

# Gas-Phase Formation of 1-Methylcyclopropene and 3-Methylcyclopropene via the Reaction of the Methylidyne Radical ( $\text{CH}; X^2\Pi$ ) with Propylene ( $\text{CH}_3\text{CHCH}_2; X^1\text{A}'$ )

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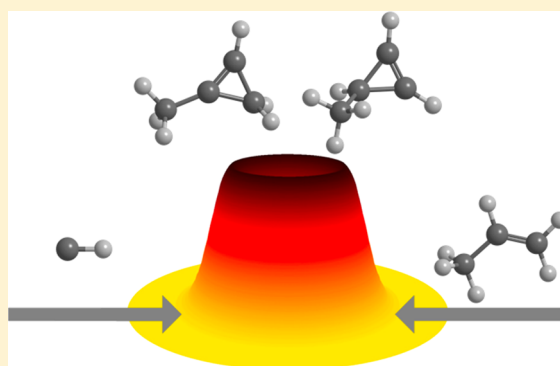
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## Supporting Information

**ABSTRACT:** The crossed molecular beam reactions of the methylidyne radical ( $\text{CH}; X^2\Pi$ ) with propylene ( $\text{CH}_3\text{CHCH}_2; X^1\text{A}'$ ) along with (partially) substituted reactants were conducted at collision energies of  $19.3 \text{ kJ mol}^{-1}$ . Combining our experimental data with ab initio electronic structure and statistical calculations, the methylidyne radical is revealed to add barrierlessly to the carbon–carbon double bond of propylene reactant resulting in a cyclic doublet  $\text{C}_4\text{H}_7$  intermediate with a lifetime longer than its rotation period. These adducts undergo a nonstatistical unimolecular decomposition via atomic hydrogen loss through tight exit transition states forming the cyclic products 1-methylcyclopropene and 3-methylcyclopropene with overall reaction exoergicities of  $168 \pm 25 \text{ kJ mol}^{-1}$ . These  $\text{C}_4\text{H}_6$  isomers are predicted to exist even in low-temperature environments such as cold molecular clouds like TMC-1, since the reaction is barrierless and exoergic, all transition states are below the energy of the separated reactants, and both the methylidyne radical ( $\text{CH}; X^2\Pi$ ) and propylene reactant were detected in cold molecular clouds such as TMC-1.



## 1. INTRODUCTION

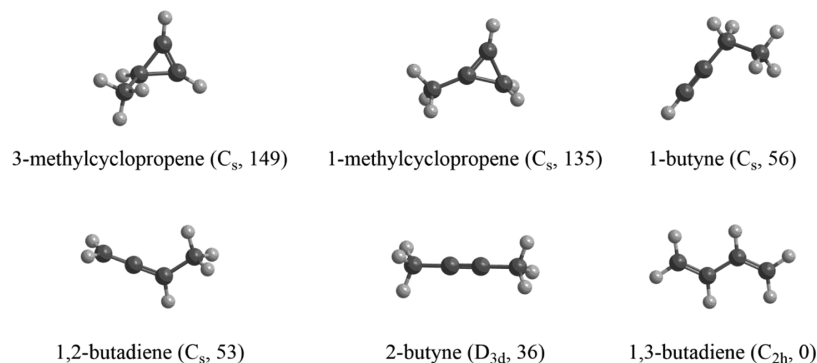
During the last decades, the  $\text{C}_4\text{H}_6$  isomers 1,3-butadiene, 1,2-butadiene, 1-butyne, and 2-butyne along with methylcyclopropene, ubiquitous hydrocarbons in fuel-rich low-pressure laminar flames,<sup>1–11</sup> have received considerable attention from the combustion, astrochemistry, and reaction dynamics communities as potential building blocks leading to the formation of polycyclic aromatic hydrocarbons (PAHs) along with their nitrogen-substituted and partially hydrogenated counterparts (Scheme 1).<sup>1–34</sup> 1,3-Butadiene, 1-butyne, and 2-butyne have been identified through their photoionization efficiency (PIE) curves in allene ( $\text{CH}_2\text{CCH}_2$ ) and propyne ( $\text{CH}_3\text{CCH}$ ) flames;<sup>3</sup> Yang et al. identified these  $\text{C}_4\text{H}_6$  isomers in butanol ( $\text{C}_4\text{H}_{10}\text{O}$ ) flames, concluding that 1,3-butadiene represents the dominant product.<sup>4</sup> Note that isomerization among these  $\text{C}_4\text{H}_6$  isomers is critical in combustion processes;<sup>9,35–37</sup> at temperatures above 1100 K, 1,2-butadiene and 2-butyne isomerize rapidly to 1,3-butadiene via hydrogen atom shifts.<sup>35</sup> The isomerization between 1-butyne and 1,3-butadiene, however, is slower than the rearrangement of 1,2-butadiene to 1,3-butadiene.<sup>35</sup> In premixed laminar 1,3-butadiene flames, 1,3-butadiene isomerizes easily to 2-butyne and 1-methylcyclopropene with nearly equal rates of  $(3.0 \times 10^{13}) \exp(-226\,000/RT) \text{ s}^{-1}$ .<sup>9,38,39</sup>

Among the  $\text{C}_4\text{H}_6$  isomers, 1,3-butadiene has been studied more deeply in the combustion chemistry community due to its important role in promoting PAH formation.<sup>2,7–9,40–47</sup> In premixed, sooting laminar flames, styrene ( $\text{C}_8\text{H}_8$ ) was speculated to be formed by the reaction between the 1,3-butadienyl radical ( $\text{C}_4\text{H}_5$ ) with 1,3-butadiene; about 80% of benzene ( $\text{C}_6\text{H}_6$ ) was proposed to originate from the vinyl radical ( $\text{C}_2\text{H}_3$ ) reacting with 1,3-butadiene in a butadiene flame.<sup>40</sup> On the other hand, reactions between butadiene and molecular oxygen lead to degradation of the hydrocarbon and production of 1,3-butadienyl ( $n\text{-C}_4\text{H}_5/i\text{-C}_4\text{H}_5$ ) along with the hydroperoxyl radical ( $\text{HO}_2$ ).<sup>44</sup> Propagation reactions with simple molecular radicals and atoms like hydroperoxyl ( $\text{HO}_2$ ), hydrogen ( $\text{H}$ ), hydroxyl ( $\text{OH}$ ), oxygen ( $\text{O}$ ), methylidyne ( $\text{CH}$ ), and vinyl ( $\text{C}_2\text{H}_3$ ) might also lead to 1,3-butadienyl ( $n\text{-C}_4\text{H}_5/i\text{-C}_4\text{H}_5$ ).<sup>44</sup> Consecutive reactions of  $i\text{-C}_4\text{H}_5/n\text{-C}_4\text{H}_5$  with acetylene ( $\text{C}_2\text{H}_2$ ) have been proposed as an important pathway to form one-ring aromatics such as benzene or its fulvene isomer in hydrocarbon-rich flames.<sup>6,9,40,41,48–52</sup> Miller et al. speculated that the reactions between  $i\text{-C}_4\text{H}_5$  and acetylene account for almost 100% of fulvene detected in 1,3-butadiene

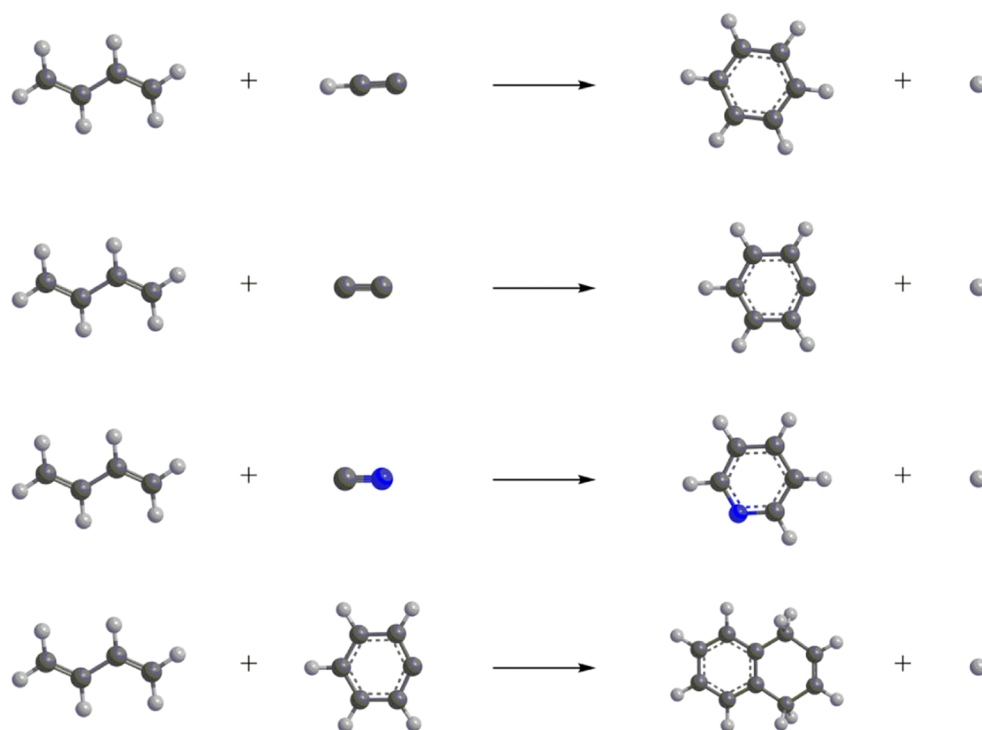
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Scheme 1. Structures of Six Low-Lying  $C_4H_6$  Isomers<sup>a</sup>

