Elucidating the Chemical Dynamics of the Elementary Reactions of the 1-Propynyl Radical (CH$_3$CC; X$^2$A$_1$) with Methylacetylene (H$_3$CCCH; X$^1$A$_1$) and Allene (H$_2$CCCH$_2$; X$^1$A$_1$)

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1. INTRODUCTION

During the last decade, the untangling of the reaction dynamics and energetics leading to the formation of distinct C$_6$H$_6$ isomers has received considerable attention from the reaction dynamics, combustion, and astrochemistry communities. Classified as the most fundamental building block of polycyclic aromatic hydrocarbons (PAHs), organic molecules composed of fused benzene rings—benzene (C$_6$H$_6$ D$_{6h}$) represents not only the simplest neutral 6π Hückel aromatic hydrocarbon molecule but also the thermodynamically most stable structure among all 216 C$_6$H$_6$ isomers (Scheme 1). Dinadayalane et al. computed the C$_6$H$_6$ potential energy surface (PES), exploiting ab initio [Møller–Plesset perturbation theory and coupled cluster single and double substitution method with a perturbative treatment of triple excitation (CCSD(T))] and hybrid density functional theory (B3LYP) calculations with the triple-ζ basis set. Mebel, Lin, and co-workers calculated the isomerization pathways between the most favorable C$_6$H$_6$ isomers and their decomposition channels using the chemically accurate G2M model chemistry approach. Scheme 1 depicts selected C$_6$H$_6$ isomers in the order of increasing relative energies with respect to benzene (0 kJ mol$^{-1}$). These isomers can be sorted into three classes: (1) monocyclic isomers with a six-membered (A) and five-membered ring (B); (2) acyclic molecules (C to J), and (3) cyclic molecules with a three-membered ring (K to M). Among these isomers, fulvene (B) was first prepared by Thiele in 1900 and represents a prototype of a class of exotic hydrocarbons formally obtained by cross-conjugating one ring and a methylidene moiety through an exocyclic carbon–carbon double bond. Several acyclic C$_6$H$_6$ isomers such as hexa-1,3-dien-5-yne (C), hexa-1,2,4,5-tetraene (G), hexa-1,2-dien-5-yne (I), and...
hexa-1,5-diyne (J) were observed in the reaction of self-recom-
bination of the propargyl radical (C3H3)29,30 and in the pyrolysis
of hexa-1,5-diyne (J).31 Isomers carrying a three-membered ring
such as 1,2,3-trimethylenecyclopropane (K), 1-methylene-2-
vinylidenecyclopropane (L), and 1-methyl-3-vinylidenecyclo-
prop-1-ene (M) are among the thermodynamically least stable
C6H6 structures and hold strong tendencies to either decyclize
or dimerize.15 Hence, these isomers have not yet been observed
in combustion flames or in the interstellar medium (ISM).32

The thermodynamically most stable isomer—benzene—has
been observed in combustion flames,2−7 in the ISM,8 and in
our solar system.33,34 The majority of the experimental and
theoretical investigations indicate that benzene (C6H6) and the
phenyl radical (C6H5) might be formed involving reactions of
resonantly stabilized free radicals including propargyl
(H2CCCH) self-combination (1),10,35 the reaction of prop-
argyl (H2CCCH) with allyl (H2CCHCH2) (2), the reaction
of acetylene (C2H2) with the n- and/or i-1,3-butadien-1-yl
radical (C4H5)5 (3), collisions of acetylene (C2H2) with the
n-1-buten-3-yn-1-yl radical (C4H3)6,36 followed by third body
stabilization (4),5,6 and the radical−radical recombination of
methyl (CH3) with cyclopentadienyl (C5H5) (5).14,37 Under
single collision conditions as provided in crossed molecular
beam experiments, benzene and phenyl are synthesized via the
barrierless, bimolecular gas-phase reactions of 1,3-butadiene
(C4H6) with ethynyl (C2H)1 and dicarbon (C2),38 respectively
(6 and 7). Fulvene, a higher energy isomer of benzene,4,7,10,39
−41 Hansen et al. pointed out that benzene
might be formed via fulvene in allene (CH 2CCH2) and
methylacetylene (CH3CCH) flames involving reactions of
propargyl (C3H3) with C2H4 molecules (8) 40−42 Fulvene is
predicted to be the major product in the reactions of C3H3 +
C3H3 (1), C3H3 + C2H4 (2), and C2H4 + CH4 (5) under
combustion conditions4,10,35,36,39 The key pathways to
benzene are suggested to involve hydrogen atom-assisted
isomerization of fulvene.4,10,18,39

\[
H_4CCCH + H_2CCCH \rightarrow C_6H_6 \\
H_4CCCH + H_2CCHCH_2 \rightarrow C_6H_6 + H + H \\
n-C_4H_5/i-C_4H_5 + C_2H_2 \rightarrow C_6H_6 + H \\
n-C_4H_5 + C_2H_2 \rightarrow C_6H_5 \\
C_4H_5 + CH_3 \rightarrow C_6H_6 + H + H \\
C_4H_5 + C_2H \rightarrow C_6H_6 + H \\
C_4H_6 + C_2 \rightarrow C_6H_5 + H \\
H_4CCCH + H_2CCHCH_2 \rightarrow C_6H_6 + H
\]

The aforementioned compilation reveals that the untangling
of the formation mechanisms of fulvene along with its isomers
under single collision conditions is still in its infancy. Here, we
access the C6H6 and C6H7 PESs via the barrierless reactions of
the 1-propynyl radical (CH3CC) with methylacetylene (CH3-
CCH) and allene (CH2CCH2). By combining the experimental
results, including selective isotopic labeling with electronic struc-
ture calculations, we provide compelling evidence that several
high-energy C6H6 isomers—among them fulvene—can be for-
med via barrierless elementary reactions under single collision
conditions excluding hydrogen-assisted isomerization pro-
cesses, thus providing an unprecedented approach of
elucidating the primary reaction products formed.

