# A Combined Experimental and Computational Study on the Reaction Dynamics of the 1-Propynyl (CH<sub>3</sub>CC)–Acetylene (HCCH) System and the Formation of Methyldiacetylene (CH<sub>3</sub>CCCCH)

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**ABSTRACT:** We investigated the 1-propynyl (CH<sub>3</sub>CC; X<sup>2</sup>A<sub>1</sub>) plus acetylene/ acetylene- $d_2$  (HCCH/DCCD; X<sup>1</sup> $\Sigma_g^+$ ) under single-collision conditions using the crossed molecular beams method. The reaction was found to produce C<sub>5</sub>H<sub>4</sub> plus atomic hydrogen (H) via an indirect reaction mechanism with a reaction energy of  $-123 \pm 18$  kJ mol<sup>-1</sup>. Using the DCCD isotopologue, we confirmed that the hydrogen atom is lost from the acetylene reactant. Our computational analysis suggests the reaction proceeds by the barrierless addition of the 1-propynyl radical to acetylene, resulting in C<sub>5</sub>H<sub>5</sub> intermediate(s) that dissociate preferentially to methyldiacetylene (CH<sub>3</sub>CCCCH; X<sup>1</sup>A<sub>1</sub>) via hydrogen atom emission with a computed reaction energy of  $-123 \pm 4$  kJ mol<sup>-1</sup>. The barrierless nature of this reaction scheme suggests the 1-



propynyl radical may be a key intermediate in hydrocarbon chain growth in cold molecular clouds like TMC-1, where methylsubstituted (poly)acetylenes are known to exist.

## 1. INTRODUCTION

During the last decades, hydrocarbon research has increasingly focused on unraveling the formation mechanisms of polycyclic aromatic hydrocarbons (PAHs)-organic molecules carrying fused benzene rings-and the role they play in soot formation,<sup>1</sup> which is both a marker of combustion inefficiency<sup>2</sup> and a public health hazard.<sup>3,4</sup> Besides being byproducts of incomplete hydrocarbon combustion, PAHs are believed to proliferate in the interstellar medium (ISM), where spectroscopic signatures for aromatic hydrocarbons have been observed in the ultraviolet (200-400 nm)<sup>5-7</sup> and infrared  $(3-20 \ \mu m)^{8-10}$  regions of the electromagnetic spectrum. A complete understanding of the PAH reaction cycle, including knowledge of all precursors and intermediates, thus has broadreaching applications to unravel the interstellar carbon budget and also to elucidate the underlying pathways to PAH formation in combustion systems.

The hydrogen-abstraction–acetylene addition (HACA) mechanism is suggested to present a facile route by which PAH growth occurs under thermal conditions.<sup>11,12</sup> Under conditions of acetylene (HCCH) enrichment, hydrogen atom abstractions from aromatic hydrocarbon precursors [benzene  $(C_6H_6)$ , naphthalene  $(C_{10}H_8)$ , biphenyl  $(C_{12}H_{10})$ , and phenanthrene  $(C_{14}H_{10})$ ], followed by the sequential addition of acetylene molecule(s), results in the addition of five- and six-membered rings leading to naphthalene,<sup>13</sup> acenaphthylene,<sup>14</sup> phenanthrene,<sup>15</sup> and pyrene,<sup>16</sup> respectively. Odd-carbon radicals tend to be resonantly stabilized free radicals (RSFRs) and have been shown to be drivers of PAH formation and growth under combustion conditions.<sup>17,18</sup> Arguably the

most important in this context is suggested to be the propargyl (CH<sub>2</sub>CCH) radical for its role in building the first aromatic species, namely, phenyl  $(C_6H_5)$  and benzene, by propargyl selfreaction.<sup>19,20</sup> Additionally, propargyl has been shown to proceed directly to larger RSFRs such as cyclopentadienyl (c- $C_{5}H_{5}$ ) via reaction with acetylene  $(C_{2}H_{2})$ .<sup>21</sup> Once formed, the cyclopentadienyl radical can react with acetylene to form the cylcopentafused PAH indene  $(C_0H_8)$  via a high-energy tropyl  $(C_7H_7)$  intermediate<sup>22</sup> or undergo self-reaction to yield naphthalene  $(C_{10}H_8)^{23,24}$  in a multistep reaction, skipping the HACA mechanism altogether. Another alternative route for PAH growth involves aromatic radical addition<sup>25</sup> to the unsaturated hydrocarbon vinylacetylene  $(HCCC_2H_3)^{26,27}$ through the hydrogen-abstraction-vinylacetylene addition (HAVA) route and 1,3-butadiene (CH<sub>2</sub>CHCHCH<sub>2</sub>).<sup>28,29</sup> Propargyl clearly plays an important role in the PAH growth cycle as a precursor to cyclic RSFRs and aromatics, but it is only one of six stable  $C_3H_3$  isomers (Figure 1). Difficulties in the preparation of five high-energy C<sub>3</sub>H<sub>3</sub> isomers has restricted their study mostly to theory, and therefore any role they might play in hydrocarbon growth schemes may, at present, be underrepresented.

One such species is the 1-propynyl (CH<sub>3</sub>CC) radical, a highenergy and nonresonant  $C_3H_3$  isomer. The propynyl radical holds a  $C_{3\nu}$  symmetric point group with an  $X^2A_1$  electronic ground state<sup>30</sup> and lies 168 kJ mol<sup>-1</sup> (0 K) above the propargyl

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Figure 1. Structural isomers of the  $C_3H_3$  radical. Point groups and energies (kJ mol<sup>-1</sup>) relative to propargyl are also shown. Energies were obtained from ref 31.

radical.<sup>31,32</sup> Literature on the availability and reactivity of 1propynyl during combustion is scarce. Geppert et al.<sup>33</sup> suggested that higher-energy C3H3 isomers like 1-propynyl might represent up to 14% of the total C<sub>3</sub>H<sub>3</sub> yield in crossed molecular beams studies on the reaction of atomic carbon  $(C(^{3}P))$  with ethylene  $(CH_{2}CH_{2})$  at a collision energy of 30.8 kJ mol<sup>-1,33,34</sup> However, recent studies on this system were unable to confirm their hypothesis.<sup>35,36</sup> Methylacetylene (propyne; CH<sub>3</sub>CCH) could be a source of 1-propynyl radicals, but considering the bond energies of the acetylenic hydrogen bond to those of the acetylene-methyl  $(C-CH_3)$  and methyl hydrogen bonds  $(H-C_2H)$ , the yield would be extremely small.<sup>37</sup> Indeed, hydrogen atom reactions with methylacetylene at combustion-relevant temperatures and pressures produce mainly acetylene by methyl  $(CH_3)$  displacement, allene  $(H_2CCCH_2)$  via hydrogen-assisted isomerization, and the propargyl radical by direct hydrogen abstraction.<sup>38</sup>

Although thermal degradation of methylacetylene may not form appreciable quantities of 1-propynyl, photodissociation of methylacetylene by UV photons can form 1-propynyl by rupture of the acetylenic C–H bond.  $^{39-41}$  This, in part, has led to its consideration as an important reactant in cold hydrocarbon-rich systems like the atmosphere of Saturn's largest moon, Titan. Kirk et al. found that 1-propynyl reacts in overall exoergic processes with the unsaturated hydrocarbons acetylene (HCCH), ethylene (CH $_2$ CH $_2$ ), methylacetylene (CH<sub>3</sub>CCH), and propylene (CH<sub>3</sub>C<sub>2</sub>H<sub>3</sub>).<sup>42</sup> Reactions of 1propynyl with acetylene and ethylene were suggested to form only atomic hydrogen loss products methyldiacetylene (CH<sub>3</sub>CCCCH) and vinylmethylacetylene (CH<sub>3</sub>C<sub>2</sub>C<sub>2</sub>H<sub>3</sub>), respectively, while reactions with the methyl-bearing molecules preferentially formed methyl-loss products in addition to hydrogen-loss products.<sup>42</sup>

The chemistry of the 1-propynyl radical might be considered analogous to the isolobal ethynyl ( $C_2H$ ;  $X^2\Sigma^+$ ) radical, where the hydrogen atom has been replaced by a methyl group. Ethynyl has been shown to form benzene by barrierless addition to the  $\pi$  system of 1,3-butadiene following cyclization and elimination of atomic hydrogen.<sup>43</sup> Its ability to barrierlessly add to unsaturated hydrocarbons has made it increasingly relevant in the cold hydrocarbon-rich atmosphere of Titan,<sup>44</sup> where PAH growth may occur by an ethynyl addition mechanism (EAM) that proceeds similarly to the temperature-dependent HACA scheme.<sup>45,46</sup> Ethynyl has also been shown to extend the alkyne-bearing hydrocarbons acetylene (HCCH),<sup>47</sup> diacetylene (HCCCCH),<sup>48</sup> and methylacetylene (CH<sub>3</sub>CCH)<sup>49,50</sup> by one C<sub>2</sub> unit via displacement of the terminal acetylenic hydrogen atom. Therefore, reactions of 1-propynyl (CH<sub>3</sub>CC) with (poly)acetylenes are expected to result in methyl-substituted polyacetylenes. Further, reactions with 1,3-butadiene might bear the formation of the aromatic toluene (CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>) molecule.