<sup>a</sup>Point groups and energies ( $\text{kJ mol}^{-1}$ ) relative to 1,3-butadiene are also shown. Energies were obtained from NIST.<sup>85,86</sup>

Scheme 2. Barrierless Reactions of 1,3-Butadiene with Open-Shell Reactants Leading to Key Aromatic Molecules: Benzene ( $C_6H_6$ ,  $D_{6h}$ ), Phenyl ( $C_6H_5$ ,  $C_{2v}$ ), Pyridine ( $C_5H_5N$ ,  $C_{2v}$ ) and 1,4-Dihydronaphthalene ( $C_{10}H_{10}$ ,  $C_{2v}$ )

flames; 30% of benzene has been inferred to be formed by a hydrogen-assisted isomerization of fulvene.<sup>41,42</sup>

More closely related to low-temperature interstellar environments, barrierless 1,3-butadiene reactions with the ethynyl radical ( $C_2H$ ), dicarbon ( $C_2$ ), the cyano radical ( $CN$ ), and the phenyl radical ( $C_6H_5$ ) lead to aromatic systems like benzene ( $C_6H_6$ ), phenyl ( $C_6H_5$ ), 1,4-dihydronaphthalene ( $C_{10}H_{10}$ ), and small fractions of pyridine ( $C_5H_5N$ ), under single-collision conditions (Scheme 2).<sup>12–15,18,20,21,23</sup> Benzene, the simplest building block of all PAHs, can be synthesized through the addition of the ethynyl radical to one of the terminal carbon atoms of 1,3-butadiene followed by isomerization, cyclization, and hydrogen loss accompanied by aromatization.<sup>14</sup> Zhang et al. revealed that the phenyl radical represents an important product of the barrierless bimolecular reaction of triplet dicarbon and 1,3-butadiene.<sup>18,23</sup> Combined experimental and computational studies revealed that the initial collision complex formed via the addition of triplet dicarbon to one

of the terminal carbons of 1,3-butadiene will undergo ring closure and hydrogen migration, eventually leading to the phenyl radical through atomic hydrogen elimination.<sup>18,23</sup> Pyridine, formally derived from benzene by replacing a single CH moiety by a nitrogen atom, represents a minor product in the reaction of ground-state cyano radicals with 1,3-butadiene.<sup>20,21</sup> Finally, 1,4-dihydronaphthalene was identified in the reaction of the phenyl radical with 1,3-butadiene.<sup>12,13,15</sup> Similar to the aforementioned reactions, this pathway is initiated by a barrierless addition of the phenyl radical to the terminal carbon atom of 1,3-butadiene followed by ring closure, isomerization, and hydrogen atom emission.<sup>12,13,15</sup>

However, despite the fundamental importance of 1,3-butadiene in the formation of mono- and bicyclic aromatic molecules (Scheme 2), the underlying reaction pathways leading to distinct  $C_4H_6$  isomers in combustion flames and distinct exaterrestrial environments are poorly understood.<sup>53,54</sup> The reactions of methyldiyne ( $CH$ ) with propylene

(C<sub>3</sub>H<sub>6</sub>) was suggested as an important route to 1,3-butadiene. In 2004, Miller et al. explored the C<sub>4</sub>H<sub>7</sub> potential energy surface (PES), computationally identifying acyclic C<sub>4</sub>H<sub>7</sub> isomers.<sup>19</sup> Further, a detailed theoretical investigation on the C<sub>4</sub>H<sub>7</sub> surface was conducted at the B3LYP/6-311G(d,p) and G3B3 (single-point) levels of theory.<sup>16</sup> Both linear and cyclic C<sub>4</sub>H<sub>7</sub> radicals were considered with the energetics of the acyclic structures being consistent with Miller's calculation.<sup>16,19</sup> Kinetic experiments of methylidyne (CH) radicals with propylene were carried out in a low-pressure fast-flow reactor at 300 K with the hydrogen atom production channel reaching up to 78 ± 10%. 1,3-Butadiene was proposed as the main product.<sup>17</sup> Further, the reactions of CH/CD(X<sup>2</sup>Π) with propylene were explored at 298 K and 4 Torr, exploiting photoionization mass spectrometry.<sup>22</sup> 1-Methylallyl was suggested to be formed through methylidyne cycloaddition to the carbon–carbon double bond of propylene followed by ring opening and hydrogen atom elimination, eventually forming three C<sub>4</sub>H<sub>6</sub> isomers: 1,3-butadiene, 1,2-butadiene, and 1-butyne. 1,3-Butadiene was the main product with the branching fraction of 0.63 ± 0.13 with minor fractions of 1,2-butadiene (0.25 ± 0.05) and 1-butyne (0.12 ± 0.03).<sup>22</sup> Based on the aforementioned investigations, Ribeiro and Mebel conducted a systematic investigation of the C<sub>4</sub>H<sub>7</sub> PES initiated from the reaction of methylidyne (CH) with propylene (C<sub>3</sub>H<sub>6</sub>) first at a zero-pressure limit under single-collision conditions and also at 5 Torr at 300 K.<sup>55</sup> Assuming complete energy randomization and formation of an adduct via methylidyne addition to the carbon–carbon double bond, 1,3-butadiene and atomic hydrogen were predicted to be formed with branching ratios of 80% with 1,2-butadiene contributing up to 11%. If the reaction is initiated by methylidyne insertion into the terminal sp<sup>2</sup> C–H bond or into the C–C bond, the branching ratios for 1,3-butadiene and hydrogen, and 1,2-butadiene and hydrogen were predicted to be 87 and 11%, respectively. Considering an insertion of methylidyne into an sp<sup>3</sup> C–H, 1,2-butadiene and atomic hydrogen account for almost 30% of all products.

Although the formation mechanisms of C<sub>4</sub>H<sub>6</sub> isomers have been gauged previously both experimentally and theoretically, the aforementioned experimental studies only involved kinetic studies in which often hundreds of collisions might modify the nascent product distribution; likewise, hydrogen-assisted isomerization of nascent reaction products under bulk conditions presents an often-neglected complication in the identification of the initial reaction products.<sup>16,17,19,22,55</sup> Therefore, a detailed and comprehensive investigation of the reaction of methylidyne radicals with propylene under single-collision conditions is desirable.<sup>18,56–64</sup> These experiments are conducted under single-collision conditions and guarantee that truly primary reaction products are identified; this also eliminates hydrogen-assisted isomerization of these nascent products and a potential stabilization of reaction intermediates. Here, we performed reaction dynamics studies on the barrierless bimolecular reaction of the methylidyne (CH) radical with propylene (CH<sub>3</sub>CHCH<sub>2</sub>) at a collision energy (*E<sub>c</sub>*) of 19.3 kJ mol<sup>−1</sup> under single-collision conditions. These results are compared to Ribeiro and Mebel's computational study of the C<sub>4</sub>H<sub>7</sub> PES<sup>55</sup> and are expanded by conducting new statistical Rice–Ramsperger–Kassel–Marcus (RRKM) calculations to predict the branching ratios under our experimental conditions. Agreements and discrepancies between computations and experiments leading to 1-methylcyclo-propene and 3-

methylcyclo-propene are discussed, and reaction mechanism(s) are proposed. Due to the barrierless and exoergic nature of this elementary reaction, the methylidyne (CH) radical can also react with propylene (CH<sub>3</sub>CHCH<sub>2</sub>)<sup>65</sup> in cold molecular clouds such as TMC-1;<sup>66</sup> hence, implications to astrochemistry are also presented.