2. EXPERIMENTAL AND COMPUTATIONAL
METHODS

2.1. Experimental Methods. The reactions of 1-propynyl
(CH3CC; X 2A1) with methylacetylene (CH3CCH; X3A1),
methylacetylene-d4 (CD3CCH; X3A1), methyl-d4-acetylene
(CD3CCH; X1A1), methylacetylene-d4 (CH3CCD; X1A1), allylene (CH2CCH2; X1A1), and allene-d4 (CD2CCD; X1A1) were studied under single collision conditions, exploiting a universal crossed molecular beams machine at the University of Hawaii. In the primary source chamber, the pulsed 1-propynyl molecular beam was produced by photodissociation of 1-bromopropyne (CH2CCHBr; 1717 CHEM #90%, seeded at a level of 0.5% in helium (99.9999%; AirGas) at 193 nm (Complex110, Coherent, Inc.) at 60 Hz and 20 mJ per pulse. This gas mixture—stored in a Teflon-lined sample cylinder15—was regulated to 760 Torr and introduced into a piezoelectric pulsed valve operated at 60 Hz at pulse widths of 80 µs and peak voltages of ~400 V. The pulsed 1-propynyl beam passes through a skimmer and is velocity-selected by a four-slot chopper wheel rotating at 120 Hz. On-axis (Θ = 0°) characterization of the primary beam determines a peak velocity νp of 1759 m s⁻¹ and a speed ratio S of 8.3 (Table 1).

Table 1. Peak Velocities (νp) and Speed Ratios (S) of 1-Propynyl (CH3CCH), Methylacetylene (CH3CCH), Methyleneacetylene-d4 (CD3CCD), Methyl-d4-acetylene (CD2CCD), Methyleneacetylene-d3 (CH3CCD), and Allene-d4 (CD2CCD) Beams along with the Corresponding Collision Energies (Eс) and CM Angles (ΘCM) for Each Reactive Scattering Experiment

<table>
<thead>
<tr>
<th>beam</th>
<th>νp (m s⁻¹)</th>
<th>S</th>
<th>Eс (kJ mol⁻¹)</th>
<th>ΘCM (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2H4 (X2A1)</td>
<td>1767 ± 0.3</td>
<td>8.0 ± 0.3</td>
<td>37.1 ± 0.4</td>
<td>25.7 ± 0.3</td>
</tr>
<tr>
<td>CH3CCH (X2A1)</td>
<td>800 ± 0.3</td>
<td>12.0 ± 0.4</td>
<td>38.7 ± 0.4</td>
<td>27.5 ± 0.3</td>
</tr>
<tr>
<td>CD2CCD (X1A1)</td>
<td>790 ± 0.3</td>
<td>12.0 ± 0.4</td>
<td>38.3 ± 0.4</td>
<td>27.0 ± 0.3</td>
</tr>
<tr>
<td>CH3CCD (X1A1)</td>
<td>790 ± 0.3</td>
<td>12.0 ± 0.4</td>
<td>37.6 ± 0.4</td>
<td>26.2 ± 0.3</td>
</tr>
<tr>
<td>CH4 (X2A1)</td>
<td>800 ± 0.3</td>
<td>12.0 ± 0.4</td>
<td>36.4 ± 0.3</td>
<td>25.9 ± 0.3</td>
</tr>
<tr>
<td>CH2CCH2 (X1A1)</td>
<td>1750 ± 8</td>
<td>8.6 ± 0.4</td>
<td>37.3 ± 0.3</td>
<td>27.3 ± 0.3</td>
</tr>
<tr>
<td>CD2CCD2 (X1A1)</td>
<td>790 ± 0.3</td>
<td>12.0 ± 0.4</td>
<td>37.3 ± 0.3</td>
<td>27.3 ± 0.3</td>
</tr>
</tbody>
</table>

The primary beam crosses perpendicularly the secondary supersonic beam of the hydrocarbon reactant generated in the secondary source chamber. In each reaction system, the hydrocarbon backing pressure was regulated to 550 Torr and fed into the secondary pulsed valve operated at a repetition rate of 60 Hz, a pulse width of 80 µs, and a peak voltage of ~400 V. The methylacetylene and allene velocity distributions were determined to be νp = 800 ± 10 m s⁻¹ with S = 12.0 ± 0.4 resulting in nominal collision energies Eс of 37.1 ± 0.4 and 36.4 ± 0.3 kJ mol⁻¹ and center-of-mass (CM) angles ΘCM of 25.7 ± 0.3° and 25.9 ± 0.3°, respectively. The peak velocities and speed ratios along with the collision energies and CM angles for methylacetylene, methylacetylene-d4, methylacetylene-d3, methylacetylene-d4-2, methylacetylene-d2, allylene, and allene-d4 are summarized in Table 1.

The machine operates a triply differentially pumped detector rotatable in the plane defined by both sources; this detector comprises a Brink-type ionizer, a quadrupole mass spectrometer (QMS), and a Daly-type ion counter.65 The neutral products formed in the reactive scattering process enter the detector and are ionized through electron impact at an electron energy of 40 eV, at a current of 1.4 mA, and an ion flight constant of 4.25 µs amu⁻¹/² and then filtered according to mass-to-charge (m/z) ratios using the QMS (Extrel; QC 150) equipped with a 2.1 MHz oscillator. The ions are then accelerated by a negative 22.5 kV potential onto an aluminum-coated stainless steel target, thus generating a cascade of secondary electrons that is directed toward an aluminum-coated scintillator. The resulting signal is collected by a photomultiplier tube (Burle, model 8850) operated at a negative potential of 1.35 kV. The signal output is discriminated at 1.6 mV (Advanced Research Instruments, model F-100TD) and recorded by a multichannel scaler (SRS 430).

Time-of-flight (TOF) spectra were recorded at laboratory (LAB) angles in the range of 0° ≤ Θ ≤ 69° with respect to the 1-propynyl radical beam (Θ = 0°). The TOF spectra were then integrated and normalized to obtain the product angular distribution in the LAB frame. To obtain information on the reaction dynamics, a forward convolution method is used to transform the LAB data into the CM frame.47–50 This represents an iterative method, whereby the user-defined CM translational energy P(Eф) and angular T(Θ) flux distributions are varied until a suitable fit of the LAB frame TOF spectra and angular distributions are achieved. The CM functions comprise the reactive differential cross-section I(Θ,u), which is taken to be separable into its CM scattering angle Θ and CM velocity u components, I(Θ,u) ≈ P(u) × T(Θ). The differential cross-section is plotted as a flux contour map that serves as an image of the reaction. Errors of the P(Eф) and T(Θ) functions are determined within the 1σ error limits of the accompanying LAB angular distribution while maintaining a good fit of the LAB TOF spectra.