As already discussed, UV dissociation of methylacetylene yields a highly reactive propynyl radical, and the absence of stabilization by electron resonance increases its reactivity opening the possibility for low-energy reactions with closed-shell unsaturated hydrocarbons. If formed in the low-density ISM, 1-propynyl could react barrierlessly with (poly)acetylenes (Figure 2), which are known to be present in cold molecular



Figure 2. Growth of methyl (poly)acetylenes via barrierless radical additions.

clouds like TMC-1 and in circumstellar envelopes of carbon stars like IRC+10216.51-53 Such a mechanism could help explain the presence of methyldiacetylene (CH<sub>3</sub>CCCCH) and methyltriacetylene (CH<sub>3</sub>CCCCCCH) in TMC-1,<sup>54-57</sup> where methylacetylene is a known constituent.<sup>58</sup> The applicability of these considerations hinge on (a) whether these reactions face barriers that render them uncompetitive, (b) steric effects that may hinder isomerization reactions such as cyclization of any intermediates formed, and (c) the extent to which the 1propynyl methyl group remains a spectator during reaction. The aim of this article is to answer these questions regarding the reactivity the 1-propynyl radical and to search for consistencies and differences with the isolobal ethynyl reaction system by exploring the reaction dynamics of the 1-propynyl radical (CH<sub>3</sub>CC) with acetylene (HCCH) under singlecollision conditions.<sup>59-63</sup>

# 2. EXPERIMENTAL AND COMPUTATIONAL METHODS

2.1. Experimental Methods. The 1-propynyl (CH<sub>3</sub>CC;  $X^{2}A_{1}$ ) reactions with acetylene (HCCH;  $X^{1}\Sigma_{g}^{+}$ ) and acetylene $d_2$  (DCCD;  $X^1\Sigma_g^+$ ) were conducted under single-collision conditions using a crossed molecular beams machine at the University of Hawaii.<sup>64</sup> The machine employs two orthogonal fixed molecular beam sources and a detector that is rotatable in the plane of these sources. The detector comprises an electron impact ionizer,<sup>65</sup> quadrupole mass spectrometer (QMS), and a Daly-type ion counter.<sup>66</sup> Subdivided into three regions, differential pumping of the detector reduces operating pressures to less than  $2 \times 10^{-11}$  torr in the innermost section that houses the ionizer. Neutral molecules entering the detector are ionized then filtered according to mass-to-charge (m/z) ratios using the QMS (Extrel; QC 150) equipped with a 1.2 MHz oscillator. Ions that were allowed to pass the mass filter were accelerated by a negative 22.5 kV potential onto an aluminum-coated stainless-steel target, resulting in a cascade of secondary electrons that was directed toward an aluminumcoated scintillator. The resulting fluorescence was collected by a photomultiplier tube (PMT, Burle, model 8850) operated at a negative potential of 1.35 kV. The signal output was discriminated at 1.6 mV (Advanced Research Instruments, model F-100TD) and recorded by a multichannel scaler (MCS, SRS 430).

The data collection was coordinated by a four-slot (0.76 mm) chopper wheel rotating at 120 Hz equipped with an infrared photodiode that permits system-wide synchronization by acting as a time zero and trigger  $(T_0 = 0 \ \mu s)$  for the equipment discussed herein. The resulting 480 Hz signal was processed by an f/8 frequency divider and ultimately distributed among three Stanford Research Systems (SRS) DG535 delay/pulse generators (PDG I–III). The +4 V, 50  $\Omega$ outputs AB  $(A_{I} = T_{0} + 1883 \ \mu s, B_{I} = A_{I} + 80 \ \mu s)$  & CD  $(C_{I} =$  $A_{\rm I} - 56 \ \mu s$ ,  $D_{\rm I} = C_{\rm I} + 80 \ \mu s$ ) of PDG I were fed into a homemade pulse shaper and then amplified by a power amplifier (Physik Instrumente, E-421). These 60 Hz signals were sent to the primary and secondary pulsed valves (Proch-Trickl),<sup>67</sup> each containing a piezoelectric disc translator (Physik Instrumente, P-286.23), resulting in 80  $\mu$ s opening times using amplitudes of -400 V for this set of experiments. To permit background subtraction (i.e., laser-on minus laseroff), PDG I A (TTL, high impedance) was halved to 30 Hz and delivered to PDGs II and III for further distribution. PDG II AB  $(A_{II} = T_0 + 2048 \ \mu s; B_{II} = A_{II} + 15 \ \mu s)$  was used to trigger an excimer laser (Coherent: Compex110). PDG III output AB ( $A_{III} = T_0 + 1883 \ \mu s$ ;  $B_{III} = B_{III} + 5 \ \mu s$ ) was sent to the MCS. This synchronization scheme is compiled in Figure

The 1-propynyl radical was obtained by photodissociation of 1-bromopropyne (CH<sub>3</sub>CCBr; 1717 CheMall, 95%). The radical precursor was purified by multiple freeze–pump– thaw cycles then diluted to 0.5% in helium (99.9999%; AirGas) in a Teflon-lined sample cylinder (Swagelok). This mixture was regulated to 760 torr and fed into an ultrahighvacuum (UHV) preparation source chamber via a pulsed valve with a nozzle-skimmer distance of 19 ± 1 mm. A homemade Teflon extension with a 2 × 5 mm cutout was fitted to the pulsed valve nozzle, through which the 193 nm output (20 mJ pulse<sup>-1</sup>) was aligned and focused (1 × 3 mm<sup>2</sup>) and ultimately overlapped with the pulsed CH<sub>3</sub>CCBr/He mixture. On-axis ( $\Theta$ 



**Figure 3.** Pulse sequence for the crossed molecular beam experiment for the reaction of 1-propynyl (CH<sub>3</sub>CC; X<sup>2</sup>A<sub>1</sub>) radical with acetylene (HCCH; X<sup>1</sup> $\Sigma_g^+$ ) and acetylene- $d_2$  (DCCD; X<sup>1</sup> $\Sigma_g^+$ ).

 $= 0^{\circ}$ ) characterization of the primary beam at an electron impact energy in the ionizer of 34 eV suggests a peak velocity  $v_{\rm p}$  of 1759  $\pm$  7 m s<sup>-1</sup> and speed ratio S of 7.7  $\pm$  0.1 of the 1propynyl radical. The acetylene (AirGas; 99.6%) reactant was purified by removing acetone from the storage mixture by introducing an ethanol/dry ice bath in the path to the pulsed valve. The resulting acetylene (99.8%) was regulated to 500 torr and fed to the secondary pulsed valve. The acetylene velocity distribution carries  $v_p = 900 \pm 10 \text{ m s}^{-1}$  with  $S = 9.0 \pm 10 \text{ m}$ 0.2 resulting in a mean collision energy  $E_{\rm C}$  of 30.5  $\pm$  0.2 kJ mol<sup>-1</sup> and a center-of-mass angle  $\Theta_{CM}$  of 18.8  $\pm$  0.2°. The acetylene-d<sub>2</sub> (DCCD; CDN Isotopes, 99.8%) reactant was packaged without stabilizers and thus required no further purification. The acetylene- $d_2$  beam had a  $v_p = 890 \pm 10$  with *S* = 9.0  $\pm$  0.2. Therefore, this reaction system was characterized by an  $E_{\rm C} = 31.7 \pm 0.2$  kJ mol<sup>-1</sup> and  $\Theta_{\rm CM} = 20.0 \pm 0.2^{\circ}$ . These physical characteristics are summarized in Table 1. We note