## 2. METHODS

**2.1. Experimental Methods.** The bimolecular reactions of methylidyne (CH; X<sup>2</sup>Π) with propylene (CH<sub>3</sub>CHCH<sub>2</sub>; X<sup>1</sup>A') along with the corresponding fully deuterated counterpart (CD<sub>3</sub>CDCD<sub>2</sub>) and of methylidyne-*d* (CD; X<sup>2</sup>Π) with propylene (CH<sub>3</sub>CHCH<sub>2</sub>; X<sup>1</sup>A') and partially deuterated isotopologues (CD<sub>3</sub>CHCH<sub>2</sub>) were performed under single-collision conditions in a crossed molecular beam machine at the University of Hawaii.<sup>56</sup> The pulsed supersonic methylidyne beam was produced via photodissociation (COMPex 110, Coherent, Inc.; 248 nm; 30 Hz) of a helium-seeded (99.9999%; AirGas) bromoform (CHBr<sub>3</sub>, Sigma-Aldrich Chemistry, ≥99%) held in a stainless steel bubbler at 283 K at a total pressure of 2.2 atm.<sup>67–70</sup> After passing through the skimmer, the methylidyne beam was velocity-selected by a four-slot chopper wheel with a peak velocity of *v<sub>p</sub>* = 1782 ± 29 m s<sup>−1</sup> and a speed ratio *S* of 13.8 ± 1.6 (Table 1). By the use of

**Table 1.** Peak Velocities (*v<sub>p</sub>*) and Speed Ratios (*S*) of the Methylidyne (CH), Propylene (C<sub>3</sub>H<sub>6</sub>), Propylene-*d*<sub>6</sub> (C<sub>3</sub>D<sub>6</sub>), and Methylidyne-*d* (CD) Beams along with the Corresponding Collision Energies (*E<sub>c</sub>*) and Center-of-Mass Angles (Θ<sub>CM</sub>) for Each Reactive Scattering Experiment

beam	<i>v<sub>p</sub></i> (m s <sup>−1</sup> )	<i>S</i>	<i>E<sub>c</sub></i> (kJ mol <sup>−1</sup> )	Θ <sub>CM</sub> (deg)
CH (X <sup>2</sup> Π)	1782 ± 29	13.8 ± 1.6		
C <sub>3</sub> H <sub>6</sub> (X <sup>1</sup> A')	840 ± 10	11.0 ± 0.2	19.3 ± 0.4	56.7 ± 0.3
C <sub>3</sub> D <sub>6</sub> (X <sup>1</sup> A')	820 ± 10	7.8 ± 1.0	19.7 ± 0.4	59.5 ± 0.3
CD (X <sup>2</sup> Π)	1841 ± 15	13.9 ± 0.8		
C <sub>3</sub> H <sub>6</sub> (X <sup>1</sup> A')	840 ± 10	11.0 ± 0.2	21.5 ± 0.4	53.9 ± 0.3
CD <sub>3</sub> CHCH <sub>2</sub> (X <sup>1</sup> A')	830 ± 10	11.0 ± 0.2	21.8 ± 0.4	55.4 ± 0.3

laser-induced fluorescence, the methylidyne beam was determined to hold a rotational temperature of 14 ± 1 K with less than 6% of the radicals populating the first vibrationally excited level (*ν* = 1).<sup>68–70</sup> The supersonic beam of neat propylene (Sigma-Aldrich Chemistry, >99%) at a backing pressure of 550 Torr with a peak velocity of *v<sub>p</sub>* = 840 ± 10 m s<sup>−1</sup> and a speed ratio *S* of 11.0 ± 0.2 (Table 1) crossed perpendicularly with the methylidyne beam, resulting in a collision energy of 19.3 ± 0.4 kJ mol<sup>−1</sup> and a center-of mass angle Θ<sub>CM</sub> of 56.7 ± 0.3°. Each supersonic beam was generated by a piezoelectric pulse valve, which was operated at a repetition rate of 60 Hz, a pulse width of 80 μs, and a peak voltage of −400 V. The secondary pulse valve, which introduced pure propylene gas, was triggered 95 μs prior to the primary pulse valve. For the deuterated reactants, methylidyne-*d* (CD) was produced exploiting bromoform-*d* (CDBr<sub>3</sub>, Sigma-Aldrich Chemistry, >99.5%) as a photodissociation precursor. The reactions of methylidyne (CH; X<sup>2</sup>Π) with propylene-*d*<sub>6</sub> (CD<sub>3</sub>CDCD<sub>2</sub>) and of methylidyne-*d* (CD; X<sup>2</sup>Π) with propylene (CH<sub>3</sub>CHCH<sub>2</sub>; X<sup>1</sup>A') and partially deuterated isotopologues (CD<sub>3</sub>CHCH<sub>2</sub>) were performed to



elucidate the detailed positions of the atomic hydrogen and/or deuterium loss (Table 1).

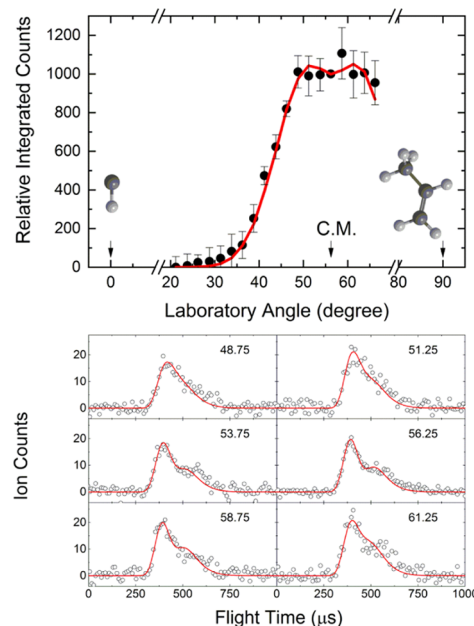
The detector is housed within a triply differentially pumped chamber and rotatable in the plane defined by both reactant beams. It consists of a Brink-type ionizer,<sup>71</sup> a quadrupole mass spectrometer (QMS), and a Daly-type ion counter.<sup>72</sup> The neutral reaction products entering the detector were ionized by electron impact (80 eV), filtered based on their mass-to-charge ratios ( $m/z$ ) utilizing a QMS (Extrel; QC 150) equipped with a 2.1 MHz oscillator, and eventually recorded by a Daly-type ion counter. Up to  $1.3 \times 10^6$  time-of-flight (TOF) spectra were collected at laboratory angles between  $0 \leq \Theta \leq 69^\circ$  with respect to the methylidyne beam ( $\Theta = 0^\circ$ ). A forward-convolution routine was used to analyze the laboratory data, which is an iterative method exploiting user-defined center-of-mass (CM) translational energy  $P(E_T)$  and angular  $T(\theta)$  flux distributions; these functions are varied iteratively until an acceptable fit of the laboratory frame (LAB) TOF spectra and angular distributions are obtained.<sup>73,74</sup> These functions define the reactive differential cross section  $I(u, \theta) \sim P(u) \times T(\theta)$  with the center-of-mass velocity  $u$ . The error ranges of the  $P(E_T)$  and  $T(\theta)$  functions are determined within  $1\sigma$  limits of the corresponding laboratory angular distribution while maintaining a good fit of the laboratory TOF spectra.

**2.2. Computational Methods.** Energy-dependent Rice–Ramsperger–Kassel–Marcus (RRKM) theory<sup>75–77</sup> was utilized in the calculations of unimolecular rate constants of various elementary steps on the  $C_4H_7$  PES relevant to the reaction of the methylidyne radical (CH) with propylene ( $C_3H_6$ ). The  $C_4H_7$  surface together with all structures and vibrational frequencies of the reactants, products, intermediates, and transition states have been described in the previous work by Ribeiro and Mebel.<sup>55</sup> In the present study, internal energy-dependent rate constants were computed within the harmonic approximation using the recently developed in-house code,<sup>78</sup> which allows for automatic processing of Gaussian 09 log files for the evaluation of numbers of states for transition states and densities of states for local minima within the direct count method. The energy-dependent RRKM rate constants were computed in the limit of zero pressure and hence are applicable to crossed molecular beam conditions. The unimolecular rate constants were utilized in the calculations of product branching ratios, which were obtained by solving first-order kinetic equations employing steady-state approximation.<sup>78,79</sup>

### 3. RESULTS

**3.1. Laboratory Frame.** For the reaction of the methylidyne radical (CH; 13 amu) with propylene ( $CH_3CHCH_2$ ; 42 amu), reactive scattering signal was collected at mass-to-charge ratios ( $m/z$ ) of 55 ( $^{13}CC_3H_6^+$ ), 54 ( $C_4H_6^+$ ), and 53 ( $C_4H_5^+$ ). The TOF spectra recorded at these mass-to-charge ratios were superimposable after scaling, suggesting that ion counts at  $m/z = 55$ , 54, and 53 originate from the same reaction channel, i.e.,  $CH$  (13 amu) +  $C_3H_6$  (42 amu)  $\rightarrow$   $C_4H_6$  (54 amu) +  $H$  (1 amu). Here, the signal at  $m/z = 53$  ( $C_4H_5^+$ ) can be linked to a dissociative electron impact ionization of the  $m/z = 54$  ( $C_4H_6^+$ ) parent in the electron impact ionizer; ion counts at  $m/z = 55$  ( $^{13}CC_3H_6^+$ ) arose from naturally occurring  $^{13}C$  isotopes in the product. Therefore, we can state that the reaction of methylidyne with propylene is dictated by atomic hydrogen loss and the formation of  $C_4H_6$  isomer(s). Since the ion counts of the parent ion  $m/z = 54$  ( $C_4H_6^+$ ) are only at a

level of  $39 \pm 4\%$  compared to those of the fragment ion  $m/z = 53$  ( $C_4H_5^+$ ), the TOF spectra were collected at the best signal-to-noise ratio at  $m/z = 53$  ( $C_4H_5^+$ ). The resulting TOFs were then normalized with respect to the center-of-mass angle and integrated to obtain the laboratory angular distribution (LAD; Figure 1). The LAD is nearly symmetric around  $\Theta_{CM}$  and