2.2. Computational Methods. Geometry optimization for the reactants, intermediates, transition states, and products on the C6H12-PES pertinent to the reactions of 1-propynyl radical with allene and methylacetylene were carried out on the density functional B3LYP level of theory,51,52 with the 6-311G(d,p) basis set. Vibrational frequencies were computed on the same B3LYP/6-311G(d,p) level and were used for the evaluation of zero-point vibrational energy (ZPE) corrections and in calculations of rate constants. Single-point energies for all stationary structures were refined by single-point calculations using the explicitly correlated coupled clusters CCSD(T)-F12 method53,54 with Dunning’s correlation-consistent cc-pVTZ-F12 basis set.55 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⁻¹ or better.56 The B3LYP and CCSD(T)-F12 calculations were performed using the GAUSSIAN 0957 and MOLPRO 201058 program packages, respectively. Energy-dependent rate constants of all unimolecular reaction steps on the C6H12-PES following initial association of the 1-propynyl radical with the C6H4 isomers were computed using the Rice–Ramsperger–Kassel–Marcus (RRKM) theory.59–61 The available internal energy was taken as a sum of the collision energy and the chemical activation energy, that is, negative of the relative energy of a species with respect to the reactants. One energy level was considered throughout as a zero-pressure limit corresponding to crossed molecular beam conditions. The numbers and densities of states were computed within the harmonic approximation using the B3LYP/6-311G(d,p) frequencies. Product branching ratios were evaluated by solving first-order kinetic equations within steady-state approximation utilizing the RRKM rate constants for individual reaction steps. Rate constants for barrierless hydrogen atom
eliminations in the unimolecular decomposition of fulvene were computed using variational transitional-state theory.\textsuperscript{62} The RRKM and branching ratio calculations were carried out using a newly developed in-house code, which processes an output of GAUSSIAN 09 frequency calculations to carry out the direct count of the number of states for transition states and the density of states for local minima.

3. RESULTS

3.1. LAB Frame. For both the reactions of the 1-propynyl radical (CH\textsubscript{3}CC; 39 amu) with methylacetylene (CH\textsubscript{2}CCH\textsubscript{2}; 40 amu) and allene (CH\textsubscript{2}CCH\textsubscript{2}; 40 amu), the reactive scattering signal was observed at mass-to-charge ratios (m/z) of 79 (\textsuperscript{13}C\textsubscript{6}H\textsubscript{5}+, 78 (C\textsubscript{6}H\textsubscript{6}+), and 77 (C\textsubscript{6}H\textsubscript{7}+ formally connected to the adduct, the hydrogen loss reaction product, and the molecular hydrogen loss product, respectively. The TOF spectra recorded at these mass-to-charge ratios exhibited identical patterns after scaling with the signal at m/z = 79 collected at a level of about 7% of m/z = 78. These findings suggest that the signals at m/z = 78 and 77 originate from the same reaction channel forming the heavy product (C\textsubscript{6}H\textsubscript{6}; 78 amu) along with atomic hydrogen (H; 1 amu); the signal at m/z = 77 can be attributed to dissociative electron impact ionization of the C\textsubscript{6}H\textsubscript{6} product in the electron impact ionizer, whereas the ion counts at m/z = 79 can be correlated with the \textsuperscript{13}C-substituted C\textsubscript{6}H\textsubscript{6} product arising from the natural distribution of carbon atom isotopes. Therefore, having evidenced the hydrogen atom loss channel, the TOF spectra of the nascent C\textsubscript{6}H\textsubscript{6} reaction product were collected at the best signal-to-noise ratio at m/z = 78 at distinct LAB angles from 15.25° to 45.25° in 2.5° intervals with up to 1.3 × 10\textsuperscript{6} TOFs per angle (Figure 1); note that the signal at m/z = 77 was detected at a level of typically 128% compared to m/z = 78. Contributions from the nonreactive scattering of the primary beam, verified by scattering with argon, were subsequently subtracted from the TOF spectra close to the primary beam. The resulting TOFs were then normalized with respect to the CM angle (\(\Theta_{CM}\)) to obtain the LAB angular distribution (LAD; Figure 2). Considering the interference from the primary beam, the lowest angle of the LAD can just reach 15.25°. The LAD distributions for both systems span nearly 30° within the scattering plane and are symmetric around \(\Theta_{CM}\). This result suggests indirect scattering dynamics and bound C\textsubscript{6}H\textsubscript{6} reaction intermediate(s) dissociating to C\textsubscript{6}H\textsubscript{6} plus atomic hydrogen.

In order to elucidate the detailed position(s) of the atomic hydrogen loss(es), the reactions of 1-propynyl radical (CH\textsubscript{3}CC; 39 amu) with (partially) deuterated methylacetylene and allene were performed as well. Isotopic substitution experiments present an ideal tool to extract the hydrogen atom loss position(s).\textsuperscript{63} First, these studies focused on the atomic hydrogen and deuterium loss channels of the 1-propynyl radical (CH\textsubscript{3}CC; 39 amu) with methylacetylene-d\textsubscript{1} (CD\textsubscript{2}CCH; X\textsubscript{A1}+; 44 amu), methyl-d\textsubscript{1}-acetylene (CD\textsubscript{3}CCH; X\textsubscript{A1}+; 43 amu), and methylacetylene-d\textsubscript{1} (CD\textsubscript{2}CCH; X\textsubscript{A1}+; 41 amu). For the 1-propynyl radical (CH\textsubscript{3}CC; 39 amu)—methylacetylene-d\textsubscript{1} (CD\textsubscript{2}CCH) system (reactions 9 and 10), TOFs recorded at m/z = 82 (C\textsubscript{6}H\textsubscript{6}D\textsubscript{4}+) (9) and m/z = 81 (C\textsubscript{6}H\textsubscript{6}D\textsubscript{3}+) (10) at the CM angle of 26.8° suggest no signal at m/z = 82 (Figure 3a); ion counts were only observed at m/z = 81. Consequently, the signal at m/z = 81 is attributed to the formation of C\textsubscript{6}H\textsubscript{6}D\textsubscript{1} resulting from an exclusive deuterium atom loss channel. Therefore, no atomic hydrogen was emitted from the methyl moiety of the 1-propynyl radical (CH\textsubscript{3}CC).