Table 1. Peak Velocities ( $\nu_p$ ) and Speed Ratios (S) of the 1-Propynyl (CH<sub>3</sub>CC), Acetylene (HCCH), and Acetylene- $d_2$ (DCCD) Beams along with the Corresponding Collision Energies ( $E_C$ ) and Center-of-Mass Angles ( $\Theta_{CM}$ )

beam	$v_p (m s^{-1})$	S	$E_{\rm C}  (\rm kJ \; mol^{-1})$	$\Theta_{\rm CM} \; (deg)$
$CH_3CC (X^2A_1)$	$1759 \pm 7$	$7.7 \pm 0.1$		
HCCH $(X^1\Sigma_g^+)$	$900 \pm 10$	$9.0 \pm 0.2$	$30.5 \pm 0.2$	$18.8\pm0.2$
DCCD $(X^1 \Sigma_g^+)$	$890\pm10$	$9.0 \pm 0.2$	$31.7 \pm 0.2$	$20.0\pm0.2$

that it is in principle possible that propargyl (CH<sub>2</sub>CCH) may be produced during preparation of 1-propynyl by photodissociation of CH<sub>3</sub>CCBr via isomerization of the 1-propynyl radical through hydrogen shift. However, the entrance channel for the propargyl plus acetylene reaction has a barrier of 51–59 kJ mol<sup>-1</sup> (0 K),<sup>21</sup> which is nearly double the collision energies used for this set of experiments. Therefore, even if propargyl is present in the 1-propynyl reactant beam, it will not contribute to the signal obtained for reactive scattering with acetylene.

Angularly resolved time-of-flight (TOF) spectra were obtained in the plane of the reactant beams at laboratory angles  $0^{\circ} \leq \Theta \leq 69^{\circ}$  with respect to the radical beam ( $\Theta = 0^{\circ}$ ). The dynamics of the reaction are encoded in the relative

motion of the system, and so it is necessary to transform the time- and angular-dependent intensities observed in the laboratory (LAB) frame to the center-of-mass (CM) frame. This is accomplished by forward-convolution of the data constrained by the reactant beam divergences, velocity spreads, and various machine parameters.<sup>68,69</sup> This is an iterative method, whereby user-defined CM translational energy  $P(E_T)$  and angular  $T(\theta)$  flux distributions are varied until a suitable fit of the laboratory-frame TOF spectra and angular distributions are achieved. The CM functions comprise the reactive differential cross section  $I(\theta, u)$ , which is taken to be separable into its CM scattering angle  $\theta$  and CM velocity u components,  $I(u, \theta) \approx P(u) \times T(\theta)$ .

2.2. Computational Methods. Geometries of the reactants, intermediates, transition states, and products of the  $CH_3CC + HCCH$  reaction were optimized at the density functional B3LYP/6-311G(d,p) level of theory.<sup>70,71</sup> Vibrational frequencies were computed at the same theoretical level and were used for the evaluation of zero-point vibrational energy corrections (ZPE) and in calculations of rate constants. Energies were refined by single-point calculations using the explicitly correlated coupled clusters CCSD(T)-F12 method<sup>72,73</sup> with Dunning's correlation-consistent cc-pVTZ-f12 basis set.<sup>74,75</sup> The CCSD(T)-F12/cc-pVTZ-f12 approach is expected to closely approximate CCSD(T)/CBS energies, that is, the energies within the coupled clusters theory with single and double excitations with perturbative treatment of triple excitations in the complete basis set limit. The expected accuracy of the CCSD(T)-F12/cc-pVTZ-f12//B3LYP/6-311G(d,p) + ZPE(B3LYP/6-311G(d,p)) relative energies is within 4 kJ mol<sup>-1</sup> or better.<sup>76</sup> The ab initio calculations were performed using the Gaussian 0977 and Molpro 201075 program packages. Note that some of the intermediates and transition states on the  $C_5H_5$  potential energy surface (PES) considered here were investigated earlier in relation to the reaction of ethynyl radical with methylacetylene and allene." Rate constants of all pertinent unimolecular reaction steps on the C<sub>5</sub>H<sub>5</sub> PES following initial association of CH<sub>3</sub>CC with acetylene were computed using Rice-Ramsperger-Kassel-Marcus (RRKM) theory,<sup>79–81</sup> as functions of available internal energy of each intermediate or transition state, where numbers and densities of states were obtained within the harmonic approximation using B3LYP/6-311G(d,p) computed frequencies. The internal energy was taken as a sum of the collision energy and a negative of the relative energy of a species with respect to the reactants (the chemical activation energy). One energy level was considered throughout as at a zero-pressure limit. Then, RRKM rate constants were utilized to compute product branching ratios by solving first-order kinetic equations within steady-state approximation.<sup>82</sup>

#### 3. RESULTS

**3.1. Laboratory Frame.** We monitored potential products formed from the reactive scattering of the 1-propynyl radical (CH<sub>3</sub>CC; 39 amu) with acetylene (HCCH; 26 amu) along  $\Theta_{CM}$  at m/z 65 (C<sub>3</sub>H<sub>3</sub><sup>+</sup>), 64 (C<sub>3</sub>H<sub>4</sub><sup>+</sup>), and 63 (C<sub>3</sub>H<sub>3</sub><sup>+</sup>), which correspond to the formation of a persistent reaction intermediate (adduct), a hydrogen loss reaction product, and molecular hydrogen loss products, respectively. Signals were observed for each m/z value. Since the TOF spectra recorded at each m/z depict nearly identical patterns after scaling, they originate from the same channel, namely, the formation of C<sub>3</sub>H<sub>4</sub> (64 amu) formed by hydrogen atom (1 amu) loss. The

signal at m/z 65 arises from the natural distribution of carbon atom isotopes yielding  ${}^{13}CC_4H_4$  at a level of ~5.5%. Therefore, we conclude that the  $C_5H_5$  reaction adduct, if formed, does not persist for the duration of flight from the collision region to the detector of 367 ± 66  $\mu$ s. The signal at m/z 63 is due to dissociative electron impact fragmentation of the  $C_5H_4$  product on electron impact ionization (EI = 80 eV).

Following confirmation of the atomic hydrogen loss product channel, we recorded distinct TOF spectra of the nascent  $C_5H_4$  reaction product in the laboratory frame at m/z 64 in 2.5° intervals from 8.75° to 36.25° (Figure 4). Contributions



**Figure 4.** TOF spectra recorded at m/z 64 ( $C_5H_4^+$ ) for the reaction of the 1-propynyl (CH<sub>3</sub>CC; X<sup>2</sup>A<sub>1</sub>) radical with acetylene (HCCH; X<sup>1</sup> $\Sigma_g^+$ ). (O) Experimental data. (red lines) Best fits.

from nonreactive scattering off the primary beam, verified by scattering with molecular nitrogen  $(N_2)$ , were centered at 200  $\mu$ s and subsequently subtracted from the reactive TOF spectra close to the primary beam at angles from 8.75° to 16.25°. The TOFs were normalized with respect to  $\Theta_{CM}$  then integrated to yield the laboratory angular distribution (Figure 5), which comprises more than  $1.8 \times 10^6$  TOF spectra. Interference from the primary beam hindered our ability to record TOFs at  $\Theta$  < 10°, and hence the LAB angular distribution terminates at  $8.75^{\circ}$ . The distribution spans nearly  $30^{\circ}$  in the LAB frame and is symmetric around  $\Theta_{CM'}$  suggesting the presence of indirect scattering dynamics and bound C<sub>5</sub>H<sub>5</sub> intermediate(s) preceding dissociation to C5H4 plus H. The laboratory data were fit by forward convolution using a single reaction channel, namely, CH<sub>3</sub>CC (39 amu) + C<sub>2</sub>H<sub>2</sub> (26 amu)  $\rightarrow$  C<sub>5</sub>H<sub>4</sub> (64 amu) + H (1 amu) with a reaction cross section proportional



**Figure 5.** Laboratory angular distribution obtained at mass-to-charge ratio (m/z) 64  $(C_5H_4^+)$  from the reaction of the 1-propynyl (CH<sub>3</sub>CC; X<sup>2</sup>A<sub>1</sub>) radical with acetylene (HCCH; X<sup>1</sup> $\Sigma_g^+$ ).

to  $E_{\rm C}^{-(1/3)}$ . The best fits of the LAB TOFs and LAB angular distribution are depicted as red lines in Figures 4 and 5.