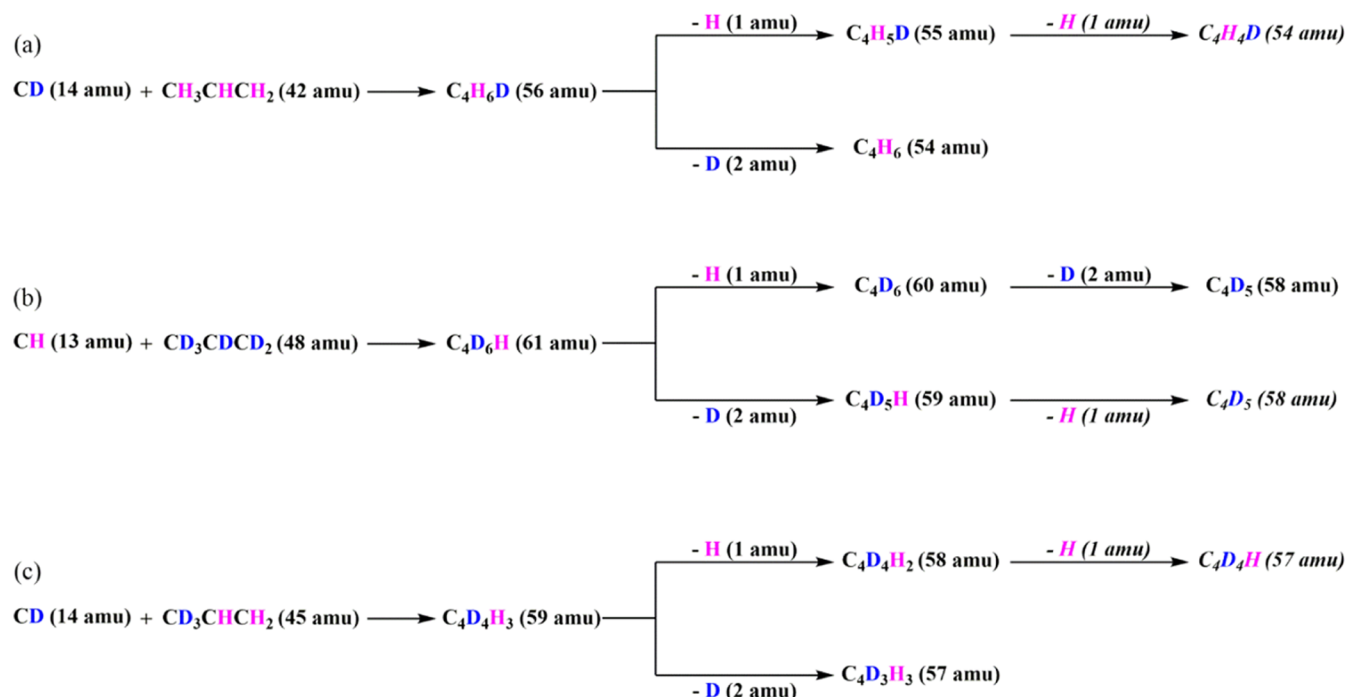


**Figure 1.** Laboratory angular distribution (top) and time-of-flight (TOF) spectra (bottom) recorded at a mass-to-charge ratio ( $m/z$ ) of 53 for the reaction of the methylidyne radical ( $CH$ ;  $C_{\infty v}$ ;  $X^2\Pi$ ) with propylene ( $C_3H_6$ ;  $C_3$ ;  $X^1A'$ ). The directions of the methylidyne radical and propylene beams are defined as 0 and  $90^\circ$ , respectively. The red solid lines represent the best-fit derived from center-of-mass functions depicted in Figure 3 with black circles defining the experimental data.

spans at least  $45^\circ$  in the laboratory frame. This result might suggest that the reaction of the methylidyne radical with propylene proceeds via indirect scattering dynamics through  $C_4H_7$  reaction intermediate(s), ultimately dissociating to  $C_4H_6$  by emitting atomic hydrogen.

The reactions of the methylidyne- $d$  radical (CD; 14 amu) with propylene ( $CH_3CHCH_2$ ; 42 amu) and of the methylidyne radical (CH; 13 amu) with propylene- $d_6$  ( $CD_3CDCD_2$ ; 48 amu) and propylene-3,3,3- $d_3$  ( $CD_3CHCH_2$ ) were also performed to extract detailed information on the position(s) of the hydrogen atom loss (Scheme 3). To probe the hydrogen and deuterium atom loss channels, the reaction of methylidyne- $d$  (CD; 14 amu) with propylene ( $CH_3CHCH_2$ ; 42 amu) was studied first (Scheme 3a). TOFs were recorded at  $m/z = 55$  ( $C_4H_5D^+$ ) and  $m/z = 54$  ( $C_4H_6^+/C_4H_4D^+$ ) at the corresponding CM angle of  $54.6^\circ$ ; a strong signal was observed at  $m/z = 54$  ( $C_4H_6^+/C_4H_4D^+$ ) with signal at  $m/z = 55$  ( $C_4H_5D^+$ ) collected at a level of only  $39 \pm 2\%$  of  $m/z = 54$  ( $C_4H_6^+/C_4H_4D^+$ ) (Figure 2a). Recall that for the reaction of the methylidyne radical (CH; 13 amu) with propylene ( $CH_3CHCH_2$ ; 42 amu), a signal at  $m/z = 54$  ( $C_4H_6^+$ ) is collected at a level of  $39 \pm 4\%$  with respect to  $m/z = 53$  ( $C_4H_5^+$ ) (Figure 2d). Since both fractions are identical within error limits, we may conclude that for the reaction of the methylidyne- $d$  radical (CD; 14 amu) with propylene ( $CH_3CHCH_2$ ; 42 amu), a signal at  $m/z = 54$  ( $C_4H_6^+/$

Scheme 3. Reaction Schematics for the Reactions of (a) Methylidyne-*d* (CD) with Propylene ( $\text{CH}_3\text{CHCH}_2$ ), (b) Methylidyne (CH) with Propylene-*d*<sub>6</sub> ( $\text{CD}_3\text{CDCD}_2$ ), and (c) Methylidyne-*d* (CD) with Propylene-3,3,3-*d*<sub>3</sub> ( $\text{CD}_3\text{CHCH}_2$ ), Leading to H- and D-Loss Products<sup>a</sup>



<sup>a</sup>Successive dissociative electron impact ionization processes of the parent ions are represented in italics.

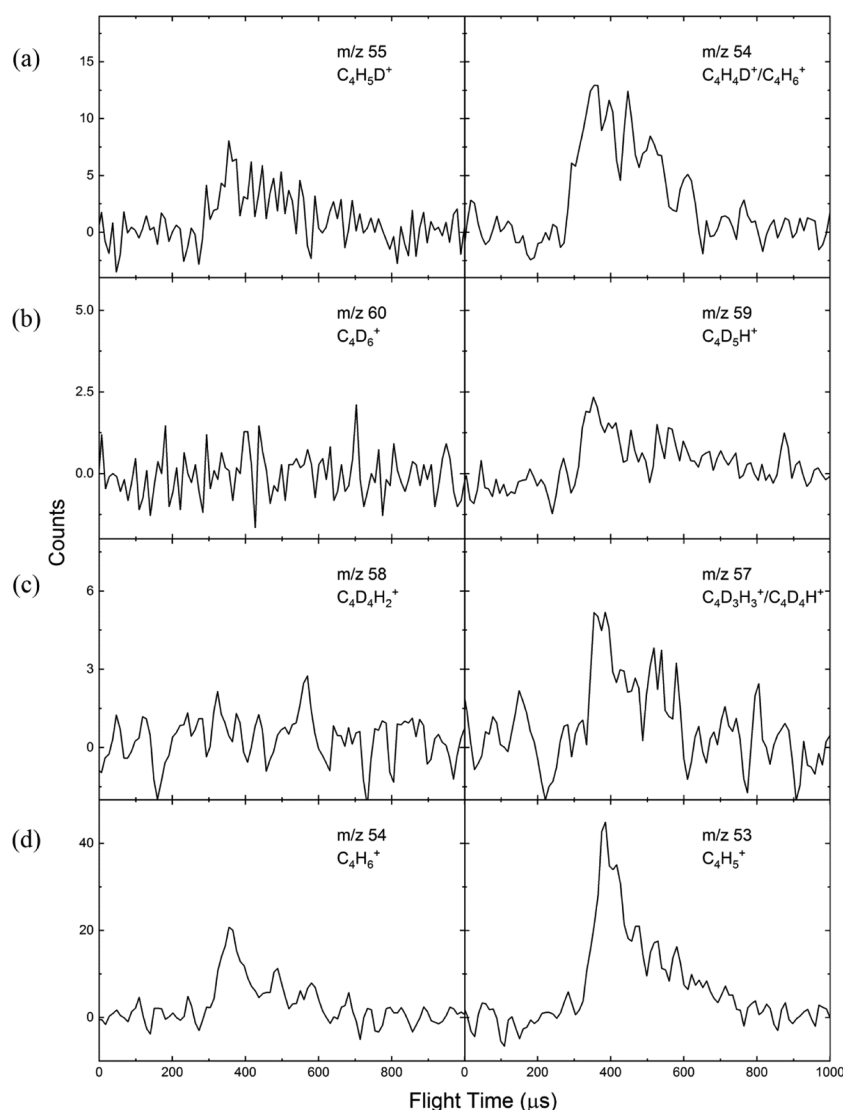
$\text{C}_4\text{H}_4\text{D}^+$ ) can be attributed to a dissociative electron impact ionization of the  $m/z = 55$  ( $\text{C}_4\text{H}_5\text{D}^+$ ) product in the electron impact ionizer. Here, the  $\text{C}_4\text{H}_5\text{D}$  product(s) was (were) formed via *hydrogen atom loss* from the propylene reactant. Consequently, no atomic hydrogen was emitted from the methylidyne radical (CH) within our detection limits.