\[
\begin{align*}
\text{H}_3\text{CCC} \text{ (39 amu) } + & \text{ D}_2\text{CCCD} \text{ (44 amu) } \\
\rightarrow & \text{ C}_6\text{H}_6\text{D}_4 \text{ (82 amu) } + \text{ H} \text{ (1 amu) } & (9) \\
\text{H}_3\text{CCC} \text{ (39 amu) } + & \text{ D}_3\text{CCCD} \text{ (44 amu) } \\
\rightarrow & \text{ C}_6\text{H}_6\text{D}_3 \text{ (81 amu) } + \text{ D} \text{ (2 amu) } & (10)
\end{align*}
\]

To further pinpoint the position of the deuterium loss from the methylacetylene reactant—methyl or ethynyl group—data were collected in the 1-propynyl (CH\textsubscript{3}CC; 39 amu)—methyl-d\textsubscript{1}-acetylene (CD\textsubscript{3}CCH; 43 amu) system at m/z = 81 (C\textsubscript{6}H\textsubscript{6}D\textsubscript{4}+) (11) and m/z = 80 (C\textsubscript{6}H\textsubscript{6}D\textsubscript{3}+) (12) for potential hydrogen and/or deuterium atom losses from the acetylenic hydrogen and/or the methyl-d\textsubscript{1} group at methylacetylene. A signal was observed at m/z = 81 (C\textsubscript{6}H\textsubscript{6}D\textsubscript{4}+) and m/z = 80 (C\textsubscript{6}H\textsubscript{6}D\textsubscript{3}+). Therefore, the signal at m/z = 81 suggests the existence of a hydrogen atom replacement (reaction 11); since the aforementioned data reveal that no atomic hydrogen was lost from the methyl group, for the 1-propynyl (CH\textsubscript{3}CC)—methyl-d\textsubscript{1}-acetylene (CD\textsubscript{3}CCH) system, the hydrogen atom can only be emitted from the ethynyl (C\textsubscript{2}H\textsubscript{2}) moiety.

\[
\begin{align*}
\text{H}_3\text{CCC} \text{ (39 amu) } + & \text{ D}_2\text{CCCD} \text{ (43 amu) } \\
\rightarrow & \text{ C}_6\text{H}_6\text{D}_3 \text{ (81 amu) } + \text{ H} \text{ (1 amu) } & (11)
\end{align*}
\]
Further, a set of data was collected for the reaction of the 1-propynyl radical (CH$_3$CC; 39 amu) with methylacetylene-$d_1$ (CH$_3$CCD; 41 amu) to probe the hydrogen and/or deuterium losses (Figure 3c). Ion counts were observable at $m/z = 79$ (C$_6$DH$_5^+$) (reaction 13) and $m/z = 78$ (C$_6$H$_6^+$) (reaction 14). The data at $m/z = 79$ suggest that the hydrogen atom is lost from the methyl group of the methylacetylene reactant. Note that ion counts at $m/z = 78$ can also arise from dissociative electron impact ionization of the product C$_6$DH$_5$ formed via reaction 13. Therefore, the results from the 1-propynyl radical (CH$_3$CC)—methylacetylene-$d_1$ (CH$_3$CCD) system demonstrate the existence of a second hydrogen loss channel—besides reaction 9—from the methyl group (reaction 13). Accounting for the $^{13}$C isotopic contributions totaling to 6.6% for six carbon atoms and integrating the ion counts, the branching ratio of the hydrogen atom loss from the ethynyl group versus the methyl group of the methylacetylene reactant is determined to be $9.4 \pm 0.1$.

Finally, the reaction of the 1-propynyl radical (CH$_3$CC; 39 amu) with allene-$d_4$ (D$_2$CCCD$_2$; 44 amu) gauged to what extent the hydrogen loss occurs from the propynyl and/or from the allene reactant. We probed the reactive scattering signals at $m/z = 82$ (C$_6$H$_2$D$_4^+$) (reaction 15) and $m/z = 81$ (C$_6$H$_3$D$_3^+$) (reaction 16) and observed a strong signal at both the mass-to-charge ratios. This suggests that at least the atomic hydrogen loss is open (reaction 15); once again, the signal at $m/z = 81$ could also arise from dissociative electron impact ionization of the neutral C$_6$H$_2$D$_4$ product, so it is difficult to experimentally pin down the contribution of reaction 16. Because of the associated costs of the (partially) deuterated chemicals, data were only collected at the CM angles.

In summary, the isotopic experiments reveal that for the 1-propynyl (CH$_3$CC)−methylacetylene (CH$_3$CCH) system, the hydrogen loss originates solely from methylacetylene with branching ratios of the ethynyl versus methyl group of 9.4 ± 0.1. However, for the reactions of the 1-propynyl radical (CH$_3$CC) with allene (CH$_2$CCH$_2$), the hydrogen loss originates at least from the 1-propynyl radical.

### 3.2. CM Frame

In both the reactions of the 1-propynyl radical (CH$_3$CC; 39 amu) with methylacetylene (CH$_3$CCH; 40 amu) and allene (CH$_2$CCH$_2$; 40 amu), TOFs and LAD angular distribution can be fit using a single reaction channel with the products of the generic formula C$_6$H$_6$ and atomic hydrogen. The best-fitting CM functions are shown in
Additional information on the reaction dynamics can be obtained by inspecting the CM angular distribution $T(\theta)$. For the reaction of the 1-propynyl radical ($\text{CH}_3\text{CC};$ 39 amu) with methylacetylene ($\text{CH}_3\text{CCH};$ 40 amu), the CM angular distribution $T(\theta)$ (Figure 4a) displays nonzero intensity over all angular range, suggesting that the product was formed via indirect scattering dynamics via activated $\text{C}_6\text{H}_7$ complex(es). Second, the forward-backward symmetry of $T(\theta)$ suggests the lifetime of the intermediate being longer than its rotational period. For the reaction of the 1-propynyl radical ($\text{CH}_3\text{CC}$) with allene ($\text{CH}_2\text{CCH}_2$), the CM angular distribution $T(\theta)$ (Figure 4b) displays similar features compared to the reaction of the 1-propynyl radical ($\text{CH}_3\text{CC}$) with methylacetylene ($\text{CH}_3\text{CCH};$ 40 amu). $T(\theta)$, with a nonzero intensity at all angles and forward-backward symmetry, indicates that the product was formed via a relatively long-lived activated $\text{C}_6\text{H}_7$ complex via indirect scattering dynamics as well.