We also performed a second set of experiments with CH<sub>3</sub>CC (39 amu) plus DCCD (28 amu) to determine if the hydrogen loss occurs from the propynyl or from the acetylene reactant. We monitored for reactive scattering signals at m/z 65 (C<sub>5</sub>H<sub>3</sub>D<sup>+</sup>) and 66 (C<sub>5</sub>H<sub>2</sub>D<sub>2</sub><sup>+</sup>) at the CM angle of 20.0 ± 0.2° and observed a strong signal at m/z 65. A weak signal is discernible in the baseline of m/z 66, which can account for the <sup>13</sup>C signature of m/z 65 (Figure 6). Therefore the signal at



**Figure 6.** TOF data for the reaction of the 1-propynyl (CH<sub>3</sub>CC;  $X^2A_1$ ) radical with acetylene- $d_2$  (DCCD;  $X^1\Sigma_g^+$ ) at (a) m/z 65 (C<sub>5</sub>H<sub>3</sub>D<sup>+</sup>) and (b) m/z 66 (C<sub>5</sub>H<sub>2</sub>D<sub>2</sub><sup>+</sup>). (O) Experimental data. (red line) Fit obtained from the forward-convolution routine.

m/z 65 is attributed to the formation of C<sub>5</sub>H<sub>3</sub>D, while that at m/z 66 is from <sup>13</sup>CC<sub>4</sub>H<sub>3</sub>D. Hence, we conclude that only the deuterium atom loss channel is observed. Importantly, the TOF recorded at  $\Theta_{\rm CM}$  can be fit using the CM functions derived from the hydrogenated system, which suggests the products formed in each experiment are isotopologues.

**3.2.** Center-of-Mass Frame. The best-fitting CM functions are depicted in Figure 7 with hatched areas of the  $P(E_T)$  and  $T(\theta)$  functions determined within the  $1\sigma$  error



**Figure** 7. CM translational energy (a) and angular (b) flux distributions for the formation of  $C_5H_4$  plus atomic hydrogen via the reaction of the 1-propynyl (CH<sub>3</sub>CC; X<sup>2</sup>A<sub>1</sub>) radical with acetylene (HCCH; X<sup>1</sup> $\Sigma_g^+$ ). (hatched areas) Regions of acceptable fits.

limits of the LAB angular distribution. The translational energy flux distribution  $P(E_T)$  for nascent C<sub>5</sub>H<sub>4</sub> (Figure 7a) is best understood within the limits of the maximum energy  $E_{max}$ available for product translation,  $E_{max} = E_C - \Delta_r G$ . The derived  $P(E_{\rm T})$  terminates at 154 ± 18 kJ mol<sup>-1</sup> and corresponds to  $E_{\rm max}$  for this system under our experimental conditions. Accordingly, we derived a reaction energy of  $-123 \pm 18$  kJ  $mol^{-1}$  for the hydrogen loss product. The peaking of  $P(E_T)$  at 26 kJ mol<sup>-1</sup> suggests that C<sub>5</sub>H<sub>4</sub> is formed via a tight exit barrier. The distribution also has an average translation energy of  $47 \pm 6$  kJ mol<sup>-1</sup>. That only 31% of the energy following reaction is released into product translation is suggestive of an indirect reaction mechanism. Finally, the  $T(\theta)$  (Figure 7b) depicts nonzero intensity at all angles, suggesting the reaction mechanism proceeds to product formation indirectly via an activated C<sub>5</sub>H<sub>5</sub> intermediate state. The intensity at 90° could be varied significantly while maintaining a decent fit of the data; however, the best-fitting  $T(\theta)$  is forward-backward symmetric and suggests the presence of an intermediate C<sub>5</sub>H<sub>5</sub> that is relatively long-lived with respect to its rotational period.

#### 4. DISCUSSION

In discussing the reaction dynamics of  $C_5H_4$  formation, we employ electronic structure calculations to help elucidate the underlying reaction mechanism and to suggest which  $C_5H_4$  is formed. We observed reactive scattering signal at m/z 64



Figure 8. PES for the bimolecular reaction of the 1-propynyl (CH<sub>3</sub>CC;  $X^2A_1$ ) radical with acetylene (HCCH;  $X^1\Sigma_g^+$ ) leading to  $C_5H_4$  plus H products.

 $(C_5H_4^+)$ , which was determined to originate from the CH<sub>3</sub>CC  $(39 \text{ amu}) + \text{HCCH} (26 \text{ amu}) \rightarrow \text{C}_{5}\text{H}_{4}(64 \text{ amu}) + \text{H} (1 \text{ amu})$ reaction. The divergence of C<sub>5</sub>H<sub>4</sub> in the LAB frame along with its symmetry about the CM angle suggests the presence of an exoergic product channel that involves a relatively long-lived  $C_5H_5$  adduct. Reconsidered in the CM frame, the  $C_5H_4$ translational energy flux distribution  $P(E_{\rm T})$  suggests the formation of mostly excited C5H4 species, where the average translational energy is only 31% of the total available energy  $E_{\text{max}}$ . Considering the maximum kinetic energy release we determine that the detected C5H4 product is formed exoergically with a reaction energy of  $-123 \pm 18$  kJ mol<sup>-1</sup>. The CM angular flux distribution of C5H4 is forwardbackward symmetric, which further suggests the presence of bound  $C_5H_5$  intermediate(s). Since the hydrogen atom lost in product formation can originate from either of the 1-propynyl and acetylene reactants, we performed a second experiment with the acetylene- $d_2$  (DCCD) and observed only the deuterium loss product channel C<sub>5</sub>H<sub>3</sub>D indicating that, in the analogous hydrogenated reaction system, the H-atom is lost predominantly from the acetylene reactant. Furthermore, the resulting TOF spectra is well-approximated by the CM functions derived from the C5H4 plus atomic hydrogen channel, suggesting that the species produced in each experiment are isotopologues. This suggests the methyl group is a spectator in the reaction and is retained in product formation.

Our electronic structure calculations suggest at least three  $C_{S}H_{4}$  isomers are relevant for discussion of the reaction at hand. The methyldiacetylene (**p1**,  $C_{3\nu}$ ), pentatetraene (**p2**,  $D_{2d}$ ), and ethenylidenecyclopropene (**p3**,  $C_{2\nu}$ ) isomers can be formed along with the light hydrogen atom with computed reaction energies of -123, -87, and 9 kJ mol<sup>-1</sup>, respectively (Figure 8). These energies are accurate to within 4 kJ mol<sup>-1</sup>. The computed reaction energy for the formation of methyldiacetylene (**p1**) plus atomic hydrogen of  $-123 \pm 4$  is in strong agreement with our experimentally derived reaction

energy of  $-123 \pm 18$  kJ mol<sup>-1</sup>. Regarding the high-energy p2 & p3 isomers, a comparison of the experimental and computed reaction energetics is not sufficient to exclude their formation as well, since they might be masked in the low section of the center-of-mass translational energy distribution. If formed, the translational energy distributions for p2 and p3 would terminate near 118 and 22 kJ mol<sup>-1</sup>, respectively, resulting in narrow laboratory angular distributions that lie within the distribution limits of the prevailing methyldiacetylene plus hydrogen atom product channel (Figure 9).



**Figure 9.** Newton diagram for the reaction of 1-propynyl (CH<sub>3</sub>CC;  $X^2A_1$ ) plus acetylene (HCCH;  $X^1\Sigma_g^+$ ) leading to  $C_5H_4$  product isomers **p1**, **p2**, and **p3** via atomic hydrogen loss. The Newton circles have radii equal maximum CM recoil velocity of the corresponding  $C_5H_4$  isomers under the conditions of our experiment using the reaction energies determined by our computational methods.