To confirm this conclusion, we carried out the reaction of the methylidyne radical (CH; 13 amu) with propylene-*d*<sub>6</sub> ( $\text{CD}_3\text{CDCD}_2$ ; 48 amu) (Scheme 3b). Signal was collected at mass-to-charge ratios ( $m/z$ ) of 60 ( $\text{C}_4\text{D}_6^+$ ), 59 ( $\text{C}_4\text{D}_5\text{H}^+$ ), and 58 ( $\text{C}_4\text{D}_5^+$ ) (Figure 2b). Note that ions at  $m/z = 60$  ( $\text{C}_4\text{D}_6^+$ ) and 59 ( $\text{C}_4\text{D}_5\text{H}^+$ ) can both fragment to  $m/z = 58$  ( $\text{C}_4\text{D}_5^+$ ). Signal at  $m/z = 60$  ( $\text{C}_4\text{D}_6^+$ ) was barely visible, accounting for up to  $4 \pm 1\%$  with respect to  $m/z = 58$  ( $\text{C}_4\text{D}_5^+$ ). Signal at  $m/z = 59$  ( $\text{C}_4\text{D}_5\text{H}^+$ ) ranges at  $38 \pm 5\%$  compared to that at  $m/z = 58$  ( $\text{C}_4\text{D}_5^+$ ). Based on these data,  $m/z = 58$  ( $\text{C}_4\text{D}_5^+$ ) represents most likely a fragment from  $m/z = 59$  ( $\text{C}_4\text{D}_5\text{H}^+$ ), which suggests that the deuterium loss channel exists in the methylidyne–propylene-*d*<sub>6</sub> system. Therefore, the experimental results for the reactions of methylidyne-*d* (CD; 14 amu) with propylene ( $\text{CH}_3\text{CHCH}_2$ ; 42 amu) and methylidyne radical (CH; 13 amu) with propylene-*d*<sub>6</sub> ( $\text{CD}_3\text{CDCD}_2$ ; 48 amu) are consistent, suggesting that for the 1-methylidyne (CH)–propylene ( $\text{CH}_3\text{CHCH}_2$ ) system, the hydrogen emission originates within our error limits from the propylene reactant.

We further performed the reaction of the methylidyne-*d* radical (CD; 14 amu) with propylene-3,3,3-*d*<sub>3</sub> ( $\text{CD}_3\text{CHCH}_2$ ; 45 amu) to identify the detailed hydrogen and/or deuterium emission position(s) from the propylene-3,3,3-*d*<sub>3</sub> reactant (Scheme 3c). Signals at both  $m/z = 58$  ( $\text{C}_4\text{D}_4\text{H}_2^+$ ) and  $m/z = 57$  ( $\text{C}_4\text{D}_3\text{H}_3^+/\text{C}_4\text{D}_4\text{H}^+$ ) were collected (Figure 2c), and the ratios between these two ion counts were determined to be  $31$

$\pm 5\%$ , which is very similar to the ratio ( $39 \pm 4\%$ ) between the parent ion  $m/z = 54$  ( $\text{C}_4\text{H}_6^+$ ) and the fragment ion at  $m/z = 53$  ( $\text{C}_4\text{H}_5^+$ ) in the reaction of the methylidyne radical (CH; 13 amu) with propylene ( $\text{CH}_3\text{CHCH}_2$ ; 42 amu). The results suggest that  $m/z = 57$  ( $\text{C}_4\text{D}_3\text{H}_3^+/\text{C}_4\text{D}_4\text{H}^+$ ) is most likely a fragment from  $m/z = 58$  ( $\text{C}_4\text{D}_4\text{H}_2^+$ ) and only the H loss channel exists in the methylidyne-*d* radical (CD) with propylene-3,3,3-*d*<sub>3</sub> ( $\text{CD}_3\text{CHCH}_2$ ) reaction. Therefore, we may conclude that, in the reaction of the methylidyne radical (CH; 13 amu) with propylene ( $\text{CH}_3\text{CHCH}_2$ ; 42 amu), the H loss results from the vinyl group of the propylene reactant, but not from methylidyne radical or the  $\text{CH}_3$  group of propylene.

**3.2. Center-of-Mass Frame.** For the reaction of the methylidyne radical (CH; 13 amu) with propylene ( $\text{CH}_3\text{CHCH}_2$ ; 42 amu), the best-fit CM functions (Figure 3) are achieved, exploiting a single reaction channel with the products of  $\text{C}_4\text{H}_6$  and atomic hydrogen; the hatched areas of the  $P(E_T)$  and  $T(\theta)$  define the error ranges and were determined within the  $1\sigma$  error limits of the LAB angular distribution. Considering energy conservation, the maximum energy  $E_{\text{max}}$  of the CM translational energy distribution  $P(E_T)$  (Figure 3), the collision energy, and the reaction energy are correlated by  $E_{\text{max}} = E_C - \Delta_r G$  for those molecules born without internal excitation.  $E_{\text{max}}$  terminates at  $187 \pm 25 \text{ kJ mol}^{-1}$ , suggesting a reaction energy of  $-168 \pm 25 \text{ kJ mol}^{-1}$  to form the heavy product ( $\text{C}_4\text{H}_6$ ) and atomic hydrogen. The distribution maximum of  $P(E_T)$  is located at  $32 \pm 2 \text{ kJ mol}^{-1}$ , indicating a tight exit transition state leading to  $\text{C}_4\text{H}_6$  from the  $\text{C}_4\text{H}_7$  intermediate(s).<sup>80</sup> An average translational energy of the products was calculated to be  $52 \pm 6 \text{ kJ mol}^{-1}$ , which reveals that only  $28 \pm 3\%$  of the energy is released into product translation degrees of freedom. Additional information on the reaction dynamics can be obtained by inspecting the CM



**Figure 2.** Time-of-flight (TOF) spectra for the reaction of (a) methylidyne-*d* radical ( $\text{CD}$ ;  $C_{\infty v}$ ;  $X^2\Pi$ ) with propylene ( $\text{C}_3\text{H}_6$ ;  $C_s$ ;  $X^1A'$ ) recorded at mass-to-charge ( $m/z$ ) ratios of 55 ( $\text{C}_4\text{H}_5\text{D}^+$ ) and 54 ( $\text{C}_4\text{H}_4\text{D}^+/\text{C}_4\text{H}_6^+$ ), (b) methylidyne radical ( $\text{CH}$ ;  $C_{\infty v}$ ;  $X^2\Pi$ ) with propylene-*d*<sub>6</sub> ( $\text{C}_3\text{D}_6$ ;  $C_s$ ;  $X^1A'$ ) recorded at  $m/z$  58 ( $\text{C}_4\text{D}_5^+$ ) and 59 ( $\text{C}_4\text{HD}_5^+$ ), (c) methylidyne-*d* radical ( $\text{CD}$ ;  $C_{\infty v}$ ;  $X^2\Pi$ ) with propylene-3,3,3-*d*<sub>3</sub> ( $\text{CD}_3\text{CHCH}_2$ ;  $C_s$ ;  $X^1A'$ ) recorded at  $m/z$  58 ( $\text{C}_4\text{D}_4\text{H}_2^+$ ) and 57 ( $\text{C}_4\text{D}_3\text{H}_3^+/\text{C}_4\text{D}_4\text{H}^+$ ), and (d) methylidyne radical ( $\text{CH}$ ;  $C_{\infty v}$ ;  $X^2\Pi$ ) with propylene ( $\text{C}_3\text{H}_6$ ;  $C_s$ ;  $X^1A'$ ) recorded at  $m/z$  54 ( $\text{C}_4\text{H}_6^+$ ) and 53 ( $\text{C}_4\text{H}_5^+$ ).