4. DISCUSSION

In the case of polyatomic systems such as the reactions of the 1-propynyl radical with methylacetylene (Figures 5–9; Tables 2 and 3) and allene (Figures 10–13; Tables 4 and 5), it is beneficial to combine experimental data with the electronic structure and statistical calculations to elucidate the underlying reaction mechanism(s).

4.1. 1-Propynyl–Methylacetylene System. For the 1-propynyl–methylacetylene system, the electronic structure calculations identified five exit channels ($p_1$–$p_5$) leading via indirect scattering dynamics through multiple $\text{C}_6\text{H}_7$ intermediates ($i_1$–$i_7$) through atomic hydrogen loss ($p_1$–$p_3$, $p_5$) and methyl radical elimination ($p_4$) to distinct $\text{C}_6\text{H}_4$ and $\text{C}_4\text{H}_4$ isomers (Figure 5). With the exception of $p_5$ (+2 kJ mol$^{-1}$), the reactions are overall exoergic by 276–98 kJ mol$^{-1}$. A comparison of the computed reaction energies for the atomic hydrogen loss with the experimentally determined reaction energy of $-122 \pm 19$ kJ mol$^{-1}$ suggests the formation of at least the dimethyldiacetylene ($\text{CH}_3\text{CCCCH}_3$) isomer along with atomic hydrogen ($p_1$). On the basis of the reaction energies leading to $p_2$ and $p_5$, these isomers might be masked by the low energy tail of the CM translational energy distribution. How can the dimethyldiacetylene molecule be formed? Our calculations revealed four barrier-less entrance channels dictated by the addition of the 1-propynyl radical ($\text{CH}_3\text{CC}$) with its radical center to the carbon–carbon triple bond at C1 and/or C2 of methylacetylene leading to the cis/trans doublet radical intermediates $[i_1]/[i_2]$ and $[i_3]/[i_4]$, respectively. Considering the destabilizing steric interaction with the methyl group, $[i_3]$ and $[i_4]$ are less stable by 14 kJ mol$^{-1}$ compared to $[i_1]$ and $[i_2]$. Each cis/trans isomer pair can be converted by a low barrier of only 18–25 kJ mol$^{-1}$. The cyclic intermediate $[i_5]$ interconverts $[i_1]$ and $[i_3]$ through the migration of the 1-propynyl group; $[i_5]$ can lose a hydrogen atom forming the 1-methyltriulfene isomer ($p_5$). Intermediates $[i_6]$ and $[i_7]$ are the results of hydrogen migrations in $[i_1]$ and $[i_2]$ from the former ethynyl or methyl moieties of the methylacetylene reactant; these hydrogen shifts have significant barriers between 117 and 184 kJ mol$^{-1}$. Most importantly, intermediates $[i_1]$ and $[i_2]$ can undergo unimolecular decomposition via atomic hydrogen loss via tight exit transition states located 24 and 11–12 kJ mol$^{-1}$ above the energy of the separated products $p_1$ and $p_2$, respectively. Therefore, based on the experimentally derived energetics along with the electronic structure calculations, we can reveal that the...
1-ethynyl radical adds with its radical center without entrance barrier to the sterically more accessible C1 atom of methylacetylene forming [i1] and/or [i2], which can interconvert easily. Hereafter, these initial collision complexes can lose a hydrogen atom via tight exit transition state(s) forming at least the dimethyldiacetylene (CH₃CCCCCH₃) isomer (p1). The indirect scattering dynamics via long-lived C₆H₇ reaction intermediate(s) and the tight nature of at least one exit transition state are also verified by the CM functions (Section 3.2), with the CM translational energy distribution peaking at around 23 kJ mol⁻¹. It should be noted that because of the mismatch of the computed (−276 kJ mol⁻¹) and experimentally derived reaction energies (−122 ± 19 kJ mol⁻¹), the fulvene (p4) isomer is not formed. This pathway would require the involvement of the intermediate [i7] along with multiple isomerization processes (Section 4.2).

Having identified the dimethyldiacetylene (CH₃CCCCCH₃) isomer (p1) as at least one reaction product, we are attempting to reconcile the results of the isotopic substitution experiments (Section 3.1) with the aforementioned findings that (a)
hydrogen atom is emitted from the methylacetylene reactant and not from the methyl group of the 1-propynyl reactant and (b) two distinct C₆H₆ isomers are formed via hydrogen atom loss from the ethynyl and methyl groups of the methylacetylene reactant with a branching ratio of 9.4 ± 0.1. Figures 6–8 trace the position of the deuterium atoms incorporated in the methylacetylene reactants. Most important, the sole detection of the deuterium atom loss channel in the 1-propynyl–methylacetylene-d₄ system provides clear evidence that neither the p₄ nor the p₅ isomer is formed because their pathways are solely connected with the loss of atomic hydrogen but not deuterium (Figure 6). On the other hand, the formation of p₁ and p₂ can fully account for the deuterium loss pathway. With the exclusion of p₄ and p₅, the 1-propynyl–methylacetylene-d₃ system (Figure 7) provides conclusive evidence that p₁—dimethylacetylene (CH₃CCCHCH₃)—is formed. Tagging the deuterium atoms reveals that in principle, p₄, p₁, and p₅ can account for atomic hydrogen loss; since p₄ and p₅ were already excluded (Figure 6), only p₁ remains as a possible product of the hydrogen atom loss; this labeling experiment verifies the aforementioned identification of the dimethylacetylene isomer. Finally, the 1-propynyl–methylacetylene-d₁ system (Figure 8) helps to identify a second channel. Here, p₂, p₃, and p₅ would correlate with an atomic hydrogen loss; however, since p₄ and p₅ were already excluded (Figure 6), only p₂ remains as a possible product of the hydrogen atom loss, revealing that propynallene (H₃CCCHCCCH) is formed via decomposition of [i₁] and/or [i₂]. These pathways are compiled in Figure 9.