We developed the doublet C<sub>5</sub>H<sub>5</sub> potential energy surface, connecting the 1-propynyl radical plus acetylene bimolecular entrance channel—via four intermediates  $(C_5H_5)$  and eight transition states—to atomic hydrogen loss products p1-p3 as schematized in Figure 8. The 1-propynyl radical adds with its radical center to the  $\pi$ -electrons of acetylene without an entrance barrier forming the initial collision adducts [i1] and [i1'] (CH<sub>3</sub>CCCHCH), which can easily interconvert between the *cis/trans* variations due to a low-lying isomerization barrier. Each of the isomers [i1] and [i1'] can eliminate the internal vinylic hydrogen atom to form methyldiacetylene (p1) plus atomic hydrogen via distinct transition states lying 29 kJ mol<sup>-1</sup> above the product channel. The proximity of the radical of [i1'] to the triple bond remnant of 1-propynyl makes it susceptible to cyclization via a relatively low barrier (119 kJ mol<sup>-1</sup>) to form a tricyclic radical intermediate [i3] that can eliminate a methyl hydrogen atom to access the endoergic p3 + H channel via a loose transition state with an exit barrier of 12 kJ mol<sup>-1</sup>. Besides isomerization to [i1'] or dissociation to p1 + H, intermediate [i1] can isomerize by hydrogen migration of the internal vinylic hydrogen atom to form the resonantly stabilized and global minimum isomer 1-methylbutatrienyl [i2]. Formation of [i2] is cis/trans selective and can only be accessed via [i1], where the migrating hydrogen atom is adjacent to the radical, via a  $173 \text{ kJ} \text{ mol}^{-1}$  barrier. Decomposition of [i2] by hydrogen atom elimination from the methyl group yields p2 + H, while elimination from the terminal methylene group yields p1 + H. Finally, the direct hydrogen abstraction channel may produce the nearly isoenergetic (+1 kJ mol<sup>-1</sup>) products methylacetylene CH<sub>3</sub>CCH plus ethynyl C<sub>2</sub>H, but the respective barrier is high, 42 kJ mol<sup>-1</sup>, and exceeds the collision energy in the present experiment.

On the basis of the collision energy, the pathways leading to isomers p1-p3 are, in principle, open under our experimental conditions. However, only the reaction pathways leading to methyldiacetylene are mechanistically consistent with the observed deuterium atom loss channel in our isotopic experiment (Figure 10), where the propynyl moiety is carried into the methyldiacetylene (p1) product by atomic hydrogen (deuterium) elimination from the methyl-bearing intermediates [i1], [i1'] or [i2]. Pentatetraene (p2) and ethenylidene-



**Figure 10.** Reaction schematic for the bimolecular reaction of the 1propynyl (CH<sub>3</sub>CC;  $X^2A_1$ ) radical with acetylene- $d_2$  (DCCD;  $X^1\Sigma_g^+$ ) leading to C<sub>5</sub>H<sub>3</sub>D and C<sub>5</sub>H<sub>2</sub>D<sub>2</sub> products via atomic deuterium and hydrogen loss.

cyclopropene (**p3**) can only be formed by elimination of atomic hydrogen from the methyl group of [i2] or [i3], respectively. Considering the exit transition states to form  $C_3H_4$  plus atomic hydrogen, the loss of a deuterium atom in the isotopic experiment can only be rationalized by the formation of methyldiacetylene- $d_1$  (CH<sub>3</sub>CCCCD). This also means that methyldiacetylene (CH<sub>3</sub>CCCCH) is formed in the hydrogenated system, where both reaction systems were modeled with identical CM functions. Additionally, the most probable  $E_T$  in this experiment is 26 kJ mol<sup>-1</sup>, which closely matches the exit barrier of 29 kJ mol<sup>-1</sup> for the **p1** + H product channel.

Considering the barriers to isomerization on the C<sub>5</sub>H<sub>5</sub> PES (Figure 8), the low-energy route to methyldiacetylene (p1) via intermediates [i1] and [i1'] is anticipated to be the dominant reaction pathway, with a minor contribution of pentatetraene (p2), where the barrier to  $[i1] \rightarrow [i2]$  isomerization is located 21 kJ mol<sup>-1</sup> above the  $[i1] \rightarrow p1 + H$  exit channel. The formation of the cyclic intermediate [i3] can be formed via a relatively low barrier; however, the dissociation channel to ethenylidenecyclopropene is endoergic and therefore not expected to be competitive under our experimental conditions, where the exit barrier  $(21 \text{ kJ mol}^{-1})$  is comparable to the experimental collision energy ( $E_{\rm C} = 30.5 \text{ kJ mol}^{-1}$ ). To assess to what extent isomers p2 and p3 could be formed in this experiment we calculated the statistical yields of products p1p3 using statistical (RRKM) calculations. The collision energydependent branching ratios are tabulated in Table 2 and

Table 2. Statistical Branching Ratios (%) for the Reaction of the 1-Propynyl (CH<sub>3</sub>CC) Radical with Acetylene (HCCH) at Various Collision Energies<sup>*a*</sup>

		$E_{\rm C}~({\rm kJ~mol^{-1}})$					
	0	10	20	30.5	40		
p1 total	99.89	99.86	99.82	<b>99.</b> 77	99.73		
<b>p1</b> from [i1]/[i1']	86.52	85.55	84.69	83.88	83.24		
<b>p1</b> from [i2]	13.37	14.31	15.13	15.89	16.49		
p2	0.11	0.14	0.18	0.23	0.27		
p3	0.00	0.00	0.00	0.00	0.00		
<sup>a</sup> Here <b>n1-n3</b> are	the C.H.	isomers	methyldia	cetylene	nentate.		

"Here, p1-p3 are the C<sub>5</sub>H<sub>4</sub> isomers methyldiacetylene, pentatetraene, and ethenylidenecyclopropene.

predict that methyldiacetylene constitutes greater than 99% of the total  $C_5H_4$  yield for  $E_C \leq 40$  kJ mol<sup>-1</sup>. At the experimental  $E_C$ , dissociation from intermediates [i1] & [i1'] supply ~84% of the **p1** yield, with the remaining 16% attributed to the [i2] pathway. Trace amounts (<1%) of pentatetraene (**p2**) are also predicted, whereas isomer **p3** is not expected to form in the considered energy range. Combined, our computational analysis and experimental data indicate the formation of methyldiacetylene as the primary product formed in the bimolecular reaction of 1-propynyl with acetylene.

Lastly, we compare the results of this study with those of the ethynyl ( $C_2H$ ;  $X^2\Sigma^+$ ) plus acetylene (HCCH;  $X^1\Sigma_g^+$ ) system. An early combined CMB and computational study on the substitution of  $C_2H$  with the  $C_2D$  isotopologue identified diacetylene- $d_1$  (DCCCCH) as the major reaction product, formed by hydrogen atom elimination from a low-energy DCCCHCH intermediate.<sup>47</sup> Importantly, the deuterium atom bound to the ethynyl- $d_1$  ( $C_2D$ ) reactant was not displaced throughout the reaction mechanism, resulting in the extension of acetylene by one  $C_2$  unit. This finding parallels the present

observation of the 1-propynyl plus acetylene experiment performed here and may suggest other similarities between the propynyl and ethynyl systems are to be expected in other hydrocarbon systems.

## 5. CONCLUSION

The crossed molecular beams method was exploited to explore the formation of C5H4 isomers via the reaction of the 1propynyl (CH<sub>3</sub>CC; X<sup>2</sup>A<sub>1</sub>) radical with acetylene (HCCH;  $X^{1}\Sigma_{g}$ +) under single-collision conditions. We also developed the doublet  $C_5H_5$  PES to aid in identifying the isomer(s) produced in the experiment and to develop the underlying reaction mechanism. By analyzing the experimental angularly resolved TOF spectra collected at m/z ratio 64 (C<sub>5</sub>H<sub>4</sub><sup>+</sup>) and comparing the results with our electronic structure calculations, we find that the methyldiacetylene (CH<sub>3</sub>CCCCH;  $X^{1}A_{1}$ ) plus atomic hydrogen (H;  ${}^{2}S_{1/2}$ ) is formed. A follow-up experiment of CH<sub>3</sub>CC plus acetylene- $d_2$  (DCCD) confirmed this outcome, where only the D-loss channel was observed forming  $C_5H_3D$ . Therefore, of the three  $C_5H_4$  product isomers on our PES, only methyldiacetylene (p1) can be formed by Hloss from the acetylene reactant. Additionally, our statistical analysis (RRKM) suggests the p1 + H channel represents more than 99% of the total yield at collision energies less than 40 kJ  $mol^{-1}$  ( $E_{\rm C}$  = 30.5 kJ mol<sup>-1</sup> for this experiment), where the reaction most likely proceeds via intermediate(s) [i1]/[i1'] immediately followed by dissociation to  $CH_3CCCCH(p1) +$ H. This mechanism parallels the ethynyl ( $C_2H$ ;  $X^2\Sigma^+$ ) plus HCCH system, which forms diacetylene (HCCCCH) by hydrogen displacement. The 1-propynyl methyl group remains a spectator throughout reaction and, considering all barriers are below the energy of the separated reactants, chain growth via 1-propynyl addition to (poly)acetylenes is a suitable reaction scheme for cold molecular clouds like TMC-1, where kinetic temperatures are ~10 K.