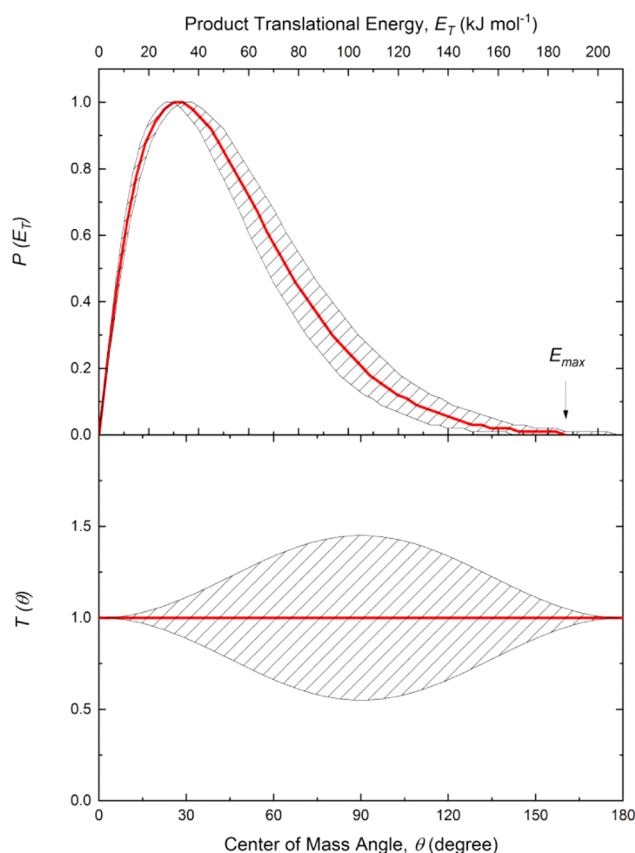
angular distribution,  $T(\theta)$  (Figure 3).  $T(\theta)$  displays a nonzero intensity from 0 to  $180^\circ$  and a forward–backward symmetry, indicating that the lifetime of the intermediate  $\text{C}_4\text{H}_7$  is longer than its rotational period(s) and that the product is formed via indirect scattering dynamics via activated  $\text{C}_4\text{H}_7$  complex(es).<sup>81</sup>

#### 4. DISCUSSION

Both hydrogen abstractions and association reactions are feasible entrance channels involved in the bimolecular reactions of methylidyne ( $\text{CH}$ ;  $X^2\Pi$ ) radical with propylene ( $\text{CH}_3\text{CHCH}_2$ ;  $X^1A'$ ). Compared to association reactions, products originating from the hydrogen abstractions lead to carbene ( $\text{CH}_2$ ) and distinct  $\text{C}_3\text{H}_5$  isomers in reactions exoergic by  $57 \text{ kJ mol}^{-1}$ . The resulting  $\text{C}_3\text{H}_5$  ( $m/z = 41$ ) isomers cannot be detected in our experiments due to the dissociative electron impact ionization of the propylene reactant leading to insurmountable background counts of the  $\text{C}_3\text{H}_5^+$  fragment. Considering the association reactions, the methylidyne ( $\text{CH}$ ) radical can add to the carbon–carbon double bond of

propylene, insert into one of its three chemically inequivalent C–H bonds, and/or may insert into the C–C single bond between the methyl and vinyl moieties. Ribeiro and Mebel examined the  $\text{C}_4\text{H}_7$  PES, computationally connecting the methylidyne radical and propylene entrance channel via 15  $\text{C}_4\text{H}_7$  intermediates and 50 transition states to methyl group losses along with  $\text{C}_3\text{H}_4$  products (**p1**, **p12**, and **p13**), atomic hydrogen loss products ( $\text{C}_4\text{H}_6$ ) (**p2–p6**, **p9–p11**),  $\text{C}_2\text{H}_3$  loss products ( $\text{C}_2\text{H}_4$ ) (**p7**), and  $\text{C}_2\text{H}_5$  loss products ( $\text{C}_2\text{H}_2$ ) (**p8**) (Figures 4–6). Here, the complete PES is subdivided into three sections: (1) cyclic structures produced by methylidyne radical ( $\text{CH}$ ) addition to the carbon–carbon double bond of propylene (Figure 4), (2) acyclic structures resulting from methylidyne radical ( $\text{CH}$ ) insertion into the terminal C–H bond or the C–C single bond of propylene (Figure 5), and (3) branched structures originated from methylidyne radical ( $\text{CH}$ ) insertion into the CH moiety of the vinyl group of propylene (Figure 6).



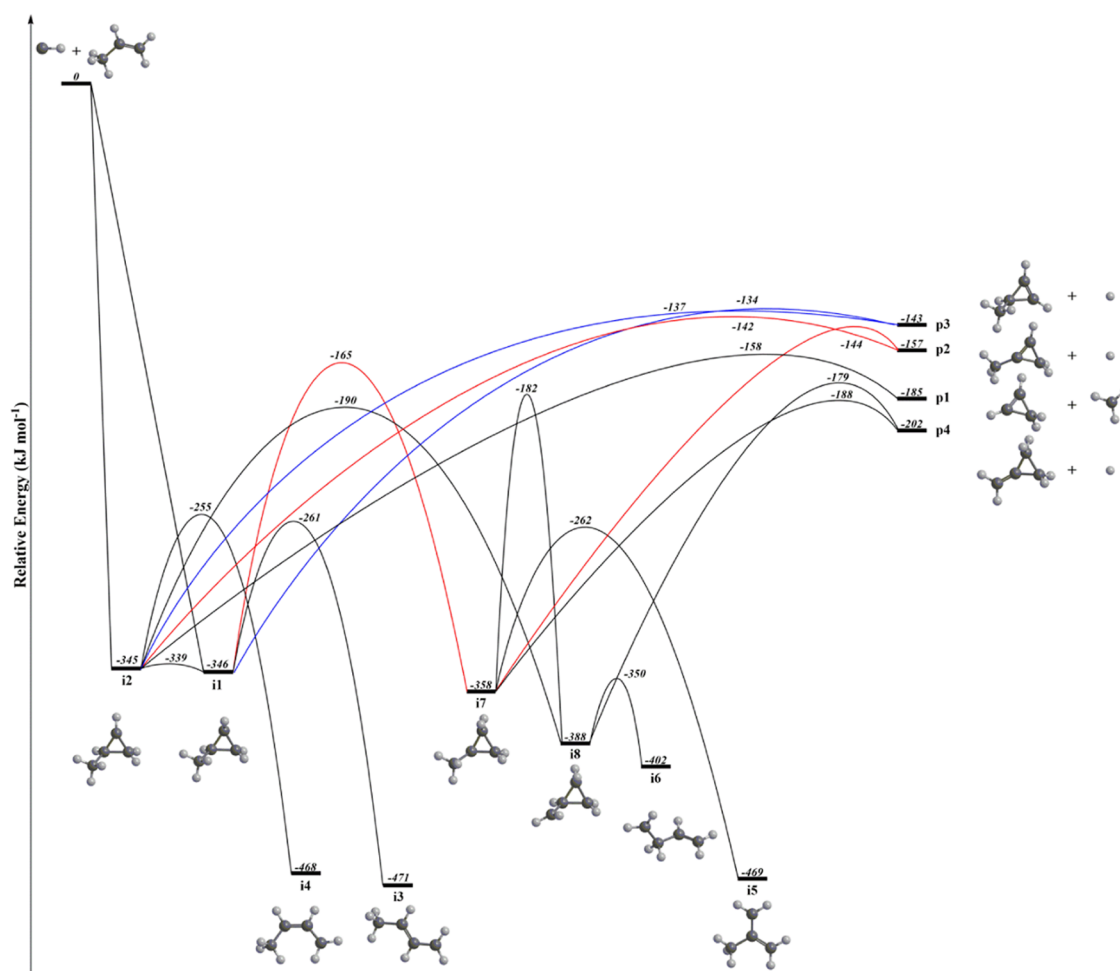


**Figure 3.** Best-fit center-of-mass translational energy ( $P(E_T)$ , upper) and angular ( $T(\theta)$ , lower) flux distributions of the reaction of the methylidyne radical with propylene to form  $C_4H_6$  molecule(s) and atomic hydrogen. The red lines reveal the best-fits; the shaded areas delimit the acceptable upper and lower error limits.  $E_{max}$  defines the maximum translational energy.

Here, we combine our experimental findings with the electronic structure and statistical calculations to reveal the underlying reaction mechanism(s) (Figures 4–6, Figures S1–S9, and Table 2). First, considering the overall reaction energies, 1-methylcyclopropene (**p2**,  $C_s$ ), 3-methylcyclopropene (**p3**,  $C_s$ ), methylenecyclopropane (**p4**,  $C_{2v}$ ), 1,3-butadiene (**p5**,  $C_{2h}$ ), 1,2-butadiene (**p6**,  $C_s$ ), 1-butyne (**p9**,  $C_s$ ), cyclobutene (**p10**,  $C_{2v}$ ), and 2-butyne (**p11**,  $D_{3d}$ ) isomers are formed along with atomic hydrogen in exoergic reactions, holding computed reaction energies of  $-157$ ,  $-143$ ,  $-202$ ,  $-284$ ,  $-234$ ,  $-229$ ,  $-235$ , and  $-250$   $\text{kJ mol}^{-1}$ , respectively. A comparison of these energies with the experimentally determined reaction energy of  $-168 \pm 25$   $\text{kJ mol}^{-1}$  suggests that the formation of 1-methylcyclopropene (**p2**) and 3-methylcyclopropene (**p3**) with reaction energies of  $-157$  and  $-143$   $\text{kJ mol}^{-1}$  correlates best with the computed data. Note that these  $C_4H_6$  isomers (**p2**–**p3**) are formed via the barrierless addition of the methylidyne radical to the double bond of propylene (Figure 4) as opposed to the insertion of methylidyne into C–H and C–C bonds under our experimental conditions. In a related reaction, Ribeiro and Mebel examined the probabilities of the entrance channels of the methylidyne (CH) radical with ethylene ( $C_2H_4$ ) reaction and proposed that the ratio between C–C double bond addition and C–H insertion is around 85:15.<sup>55</sup> Based on the chemical similarities of these two systems, methylidyne (CH) radical addition to the carbon–carbon double bond of

propylene is likely the dominant entrance channel as demonstrated below.