To further test our findings, statistical RRKM calculations were conducted to predict the branching ratios of the products, assuming that a complete energy randomization in the reaction intermediate takes place (Tables 2 and 3). The initial approach discriminates the attack of the 1-propynyl radical at the C₁ (Table 2) and C₂ carbon atoms of methylacetylene (Table 3). For the atomic hydrogen loss, at our collision energy of 37.1 kJ mol⁻¹, the statistical calculations predict a predominant formation of p₁ and p₂ with a branching ratio of 8.0 ± 0.2/1.0;
here, the uncertainty in the branching ratios was evaluated by varying the energies of critical transition states by ±4 kJ mol\(^{-1}\)—the expected uncertainty in relative energies. This branching ratio agrees very well with our experimentally determined result of 9.4 ± 0.1 if the 1-propynyl radical only attacks the C1 carbon atom of the methylacetylene reactant. This ratio only slightly varies with the collision energy from 11.1 to 7.7 when the collision energy increases from 0 to 41.8 kJ mol\(^{-1}\). An attack at the C2 carbon atom would also result in a branching ratio of \(p_1\) versus \(p_2\) of 9.0 ± 0.2/1.0. However, the methyl loss channel—which was unobserved experimentally with upper limits of 15%—should dominate the scattering dynamics if the 1-propynyl radical adds to the C2 carbon atom. Therefore, the mismatch between the predicted methyl versus atomic hydrogen for the C2 attack and the agreement with the branching ratio for the hydrogen loss and lack of methyl elimination pathway would support an initial addition of the 1-propynyl radical to the C1-atom of methylacetylene—the sterically preferred addition site.

In summary, the reaction dynamics of the 1-propynyl—methylacetylene system are dictated by an initial barrierless addition of the 1-propynyl radical with its radical center to the sterically more accessible C1 carbon atom of the methylacetylene reactant leading via indirect scattering dynamics to intermediate(s) [i1] and/or [i2]. These intermediates are likely to interconvert to each other, considering the low barrier of only 25 kJ mol\(^{-1}\). Upon unimolecular decomposition of these collision complexes via tight exit transition states, both dimethyldiacetylene (i1) (CH\(_3\)CCCD; X\(^1\)A\(_1\)) and 1-propynyllallene (p2) (H\(_2\)CCHCCH-CCH) are formed in overall exoergic reactions with an experimental branching ratio of 9.4 ± 0.1 compared to 8.0 ± 0.2/1.0, as predicted by RRKM calculations. The formation of these isomers requires the energy to “flow” from the initially formed carbon—carbon single bond over one and three bonds to form the final \(p_1\) and \(p_2\) products, respectively. It shall be noted that the experimental branching ratio was derived based on partially deuterated systems, whereas the RRKM studies exploited fully hydrogenated reactants; this might explain the slight quantitative disagreement.

4.2. 1-Propynyl—Allene System. Considering the 1-propynyl—allene system, the electronic structure calculations reveal the possible existence of 11 channels (p1–p11) leading via indirect scattering dynamics through multiple C\(_6\)H\(_7\) intermediates (i1–i23) to atomic hydrogen loss (p1–p5 and p9–p10) and elimination of heavy fragments [methyl CH\(_3\) (p6); vinyl C\(_2\)H\(_3\) (p7); and acetylene C\(_2\)H\(_2\) (p8 and p11)] in overall exoergic reactions (−406 to −12 kJ mol\(^{-1}\)) (Figures 10–13, Tables 4 and 5). Once again, a comparison of the computationally predicted reaction energies for the atomic hydrogen loss channel with the experimentally determined reaction energy of −269 ± 19 kJ mol\(^{-1}\) correlates well with the formation of at least the formation of the fulvene isomer (p4) (−280 kJ mol\(^{-1}\)). Fits attempting the inclusion of the thermodynamically more favorable benzene (p5) channel yield TOF spectra too fast and a LAD distribution too broad. On the other hand, fits accounting for the formation of 1-propynyllallene (p2) yield simulated TOFs being too slow and a LAB angular distribution too narrow. However, based on energetical constraints alone, the isomers \(p1–p3\) and \(p10\) might been hidden within the low-energy section of the CM translational energy distribution. Can the results from the 1-propynyl—allene-\(_d_4\) system eliminate any pathways? Recall that at least the atomic hydrogen elimination from the methyl group of the 1-propynyl was observed. This can account for the formation of \(p3\), \(p4\), \(p5\), and \(p10\) (Figures 11 and 12). Recall that the assumption of a benzene (p5) channel cannot fit the experimental data since the fits resulted in TOF spectra being too fast and a LAD distribution too broad. Therefore, the data of the isotopic experiment along with the energetics of the reaction propose that at least fulvene (p4) and possibly \(p3\) and/or \(p10\) are formed as well with both higher energy isomers masked in the low-energy section of the CM translational energy distribution.

On the basis of our electronic structure calculations, the 1-propynyl radical may add to the terminal or the central carbon atom of allene, forming intermediates [i1]/[i2] and [i3], respectively, without barrier to addition. Considering the barrierless nature of the reaction, large impact parameters should dominate, and hence the 1-propynyl radical should add preferentially to one of the terminal carbon atoms of allene. This position of addition is also favored by the electrophilic 1-propynyl radical because it preferentially adds to the carbon atom of the allene molecule with the highest electron density (C1/C3: −0.46;
Figure 9. Reaction schematic for the reaction of 1-propynyl (CH$_3$CC; X$^2$A$_1$) with (a) methylacetylene-d$_4$ (CD$_3$CCD), (b) methyl-d$_3$-acetylene (CD$_3$CCH), and (c) methylacetylene-d$_1$ (CH$_3$CCD), leading to D- and H-loss products.

Table 2. Statistical Branching Ratios (%) from Intermediate i$_1$ for the Reaction of the 1-Propynyl (CH$_3$CC) Radical with Methylacetylene (H$_3$CCCH) at Various Collision Energies$^a$

<table>
<thead>
<tr>
<th>$E_c$ (kJ mol$^{-1}$)</th>
<th>0</th>
<th>12.6</th>
<th>25.1</th>
<th>37.1</th>
<th>41.8</th>
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<tr>
<td>p1</td>
<td>80.1</td>
<td>81.6</td>
<td>82.5</td>
<td>82.9</td>
<td>82.9</td>
</tr>
<tr>
<td>p2</td>
<td>7.2</td>
<td>8.3</td>
<td>9.4</td>
<td>10.3</td>
<td>10.7</td>
</tr>
<tr>
<td>p3</td>
<td>12.5</td>
<td>9.8</td>
<td>7.8</td>
<td>6.5</td>
<td>6.1</td>
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<tr>
<td>p4</td>
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<td>0.3</td>
<td>0.3</td>
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<tr>
<td>p5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$^a$Here, p1–p5 are dimethyldiacetylene, hexa-1,2-dien-4-yne, methylacetylene, fulvene, and 1-methyl-3-vinylidencycloprop-1-ene.