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#### Notes

The authors declare no competing financial interest.

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# **REFERENCES**

(1) Eaves, N. A.; Dworkin, S. B.; Thomson, M. J. Assessing Relative Contributions of PAHs to Soot Mass by Reversible Heterogeneous Nucleation and Condensation. *Proc. Combust. Inst.* **2017**, *36*, 935–945.

(2) Mansurov, Z. A. Soot Formation in Combustion Processes (Review). Combust., Explos. Shock Waves 2005, 41, 727.

(3) Kim, K.-H.; Jahan, S. A.; Kabir, E.; Brown, R. J. C. A Review of Airborne Polycyclic Aromatic Hydrocarbons (PAHs) and their Human Health Effects. *Environ. Int.* **2013**, *60*, 71–80.

(4) Majumdar, D.; Rajaram, B.; Meshram, S.; Chalapati Rao, C. V. PAHs in Road Dust: Ubiquity, Fate, and Summary of Available Data. *Crit. Rev. Environ. Sci. Technol.* **2012**, *42*, 1191–1232.

(5) Duley, W. W. Polycyclic Aromatic Hydrocarbons, Carbon Nanoparticles and the Diffuse Interstellar Bands. *Faraday Discuss.* **2006**, *133*, 415–425.

(6) Steglich, M.; Bouwman, J.; Huisken, F.; Henning, Th. Can Neutral and Ionized Polycyclic Aromatic Hydrocarbons Be Carriers of the Ultraviolet Extinction Bump and the Diffuse Interstellar Bands? *Astrophys. J.* **2011**, 742, 2.

(7) Steglich, M.; Jäger, C.; Rouillé, G.; Huisken, F.; Mutschke, H.; Henning, Th. Electronic Spectroscopy of Medium-sized Polycyclic Aromatic Hydrocarbons: Implications for the Carriers of the 2175 Å UV Bump. *Astrophys. J., Lett.* **2010**, *712*, L16.

(8) Allamandola, L.; Tielens, A.; Barker, J. Interstellar Polycyclic Aromatic Hydrocarbons - The Infrared Emission Bands, the Excitation/Emission Mechanism, and the Astrophysical Implications. *Astrophys. J., Suppl. Ser.* **1989**, *71*, 733–775.

(9) Ricks, A. M.; Douberly, G. E.; Duncan, M. A. The Infrared Spectrum of Protonated Naphthalene and its Relevance for the Unidentified Infrared Bands. *Astrophys. J.* **2009**, *702*, 301–306.

(10) Tielens, A. G. G. M. Interstellar Polycyclic Aromatic Hydrocarbon Molecules. *Annu. Rev. Astron. Astrophys.* 2008, 46, 289–337.

(11) Frenklach, M.; Wang, H. Detailed Modeling of Soot Particle Nucleation and Growth. *Symp. (Int.) Combust., [Proc.]* **1991**, 23, 1559–1566.

(12) Frenklach, M. Reaction Mechanism of Soot Formation in Flames. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2028–2037.

(13) Parker, D. S. N.; Kaiser, R. I.; Troy, T. P.; Ahmed, M. Hydrogen Abstraction/Acetylene Addition Revealed. *Angew. Chem., Int. Ed.* **2014**, *53*, 7740–7744.

(14) Parker, D. S. N.; Kaiser, R. I.; Bandyopadhyay, B.; Kostko, O.; Troy, T. P.; Ahmed, M. Unexpected Chemistry from the Reaction of Naphthyl and Acetylene at Combustion-Like Temperatures. *Angew. Chem.* **2015**, *127*, 5511–5514.

(15) Yang, T.; Kaiser, R. I.; Troy, T. P.; Xu, B.; Kostko, O.; Ahmed, M.; Mebel, A. M.; Zagidullin, M. V.; Azyazov, V. N. HACA's Heritage: A Free-Radical Pathway to Phenanthrene in Circumstellar Envelopes of Asymptotic Giant Branch Stars. *Angew. Chem.* **2017**, *129*, 4586–4590.

(16) Zhao, L.; Kaiser, R. I.; Xu, B.; Ablikim, U.; Ahmed, M.; Joshi, D.; Veber, G.; Fischer, F. R.; Mebel, A. M. Pyrene Synthesis in Circumstellar Envelopes and its Role in the Formation of 2D Nanostructures. *Nature Astronomy* **2018**, *2*, 413–419.

(17) Raj, A.; Prada, I. D. C.; Amer, A. A.; Chung, S. H. A Reaction Mechanism for Gasoline Surrogate Fuels for Large Polycyclic Aromatic Hydrocarbons. *Combust. Flame* **2012**, *159*, 500–515.

(18) Park, S.; Wang, Y.; Chung, S. H.; Sarathy, S. M. Compositional Effects on PAH and Soot Formation in Counterflow Diffusion Flames of Gasoline Surrogate Fuels. *Combust. Flame* **2017**, *178*, 46–60.

(19) Constantinidis, P.; Hirsch, F.; Fischer, I.; Dey, A.; Rijs, A. M. Products of the Propargyl Self-Reaction at High Temperatures Investigated by IR/UV Ion Dip Spectroscopy. *J. Phys. Chem. A* **2017**, *121*, 181–191.

(20) Jin, H.; Frassoldati, A.; Wang, Y.; Zhang, X.; Zeng, M.; Li, Y.; Qi, F.; Cuoci, A.; Faravelli, T. Kinetic Modeling Study of Benzene and PAH Formation in Laminar Methane Flames. *Combust. Flame* **2015**, *162*, 1692–1711.

(21) da Silva, G. Mystery of 1-Vinylpropargyl Formation from Acetylene Addition to the Propargyl Radical: An Open-and-Shut Case. J. Phys. Chem. A 2017, 121, 2086–2095.

(22) Savee, J. D.; Selby, T. M.; Welz, O.; Taatjes, C. A.; Osborn, D. L. Time- and Isomer-Resolved Measurements of Sequential Addition of Acetylene to the Propargyl Radical. *J. Phys. Chem. Lett.* **2015**, *6*, 4153–4158.

(23) Mebel, A. M.; Kislov, V. V. Can the  $C_5H_5 + C_5H_5 \rightarrow C_{10}H_{10} \rightarrow C_{10}H_9 + H/C_{10}H_8 + H_2$  Reaction Produce Naphthalene? An Ab Initio/RRKM Study. *J. Phys. Chem. A* **2009**, *113*, 9825–9833.

(24) Knyazev, V. D.; Popov, K. V. Kinetics of the Self Reaction of Cyclopentadienyl Radicals. J. Phys. Chem. A 2015, 119, 7418-7429.

(25) Vereecken, L.; Peeters, J.; Bettinger, H. F.; Kaiser, R. I.;
Schleyer, P. v. R.; Schaefer, H. F. Reaction of Phenyl Radicals with Propyne. J. Am. Chem. Soc. 2002, 124, 2781–2789.

(26) Parker, D. S. N.; Zhang, F.; Kim, Y. S.; Kaiser, R. I.; Landera, A.; Kislov, V. V.; Mebel, A. M.; Tielens, A. G. G. M. Low Temperature Formation of Naphthalene and its Role in the Synthesis of PAHs (Polycyclic Aromatic Hydrocarbons) in the Interstellar Medium. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 53–58.

(27) Zhao, L.; Kaiser, R. I.; Xu, B.; Ablikim, U.; Ahmed, M.; Zagidullin, M. V.; Azyazov, V. N.; Howlader, A. H.; Wnuk, S. F.; Mebel, A. M. VUV Photoionization Study of the Formation of the Simplest Polycyclic Aromatic Hydrocarbon: Naphthalene ( $C_{10}H_8$ ). J. Phys. Chem. Lett. **2018**, 9, 2620–2626.