**4.1. Methylidyne Radical (CH) Addition to the Carbon–Carbon Double Bond.** The calculations reveal that the methylidyne radical (CH) can barrierlessly add to the carbon–carbon double bond of propylene, forming the initial adducts **i1** (*cis*- $CH_3$ - $cCH^{\bullet}CHCH_2$ ) and **i2** (*trans*- $CH_3$ - $cCH^{\bullet}CHCH_2$ ) (Figure 4). Both isomers can be interconverted easily due to a low-lying transition state of only 6  $\text{kJ mol}^{-1}$  above intermediate **i1** and 6  $\text{kJ mol}^{-1}$  above intermediate **i2**. The latter can eliminate the methyl group to form cyclopropene (**p1**) via a tight transition state lying 27  $\text{kJ mol}^{-1}$  above the separated products. What are the products of the hydrogen loss pathways of intermediates **i1** and **i2**? Intermediates **i1** and **i2** may eliminate atomic hydrogen from the CH group of the  $CH(CH_3)$  moiety yielding 1-methylcyclopropene (**p2**) via tight translation states located about 15  $\text{kJ mol}^{-1}$  above the separated products. The  $CH_2$  groups of **i1** and **i2** are also susceptible to hydrogen loss forming the 3-methylcyclopropene (**p3**) isomer. A hydrogen atom migration between the adjacent carbon atoms from the  $CH(CH_3)$  to the CH moiety in **i1** leads to **i7** ( $CH_3$ - $c^{\bullet}CCH_2CH_2$ ), whereas a hydrogen atom shift in **i2** from the methyl group to the CH moiety forms **i8** ( $^{\bullet}CH_2$ - $cCHCH_2CH_2$ ). Intermediates **i7** and **i8** are connected via a significant barrier of 176  $\text{kJ mol}^{-1}$  above **i7**; the decomposition of the latter may ultimately give rise to methylenecyclopropane (**p4**) via hydrogen atom loss from the  $CH_3$  group of **i7** and from the CH group of **i8**. 1-Methylcyclopropene (**p2**) can also be formed by a hydrogen atom emission from the  $CH_2$  group of **i7**. In brief, **p1** can be accessed via a methyl ( $CH_3$ ) group emission from intermediate **i2**. Product **p2** can be formed via three pathways with atomic hydrogen eliminated from the  $CH(CH_3)$  moiety of **i2** and/or from **i1** and after isomerization of **i1** to **i7** followed by atomic hydrogen loss from one of the  $CH_2$  moieties. An atomic hydrogen loss from the  $CH_2$  group of **i1** and/or of **i2** will lead to **p3**. There are two pathways resulting in **p4** by atomic hydrogen elimination originating from the CH group and/or from the  $CH_3$  group. Considering the experimentally derived reaction energy of  $-168 \pm 25$   $\text{kJ mol}^{-1}$ , 1-methylcyclopropene (**p2**) and 3-methylcyclopropene (**p3**) with reaction energies of  $-157$  and  $-143$   $\text{kJ mol}^{-1}$  are the most likely products. Most important, the results of our isotopic substitution experiments revealed that the hydrogen atom emission originated from the vinyl group of the propylene reactant. Figures S1–S9 trace the hydrogen versus deuterium loss in the isotopic substitution systems, methylidyne–propylene- $d_6$ , methylidyne- $d$  with propylene, and partially deuterated isotopologue ( $CD_3CHCH_2$ ) reactions. Here, the unimolecular decomposition of partially deuterated **i1** and **i2** from the methylene moiety of the vinyl group can account for the formation of **p3**. Likewise, the decomposition of **i1** and **i2** via hydrogen atom loss from the  $CH(CH_3)$  group can rationalize the formation of **p2**. Note that **i8** and hence the formation of **p4** can be ruled out since this pathway would require a hydrogen atom loss from the methyl group, which was not observed in the isotopically labeled experiments. Further, **i7** can likely be excluded as a decomposing complex to **p2** since both hydrogen atom and deuterium atom losses should be both observable. Hence, we can conclude that the lifetimes of **i1** and **i2** are too short to allow hydrogen shifts to form **i7** and **i8**, respectively.



**Figure 4.** Portion of the  $C_4H_7$  PES following CH radical addition to the carbon–carbon double bond of propylene. Pathways leading to **p2** and **p3** are colored in red and blue, respectively.

**4.2. Methylidyne Radical (CH) Insertion into the C–H Bonds of the Methyl and Methylidyne Moieties of Propylene.** Acyclic intermediates can be formed via the insertion of the methylidyne radical into terminal C–H single bonds (Figure 5). When CH is inserted into the terminal  $sp^2$  C–H bond of propylene of the  $CH_2$  moiety, intermediates **i4** (*cis*- $CH_3CHCH^{\bullet}CH_2$ ) and **i3** (*trans*- $CH_3CHCH^{\bullet}CH_2$ ) are formed. The ring opening in **i1** (*cis*- $CH_3-cCH^{\bullet}CHCH_2$ ) also leads to **i3** (*trans*- $CH_3CHCH^{\bullet}CH_2$ ), while **i4** (*cis*- $CH_3CHCH^{\bullet}CH_2$ ) can be accessed via the ring opening of **i2** (*trans*- $CH_3-cCH^{\bullet}CHCH_2$ ). Intermediate **i6** ( $^{\bullet}CH_2CH_2CHCH_2$ ) can be generated via CH insertion into any of the C–H bonds of the methyl group of propylene. Starting from intermediates **i3**, **i4**, and **i6**, hydrogen atom migrations between adjacent and nonadjacent carbon atoms are feasible. In brief, intermediates **i3**–**i6** and **i8**–**i15** are involved, eventually leading to multiple atomic hydrogen loss channels (**p5**–**p6**, **p9**–**p11**), the methyl group loss channel (**p13**), and the vinyl group emission pathway (**p7**). The computed reaction energies of five atomic hydrogen loss products (**p5**–**p6**, **p9**–**p11**) are  $-284$ ,  $-234$ ,  $-229$ ,  $-235$ , and  $-250$   $\text{kJ mol}^{-1}$ , respectively. These pathways are more exoergic than observed experimentally. Therefore, the products **p5**–**p6**, **p9**–**p11** may not be formed under our experimental condition. For instance, the isotopic labeling experiments revealed that **p5** is not formed; here, atomic hydrogen elimination from the

$CH_3$  group of **i3**, **i4** and/or from  $CH_2$  group of **i6** leading to 1,3-butadiene (**p5**) would require a hydrogen atom loss from the methyl group of the propylene reactant (Figures S2, S5, and S8); this is inconsistent with the aforementioned isotopic substitution experiments revealing that the hydrogen atom is emitted from the vinyl moiety. Further, for 1,2-butadiene (**p6**), the hydrogen atom had to be emitted from intermediate **i9**/**i10** from the methylidyne radical and/or from the  $CH_3$  group of the propylene reactant; likewise, atomic hydrogen emission can take place from **i12** accessed from **i6** and/or **i3**; these processes would require a hydrogen atom loss from the methylidyne radical and/or the methyl group of the propylene reactant. Considering the product 1-butyne (**p9**), the reaction sequence  $CH + C_3H_6 \rightarrow [i4 \rightarrow i12]/[i3 \rightarrow i12]/[i4 \rightarrow i6 \rightarrow i12]/[i3 \rightarrow i6 \rightarrow i12]/[i3 \rightarrow i14 \rightarrow i6 \rightarrow i12] \rightarrow p9 + H$  would require a hydrogen atom loss from the methylidyne radical and/or the methyl group of propylene. The pathways leading to **p6** and **p9** can be ruled out due to the mismatch with the isotopic substitution experiments.