Table 3. Statistical Branching Ratios (%) from Intermediate i$_3$ for the Reaction of the 1-Propynyl (CH$_3$CC) Radical with Methylacetylene (H$_3$CCCH) at Various Collision Energies$^a$

<table>
<thead>
<tr>
<th>$E_c$ (kJ mol$^{-1}$)</th>
<th>0</th>
<th>12.6</th>
<th>25.1</th>
<th>37.1</th>
<th>41.8</th>
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<tbody>
<tr>
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<td>3.3</td>
<td>2.7</td>
<td>2.5</td>
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<tr>
<td>p2</td>
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<td>0.3</td>
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<tr>
<td>p3</td>
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<td>95.3</td>
<td>96.3</td>
<td>96.9</td>
<td>97.2</td>
</tr>
<tr>
<td>p4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>p5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$^a$Here, p1–p5 are dimethyldiacetylene, hexa-1,2-dien-4-yne, methylacetylene, fulvene, and 1-methyl-3-vinylidencycloprop-1-ene.
Figure 10. PES for the bimolecular reaction of the 1-propynyl (CH$_3$CC; X$^2$A$_1$) radical with allene (CH$_2$CCH$_2$; X$^1$A$_1$).

Figure 11. PES for the bimolecular reaction of the 1-propynyl (CH$_3$CC; X$^2$A$_1$) radical with allene-$_d_4$ (CD$_2$CCD$_2$; X$^1$A$_1$).
As a matter of fact, reactions of allene with isolobal ethynyl (C₂H) radical and cyano (CN) radical studied under single collision conditions in our laboratory revealed that the doublet radical reactant solely added to the terminal C₁/C₃ carbon atoms of allene. Therefore, we might expect an (almost) exclusive addition of the 1-propynyl radical to the terminal C₁/C₃ atoms of allene leading to \([i₁]/[i₂]\). It should be noted though that the addition of the 1-propynyl radical to the C₂ carbon would produce a resonantly stabilized radical \([i₃]\), which is 105 kJ mol\(^{-1}\) lower in energy than \([i₁]/[i₂]\). The intermediates \([i₃]\) and \([i₁]/[i₂]\) can interconvert relatively easily via barriers, which are lower than those for any of their decomposition channels. With respect to the formation of fulvene, we are focusing now on the 1-propynyl–allene-\(d₄\) system and the experimentally verified atomic hydrogen loss (Figures 11 and 12). Note that two distinct fulvene isotopologues can be formed via atomic hydrogen (from \([i₉]\)) and deuterium loss (from \([i₁₁]\) and \([i₂₀]\)). The reaction pathways leading solely to fulvene-\(d₄\) are compiled in Figure 12. Here, two key reaction pathways can be identified. From the initial adduct \([i₁]\), the “low barrier” six-step reaction sequence \([i₁] → [i₅] → [i₆] → [i₇] → [i₈] → [i₉] → \text{fulvene} + \text{hydrogen}\) involves three hydrogen shifts, cis–trans isomerization, and cyclization with inherent barriers ranging lower than 70 kJ mol\(^{-1}\) with respect to the separated reactants. Note that \([i₁]\) can also isomerize to \([i₂]\) prior to a hydrogen shift leading to \([i₅]\). A second “high barrier” eight-step pathway involves the sequence \([i₁] → [i₂] → [i₂₄] → [i₂₅] → [i₂₆] → [i₂₇] → [i₂₈] → \text{fulvene} + \text{hydrogen}\) with a rate-limiting transition state \([i₂] → [i₂₄]\) located 36 kJ mol\(^{-1}\) below with respect to the separated reactants; note that \([i₁]\) can also isomerize to \([i₂₅]\) in one step. Overall, all reaction sequences involve an initial addition of the 1-propynyl radical to the C₁/C₃ carbon atoms of allene leading to \([i₁]\) and eventually form the decomposing intermediate \([i₉]\) (Figure 13). On the basis of the energies of the transition states, the
low barrier route to fulvene should be preferred among various fulvene formation pathways. However, statistical RRKM calculations (Tables 4 and 5) only propose a relatively small branching ratio of fulvene (2.5–3.4%) with isomers $p_1$ and $p_2$ suggested to dominate. We should recall that our aforementioned discussions could not rule out the formation of thermodynamically less stable isomers; further, isomers $p_1$ and $p_2$ should be formed exclusively via atomic deuterium loss (Figure 11), which was masked in the 1-propynyl–allene–$d_4$ system because of dissociative ionization of the C$_6$H$_2$D$_4$ parent (Section 3.2). Therefore, fulvene can be clearly identified as a reaction product, albeit with small branching ratios, with predicted scattering signal arising for $p_1$ and $p_2$. Note that the failed identification absence of benzene formation can be rationalized through a comparison of the barriers involved in the benzene versus fulvene formation (Figure 10). The formation of benzene ($p_5$) has to proceed via the sequence $[i9] \rightarrow [i21] \rightarrow [i22] \rightarrow [i23] \rightarrow$ benzene + hydrogen where the computed rate constant for the rate limiting isomerization, $[i9] \rightarrow [i21]$, is $2.3 \times 10^8$ s$^{-1}$. The computed rate constant for the competing decomposition of the $[i9]$ isomer to fulvene + H bimolecular product is higher by a factor of 6, $1.4 \times 10^9$ s$^{-1}$.