(28) Kaiser, R. I.; Parker, D. S. N.; Zhang, F.; Landera, A.; Kislov, V. V.; Mebel, A. M. PAH Formation under Single Collision Conditions: Reaction of Phenyl Radical and 1,3-Butadiene to Form 1,4-Dihydronaphthalene. *J. Phys. Chem. A* **2012**, *116*, 4248–4258.

(29) Thomas, A. M.; Lucas, M.; Yang, T.; Kaiser, R. I.; Fuentes, L.; Belisario-Lara, D.; Mebel, A. M. A Free-Radical Pathway to Hydrogenated Phenanthrene in Molecular Clouds—Low Temperature Growth of Polycyclic Aromatic Hydrocarbons. *ChemPhysChem* **2017**, *18*, 1971–1976.

(30) Zhou, J.; Garand, E.; Eisfeld, W.; Neumark, D. M. Slow Electron Velocity-Map Imaging Spectroscopy of the 1-Propynyl Radical. *J. Chem. Phys.* **2007**, *127*, 034304.

(31) Maksyutenko, P.; Zhang, F.; Gu, X.; Kaiser, R. I. A Crossed Molecular Beam Study on the Reaction of Methylidyne Radicals [CH  $(X^2\Pi)$ ] with Acetylene [ $C_2H_2$  ( $X^1\Sigma_g^+$ )]—Competing  $C_3H_2$  + H and  $C_3H$  + H<sub>2</sub> Channels. *Phys. Chem. Chem. Phys.* **2011**, *13*, 240–252.

(32) Nguyen, T. L.; Mebel, A. M.; Kaiser, R. I. A Theoretical Investigation of the Triplet Carbon Atom  $C({}^{3}P)$  + Vinyl Radical  $C_{2}H_{3}({}^{2}A')$  Reaction and Thermochemistry of  $C_{3}H_{n}$  (n = 1–4) Species. J. Phys. Chem. A 2001, 105, 3284–3299.

(33) Geppert, W. D.; Naulin, C.; Costes, M.; Capozza, G.; Cartechini, L.; Casavecchia, P.; Gualberto Volpi, G. Combined Crossed-Beam Studies of  $C({}^{3}P_{J}) + C_{2}H_{4} \rightarrow C_{3}H_{3} + H$  Reaction Dynamics between 0.49 and 30.8 kJ mol<sup>-1</sup>. J. Chem. Phys. **2003**, 119, 10607–10617.

(34) Kaiser, R. I.; Lee, Y. T.; Suits, A. G. Crossed-Beam Reaction of Carbon Atoms with Hydrocarbon Molecules. I. Chemical Dynamics of the Propargyl Radical Formation,  $C_3H_3$  ( $X^2B_2$ ), from Reaction of  $C(^3P_j)$  with Ethylene,  $C_2H_4(X^1A_g)$ . J. Chem. Phys. **1996**, 105, 8705–8720.

(35) Chin, C.-H.; Chen, W.-K.; Huang, W.-J.; Lin, Y.-C.; Lee, S.-H. Exploring the Dynamics of Reaction  $C(^{3}P) + C_{2}H_{4}$  with Crossed Beam/Photoionization Experiments and Quantum Chemical Calculations. J. Phys. Chem. A **2012**, 116, 7615–7622.

(36) Mandal, M.; Ghosh, S.; Maiti, B. Dynamics of the  $C(^{3}P)$  + Ethylene Reaction: A Trajectory Surface Hopping Study. J. Phys. Chem. A **2018**, 122, 3556–3562.

(37) Ryazantsev, M. N.; Jamal, A.; Maeda, S.; Morokuma, K. Global Investigation of Potential Energy Surfaces for the Pyrolysis of C1-C3 Hydrocarbons: Toward the Development of Detailed Kinetic Models from First Principles. *Phys. Chem. Chem. Phys.* **2015**, *17*, 27789– 27805.

(38) Rosado-Reyes, C. M.; Manion, J. A.; Tsang, W. Kinetics of the Thermal Reaction of H Atoms with Propyne. *J. Phys. Chem. A* **2010**, *114*, 5710–5717.

(39) Harich, S.; Lin, J. J.; Lee, Y. T.; Yang, X. Photodissociation Dynamics of Propyne at 157 nm. *J. Chem. Phys.* **2000**, *112*, 6656–6665.

(40) Sun, W.; Yokoyama, K.; Robinson, J. C.; Suits, A. G.; Neumark, D. M. Discrimination of Product Isomers in the Photodissociation of Propyne and Allene at 193 nm. *J. Chem. Phys.* **1999**, *110*, 4363–4368.

(41) Ganot, Y.; Rosenwaks, S.; Bar, I. H and D Release in ~ 243.1 nm Photolysis of Vibrationally Excited  $3\nu_1$ ,  $4\nu_1$ , and  $4\nu_{CD}$  Overtones of Propyne-d<sub>3</sub>. *J. Chem. Phys.* **2004**, *120*, 8600–8607.

(42) Kirk, B. B.; Savee, J. D.; Trevitt, A. J.; Osborn, D. L.; Wilson, K. R. Molecular Weight Growth in Titan's Atmosphere: Branching Pathways for the Reaction of 1-Propynyl Radical  $(H_3CC\equiv C \cdot)$  with Small Alkenes and Alkynes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 20754–20764.

(43) Jones, B. M.; Zhang, F.; Kaiser, R. I.; Jamal, A.; Mebel, A. M.; Cordiner, M. A.; Charnley, S. B. Formation of Benzene in the Interstellar Medium. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 452– 457.

(44) Woon, D. E.; Park, J.-Y. Modeling Chemical Growth Processes in Titan's Atmosphere 2. Theoretical Study of Reactions between  $C_2H$  and Ethene, Propene, 1-Butene, 2-Butene, Isobutene, Trimethylethene, and Tetramethylethene. *Icarus* **2009**, *202*, 642–655.

(45) Mebel, A. M.; Kislov, V. V.; Kaiser, R. I. Photoinduced Mechanism of Formation and Growth of Polycyclic Aromatic Hydrocarbons in Low-Temperature Environments via Successive Ethynyl Radical Additions. *J. Am. Chem. Soc.* **2008**, *130*, 13618–13629.

(46) Landera, A.; Kaiser, R. I.; Mebel, A. M. Addition of One and Two Units of  $C_2H$  to Styrene: A Theoretical Study of the  $C_{10}H_9$  and  $C_{12}H_9$  Systems and Implications Toward Growth of Polycyclic Aromatic Hydrocarbons at Low Temperatures. *J. Chem. Phys.* 2011, 134, 024302.

(47) Kaiser, R. I.; Stahl, F.; Schleyer, P. v. R.; Schaefer, H. F., III Atomic and Molecular Hydrogen Elimination in the Crossed Beam Reaction of D1-Ethinyl Radicals  $C_2D(X^2\Sigma^+)$  with Acetylene,  $C_2H_2(X^1\Sigma_g^+)$ : Dynamics of D1-Diacetylene (HCCCCD) and D1-Butadiynyl (DCCCC) Formation. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2950–2958.

(48) Gu, X.; Kim, Y. S.; Kaiser, R. I.; Mebel, A. M.; Liang, M. C.; Yung, Y. L. Chemical Dynamics of Triacetylene Formation and Implications to the Synthesis of Polyynes in Titan's Atmosphere. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 16078–16083.

(49) Kaiser, R. I.; Chiong, C. C.; Asvany, O.; Lee, Y. T.; Stahl, F.; von R Schleyer, P.; Schaefer, H. F. Chemical Dynamics of D1-Methyldiacetylene (CH<sub>3</sub>CCCCD; X<sup>1</sup>A<sub>1</sub>) and D1-Ethynylallene (H<sub>2</sub>CCCH(C<sub>2</sub>D); X<sup>1</sup>A') Formation from Reaction of C<sub>2</sub>D(X<sup>2</sup>Σ<sup>+</sup>) with Methylacetylene, CH<sub>3</sub>CCH(X<sup>1</sup>A<sub>1</sub>). J. Chem. Phys. **2001**, 114, 3488–3496.

(50) Stahl, F.; von Ragué Schleyer, P.; Bettinger, H. F.; Kaiser, R. I.; Lee, Y. T.; Schaefer, H. F. Reaction of the Ethynyl Radical,  $C_2H$ , with Methylacetylene, CH<sub>3</sub>CCH, Under Single Collision Conditions: Implications for Astrochemistry. *J. Chem. Phys.* **2001**, *114*, 3476–3487.

