathway is the preferred one among the three. However, the formation of both d_3 -butatriene and d_3 -methylenecyclopropene molecules needs extra steps with high barriers and is clearly less favorable.

The computational findings are fully supported by our experimental results. First, we verified the formation of the d_3 -vinylacetylene by comparing the experimentally determined reaction energy with literature values (NIST database) and also the computed reaction energy. Also, recall that the deuterium atom elimination was observable but not the loss of a hydrogen atom; a hydrogen loss pathway would have resulted in the formation of d_4 -butatriene via intermediate **i5**. However, the formation of butatriene could be clearly ruled out because the hydrogen loss pathway was not observed; also, the derived reaction energy does not correlate with the experimental data. Second, the indirect nature of the reaction via an addition–elimination reaction mechanism was clearly validated by the shape of the center-of-mass angular distribution, which depicted intensity over the complete angular range. Third, the existence of an exit barrier of the decomposition of **i1** via a deuterium loss pathway was also derived from the off-zero peaking of the center-of-mass translational energy distribution. Finally, the “sideways” scattering of the center-of-mass angular distribution, which suggests that the deuterium atom is emitted almost perpendicularly to the rotating plane of the decomposing complex, was confirmed in our electronic structure calculations. Here a detailed analysis of the geometry of the exit transition state connecting **i1** and d_3 -vinylacetylene plus a deuterium atom clearly depicts an angle of 107.6° between the departing deuterium atom and the principal rotation axis (Figure 6).

A similar addition–elimination reaction mechanism was also found in the related reaction of cyano radicals $\text{CN}(X^2\Sigma^+)$ with ethylene.^{74,75} The cyano–ethylene reaction has no entrance barrier and is initiated by an attack of the cyano radical to the

π -electron density of the ethylene molecule to form a $\text{CH}_2\text{CH}_2\text{CN}$ intermediate. Then, about 40% of this intermediate shows a C–H bond rupture via a tight exit barrier, the remaining 60% of the collision complex undergoes a 1,2-H-atom shift to CH_3CHCN prior to a hydrogen atom release and the formation of vinylcyanide.

5. Conclusions

In this study, we have investigated the crossed molecular beams reaction of ground-state ethynyl radicals, C_2H ($X^2\Sigma^+$), with d_4 -ethylene, $\text{C}_2\text{D}_4(X^1A_1)$, under single collisions at a collision energy of 20.6 kJ mol^{-1} . The results suggest that this reaction undergoes an indirect mechanism via a C_4HD_4 intermediate, which is formed by the initial barrierless addition of the ethynyl radical to the carbon atom of the d_4 -ethylene molecule. This collision complex would then release a deuterium atom to yield a product with a gross formula of C_4HD_3 through a tight exit transition state. This product was identified as d_3 -vinylacetylene. The other two energetically accessible reaction pathways to form d_3 -butatriene and methylenecyclopropene plus deuterium atom, which both involve a 1,3-deuterium shifting after the initial ethynyl radical addition, were found to be insignificant contributors. There are many similarities between this reaction and that of the isoelectronic cyano radicals with the ethylene system.^{74,75} Both reactions are exoergic and follow indirect reaction dynamics that involve a barrierless addition of the radicals to the carbon atom of the unsaturated carbon–carbon bond to form intermediates, followed by an atomic hydrogen/deuterium emission through exit barriers lying below the energy level of separate reactants to form the final product. Therefore, this study provides evidence that vinylacetylene can be synthesized in a low-temperature environment such as Titan's atmosphere because both reactants exist there.

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