5. SUMMARY

Crossed molecular beam reactions of the 1-propynyl radical (CH$_3$CC; $X^2A_1$) with two C$_3$H$_4$ isomers, methylacetylene (H$_3$CCCH; $X^1A_1$) and allene (H$_2$CCCH$_2$; $X^1A_1$), along with their (partially) deuterated counterparts were investigated at collision energies of around 37 kJ mol$^{-1}$ to elucidate the chemical reaction dynamics to form distinct C$_6$H$_6$ isomers under single collision conditions. The forward convolution fitting of the LADs and TOF spectra combined with ab initio and statistical (RRKM) calculations exposed that both systems have no entrance barrier, proceed via indirect (complex-forming)
reaction dynamics involving C6H6, holding life times longer than their rotation period(s), and are initiated by the addition of the 1-propynyl radical with its radical center to the π-electron density of the unsaturated hydrocarbon at the terminal carbon atoms of methylacetylene (C1) and allene (C1/C3). In the methylacetylene system, the experimental data and computations can be reconciled by proposing that the initial collision complex [i1] and possibly [i2], which can easily interconvert to [i1], undergo unimolecular decomposition via tight exit transition states through atomic hydrogen loss, yielding dimethylacetylene p1 (CH3CCCCH3) and 1-propynylallene p2 (HCCCHCCCH) in overall exoergic reactions (123 and 98 kJ mol$^{-1}$) with an experimental branching ratio of 9.4 ± 0.1. In simple terms, the formation of these isomers requires the energy to “flow” from the initially formed carbon–carbon single bond over one and three bonds to form the products p1 and p2, respectively, suggesting that the methyl group of the 1-propynyl reactant acts solely as a spectator. Here, the pathway to fulvene, [i1] → [i7] → p4, requires hydrogen atom migration from the methyl group in the methylacetylene moiety via a 177 kJ mol$^{-1}$ barrier. For comparison, the atomic hydrogen elimination pathways to the p1 and p2 products exhibit 152 and 165 kJ mol$^{-1}$ barriers, respectively, and also are favored by entropy. The computed rate constant for the [i1] → [i7] isomerization, 9.6 × 10$^{8}$ s$^{-1}$, is much lower than those for the hydrogen atom elimination pathways [i1] → p1, 2.3 × 10$^{9}$ s$^{-1}$ and [i1] → p2, 2.9 × 10$^{9}$ s$^{-1}$. As a result, the reaction dynamics of the 1-propynyl–methylacetylene system mirror the reaction mechanisms unraveled for the ethynyl (C,H)–methylacetylene$^{56,72}$ and cyano (CN)–methylacetylene$^{53,65,73}$ systems studied previously. These reactions are also initiated by the barrierless addition of the doublet radical reactant with its radical center at the carbon atom to the sterically more accessible C1 carbon atom holding the acetylenic hydrogen atom; for each system, the reaction intermediates decompose via two exit channels via tight exit transition states, leading to cyanomethylacetylene (CH$_3$CCCN) [1] along with cyanomethylacetylene (HCCHCN) [4] and methylidacetylene (CH$_3$CCCH) [2] together with ethynyllallene (H$_2$CCCHCCCH) [3], with cyanomethylacetylene and methylidacetylene being lower in energy by typically 17 kJ mol$^{-1}$ compared to their allyl-type isomers (Figure 14). On the other hand, in the allene system, our experimental investigations propose the formation of the fulvene (c-C$_6$H$_6$CH$_3$) isomer via a six-step reaction sequence with two higher energy isomers—hexa-1,2-dien-4-yne (HCCCHCCCH$_3$) and hexa-1,4-diyne (HCCCH$_2$CCCH$_3$)—predicted based on our statistical calculations. While the pathways to these acyclic C$_6$H$_6$ isomers are statistically preferable, peculiar vibrational features of the initial complexes [i1]/[i2] may favor the fulvene formation channel dynamically. In particular, these complexes possess two low-energy vibrational modes of about 71 and 140 cm$^{-1}$, which include significant contributions of CCC and CCH bending involving the central CH$_3$ group and thus could promote the hydrogen atom shift from CH$_3$ to the neighboring carbon atom, that is, the [i1]/[i2] → [i5] rearrangement, and then starting from [i5], the channel to produce fulvene overwhelmingly dominates statistically. High-energy content in these low-frequency bending modes from the initial chemical activation may increase the life time of [i1]/[i2] and hence make the rearrangement to [i5] and eventual yield to fulvene more likely than predicted by the statistical calculations. This hypothesis on the non-RRKM behavior may be tested in the future via quasi-classical trajectory calculations, that is, a direct dynamics study on flight, which at present remains a very challenging and extremely computationally demanding task. The pathway to fulvene is quite unique compared to the reactions of allene with the isosbolar ethynyl (C$_2$H) and cyano radicals (CN) (Figure 14) and advocates that in the allene–1-propynyl system, the methyl group of the 1-propynyl reactant is actively engaged in the reaction mechanism to form fulvene. Finally, it is important highlighting that since both reactions are barrierless and exoergic and all transition states reside below the energy of the separated reactants, all hydrogen-deficient C$_6$H$_6$ isomers inferred in our investigation are predicted to be synthesized in low-temperature environments such as in hydrocarbon rich atmospheres of planets and their moons such as Titan, holding mole fractions up to a few 10$^{-5}$ at 900 km,$^{74,75}$ along with cold molecular clouds such as Taurus Molecular Cloud-1. Considering the isosbolar concept of the ethynyl and the 1-propynyl radicals, the reactions of 1-popynyl with both methylacetylene and allene are expected to proceed with rate constants of a few 10$^{-10}$ cm$^{-3}$s$^{-1}$ similar to those rates determined for the ethynyl–allene and ethynyl–methylacetylene systems. Here, the 1-propynyl radical can be generated via photodissociation of methylacetylene$^{77}$ both in our solar

Figure 14. Product channels detected in the reaction of methylacetylene and allene with ethynyl (C$_2$H) and cyano (CN) radicals under single collision conditions.

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system and in the ISM; upon reaction with methylacetylene and/or allene, the hitherto undetected C₆H₄ isomers, hexa-1,2-dien-4-yne (H₂CCCHCCH₃) (0.45 D), hexa-1,4-diyne (H₂CCCH₂CCH) (0.80 D), methyldiacetylene (CH₃CCCH) (1.28 D), and fulvene (c-C₆H₄CH₂) (0.23 D), can be searched for in deep space by exploiting the Atacama Large Millimeter/submillimeter Array.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b03746.

Optimized cartesian coordinates and vibrational frequencies for all intermediates, transition states, reactants, and products involved in the reactions of the propynyl radical with C₃H₄ isomers, methylacetylene and allene (PDF)

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The authors declare no competing financial interest.

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