(51) Lacy, J.; Evans, N. J.; Achtermann, J.; Bruce, D.; Arens, J.; Carr, J. Discovery of Interstellar Acetylene. *Astrophys. J.* **1989**, 342, L43–L46.

(52) Ridgway, S. T.; Hall, D. N. B.; Kleinmann, S. G.; Weinberger, D. A.; Wojslaw, R. S. Circumstellar Acetylene in the Infrared Spectrum of IRC +  $10^{\circ}$  216. *Nature* **1976**, 264, 345–346.

(53) Cernicharo, J.; Heras, A. M.; Tielens, A. G. G. M.; Pardo, J. R.; Herpin, F.; Guélin, M.; Waters, L. B. F. M. Infrared Space Observatory's Discovery of  $C_4H_2$ ,  $C_6H_2$ , and Benzene in CRL 618. *Astrophys. J.* **2001**, 546, L123–L126.

(54) Walmsley, C. M.; Jewell, P. R.; Snyder, L. E.; Winnewisser, G. Detection of Interstellar Methyldiacetylene ( $CH_3C_4H$ ) in the Dark Dust Cloud TMC 1. *Astron. Astrophys.* **1984**, *134*, L11–L14.

(55) MacLeod, J. M.; Avery, L. W.; Broten, N. W. The Detection of Interstellar Methyldiacetylene ( $CH_3C_4H$ ). Astrophys. J. **1984**, 282, L89–L92.

(56) Loren, R. B.; Wootten, A.; Mundy, L. G. The Detection of Interstellar Methyl-Diacetylene. *Astrophys. J.* **1984**, *286*, L23–L26.

(57) Remijan, A. J.; Hollis, J. M.; Snyder, L. E.; Jewell, P. R.; Lovas, F. J. Methyltriacetylene ( $CH_3C_6H$ ) toward TMC-1: The Largest Detected Symmetric Top. *Astrophys. J.* **2006**, 643, L37–L40.

(58) Irvine, W. M.; Hoglund, B.; Friberg, P.; Askne, J.; Ellder, J. The Increasing Chemical Complexity of the Taurus Dark Clouds: Detection of  $CH_3CCH$  and  $C_4H$ . *Astrophys. J.* **1981**, *248*, L113–L117.

(59) Kaiser, R. I.; Balucani, N.; Charkin, D. O.; Mebel, A. M. A Crossed Beam and Ab Initio Study of the  $C_2(X^1\Sigma_g^+/a^3\Pi_u) + C_2H_2(X^1\Sigma_g^+)$  Reactions. *Chem. Phys. Lett.* **2003**, 382, 112–119.

(60) Balucani, N.; Asvany, O.; Kaiser, R. I.; Osamura, Y. Formation of Three C<sub>4</sub>H<sub>3</sub>N Isomers from the Reaction of CN ( $X^{2}\Sigma^{+}$ ) with Allene, H<sub>2</sub>CCCH<sub>2</sub> (XA<sub>1</sub>), and Methylacetylene, CH<sub>3</sub>CCH (X<sup>1</sup>A<sub>1</sub>): A Combined Crossed Beam and Ab Initio Study. *J. Phys. Chem. A* **2002**, *106*, 4301–4311.

(61) Kaiser, R. I.; Mebel, A. M.; Chang, A. H. H.; Lin, S. H.; Lee, Y. T. Crossed-Beam Reaction of Carbon Atoms with Hydrocarbon Molecules. V. Chemical Dynamics of  $n-C_4H_3$  Formation from Reaction of  $C({}^{3}P_{j})$  with Allene,  $H_2CCCH_2(X {}^{1}A_1)$ . J. Chem. Phys. **1999**, 110, 10330–10344.

(62) Kaiser, R. I.; Hahndorf, I.; Huang, L. C. L.; Lee, Y. T.; Bettinger, H. F.; Schleyer, P. v. R.; Schaefer, H. F.; Schreiner, P. R. Crossed Beams Reaction of Atomic Carbon,  $C({}^{3}P_{j})$ , with D6-Benzene,  $C_{6}D_{6}(X {}^{1}A_{1g})$ : Observation of the Per-Deutero-1,2-Didehydro-Cycloheptatrienyl Radical,  $C_{7}D_{5}(X^{2}B_{2}$ . J. Chem. Phys. **1999**, 110, 6091–6094.

(63) Balucani, N.; Mebel, A. M.; Lee, Y. T.; Kaiser, R. I. A Combined Crossed Molecular Beam and ab Initio Study of the Reactions  $C_2(X^{1}\Sigma_{g}^{+}, a^{3}\Pi_{u}) + C_2H_4 \rightarrow n \cdot C_4H_3(XA') + H(^{2}S_{1/2})$ . J. Phys. Chem. A **2001**, 105, 9813–9818.

(64) Kaiser, R. I.; Maksyutenko, P.; Ennis, C.; Zhang, F.; Gu, X.; Krishtal, S. P.; Mebel, A. M.; Kostko, O.; Ahmed, M. Untangling the Chemical Evolution of Titan's Atmosphere and Surface - From Homogeneous to Heterogeneous Chemistry. *Faraday Discuss.* **2010**, *147*, 429–478.

(65) Brink, G. O. Electron Bombardment Molecular Beam Detector. *Rev. Sci. Instrum.* **1966**, *37*, 857–860.

(66) Daly, N. R. Scintillation Type Mass Spectrometer Ion Detector. *Rev. Sci. Instrum.* **1960**, 31, 264–267.

(67) Proch, D.; Trickl, T. A High-Intensity Multi-Purpose Piezoelectric Pulsed Molecular Beam Source. *Rev. Sci. Instrum.* **1989**, 60, 713–716.

(68) Weiss, P. S. The Reaction Dynamics of Electronically Excited Alkali Atoms with Simple Molecules. Ph.D. Dissertation, University of California: Berkeley, CA, 1986.

(69) Vernon, M. F. Molecular Beam Scattering. Ph.D. Dissertation, University of California: Berkeley, CA, 1983.

(70) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. J. Chem. Phys. **1993**, 98, 5648–5652.

(71) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.

(72) Adler, T. B.; Knizia, G.; Werner, H.-J. A Simple and Efficient CCSD(T)-F12 Approximation. J. Chem. Phys. 2007, 127, 221106.

(73) Knizia, G.; Adler, T. B.; Werner, H.-J. Simplified CCSD(T)-F12 Methods: Theory and Benchmarks. *J. Chem. Phys.* **2009**, *130*, 054104.

(74) Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. J. Chem. Phys. **1989**, 90, 1007–1023.

(75) Werner, H.-J.; Knowles, P.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Rauhut, G.; Amos, R.; Bernhardsson, A. *MOLPRO*, Version 2010.1, A Package of Ab Initio Programs; University of Cardiff: Cardiff, UK, 2010, see http://www.molpro.net.

(76) Zhang, J.; Valeev, E. F. Prediction of Reaction Barriers and Thermochemical Properties with Explicitly Correlated Coupled-Cluster Methods: A Basis Set Assessment. J. Chem. Theory Comput. 2012, 8, 3175–3186.

(77) Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. *Gaussian 09,* Revision A.1; Gaussian Inc.: Wallingford, CT, 2009.

(78) Jamal, A.; Mebel, A. M. An Ab Initio/RRKM Study of the Reaction Mechanism and Product Branching Ratios of the Reactions of Ethynyl Radical with Allene and Methylacetylene. *Phys. Chem. Chem. Phys.* **2010**, *12*, 2606–2618.

(79) Robinson, P. J.; Holbrook, K. A. Unimolecular Reactions; John Wiley & Sons, Ltd.: New York, NY, 1972.

- (80) Eyring, H.; Lin, S. H.; Lin, S. M. Basic Chemical Kinetics; John Wiley and Sons, Inc.: New York, NY, 1980.
- (81) Steinfield, J.; Francisco, J.; Hase, W. Chemical Kinetics and Dynamics; Prentice Hall: Englewood Cliffs, NJ, 1982.

(82) Kislov, V. V.; Nguyen, T. L.; Mebel, A. M.; Lin, S. H.; Smith, S. C. Photodissociation of Benzene under Collision-Free Conditions: An Ab Initio/Rice-Ramsperger-Kassel-Marcus Study. *J. Chem. Phys.* 2004, 120, 7008–7017.