**4.3. Methylidyne Radical (CH) Insertion into the CH Moiety of the Vinyl Group of Propylene.** The acyclic intermediate **i5** ( $CH_3C(^{\bullet}CH_2)CH_2$ ) may be formed via methylidyne radical (CH) insertion into the central C–H bond of propylene (Figure 6). Ring closure will lead to intermediate **i7** ( $CH_3-c^{\bullet}CH_2CH_2CH_2$ ), which is also connected to the section of the PES as shown in Figure 4. A





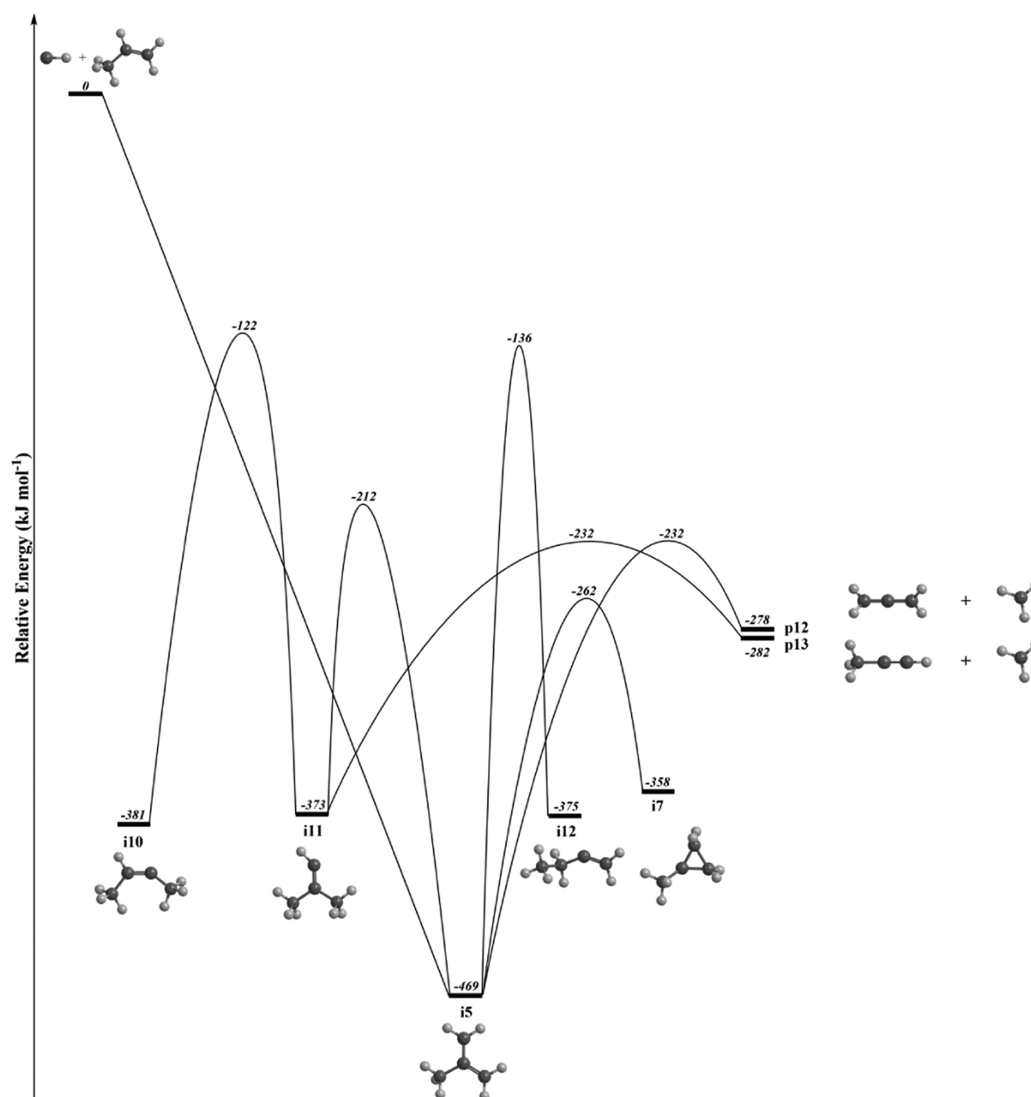


Figure 6. Portion of the  $C_4H_7$  PES corresponding to CH radical insertion into the C–H bond of the CH moiety of the vinyl group of propylene.

Table 2. Statistical Branching Ratios (%) for the Reaction of the Methylidyne (CH) Radical with Propylene ( $CH_3CHCH_2$ ) at Collision Energy  $E_C = 19.3 \text{ kJ mol}^{-1a}$

initial intermediate	i1	i2	i3	i4	i5	i6
	100	100	100	100	100	100
p1	1.2796	1.0229	0.0243	0.0246	0.0007	0.0025
p2	0.0701	0.0559	0.0013	0.0014	0.2155	0.0002
p3	0.2114	0.2008	0.0049	0.0049	0.0002	0.0005
p4	0.0094	0.0070	0.0010	0.0010	1.6341	0.0073
p5	83.4638	83.5392	80.4935	80.4319	0.087	16.1737
p6	1.4382	1.4335	1.0402	1.376	0.0030	0.1642
p7	12.7444	12.9762	17.4795	17.2215	0.1958	78.6169
p8	0.4653	0.4717	0.6431	0.59	0.0058	4.5521
p9	0.0812	0.0821	0.1129	0.142	0.0089	0.2873
p10	0.0145	0.0147	0.0199	0.0196	0.0002	0.1786
p11	0.0156	0.0157	0.022	0.0226	0.0	0.0015
p12	0.0949	0.0687	0.0022	0.0023	95.0226	0.0048
p13	0.1116	0.1115	0.1552	0.1623	2.8262	0.0106

<sup>a</sup>Here, p1–p13 are cyclopropene, 1-methylcyclopropene, 3-methylcyclopropene, methylenecyclopropane, 1,3-butadiene, 1,2-butadiene, ethylene, acetylene, 1-butyne, cyclobutene, 2-butyne, allene, and propyne.

our experimental data with ab initio electronic structure and statistical calculations, the methylidyne radical is revealed to

add barrierlessly to the carbon–carbon double bond of the propylene reactant, resulting in a cyclic doublet  $C_4H_7$

intermediate with a lifetime longer than its rotation period. These adducts undergo a nonstatistical, unimolecular decomposition via atomic hydrogen loss from the vinyl moiety of the propylene reactant through tight exit transition states forming the cyclic products 1-methylcyclopropene and 3-methylcyclopropene with overall reaction exoergicities of  $168 \pm 25$  kJ mol<sup>-1</sup>. Considering the experiments with partially deuterated reactants, insertion reactions of methylidyne radicals into C–C and C–H bonds of propylene could be ruled out; likewise, these studies reveal that the lifetime of the initial collision complexes is too low to allow any hydrogen migration and energy randomization to occur. These cyclic C<sub>4</sub>H<sub>6</sub> isomers are predicted to exist even in low-temperature environments such as cold molecular clouds like TMC-1, since the reaction is barrierless and exoergic, all transition states are below the energy of the separated reactants, and both the methylidyne radical (CH; X<sup>2</sup>Π) and propylene reactant were detected in cold molecular clouds such as TMC-1.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.9b09815>.

PES figures of isotopic reactions CD + CH<sub>3</sub>CHCH<sub>2</sub>, CH + CD<sub>3</sub>CHCH<sub>2</sub>, and CD + CD<sub>3</sub>CHCH<sub>2</sub>; portion of the C<sub>4</sub>H<sub>6</sub>D potential energy surface (PES) following CD radical addition and CD radical insertion to the carbon–carbon double bond and C–H bond of propylene (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Butler, R. G.; Glassman, I. Cyclopentadiene Combustion in a Plug Flow Reactor Near 1150 K. *Proc. Combust. Inst.* **2009**, *32*, 395–402.
- (2) McEnally, C. S.; Pfefferle, L. D. Species and Soot Concentration Measurements in a Methane/Air Nonpremixed Flame Doped with C<sub>4</sub> Hydrocarbons. *Combust. Flame* **1998**, *115*, 81–92.
- (3) Hansen, N.; Miller, J. A.; Taatjes, C. A.; Wang, J.; Cool, T. A.; Law, M. E.; Westmoreland, P. R. Photoionization Mass Spectrometric Studies and Modeling of Fuel-Rich Allene and Propyne Flames. *Proc. Combust. Inst.* **2007**, *31*, 1157–1164.
- (4) Yang, B.; Oßwald, P.; Li, Y.; Wang, J.; Wei, L.; Tian, Z.; Qi, F.; Kohse-Höinghaus, K. Identification of Combustion Intermediates in Isomeric Fuel-Rich Premixed Butanol–Oxygen Flames at Low Pressure. *Combust. Flame* **2007**, *148*, 198–209.
- (5) Yang, B.; Li, Y.; Wei, L.; Huang, C.; Wang, J.; Tian, Z.; Yang, R.; Sheng, L.; Zhang, Y.; Qi, F. An Experimental Study of the Premixed Benzene/Oxygen/Argon Flame with Tunable Synchrotron Photoionization. *Proc. Combust. Inst.* **2007**, *31*, 555–563.
- (6) Hansen, N.; Kasper, T.; Yang, B.; Cool, T. A.; Li, W.; Westmoreland, P. R.; Oßwald, P.; Kohse-Höinghaus, K. Fuel-Structure Dependence of Benzene Formation Processes in Premixed Flames Fueled by C<sub>6</sub>H<sub>12</sub> Isomers. *Proc. Combust. Inst.* **2011**, *33*, 585–592.
- (7) Li, W.; Law, M. E.; Westmoreland, P. R.; Kasper, T.; Hansen, N.; Kohse-Höinghaus, K. Multiple Benzene-Formation Paths in a Fuel-Rich Cyclohexane Flame. *Combust. Flame* **2011**, *158*, 2077–2089.
- (8) Marinov, N. M.; Pitz, W. J.; Westbrook, C. K.; Castaldi, M. J.; Senkan, S. M. Modeling of Aromatic and Polycyclic Aromatic Hydrocarbon Formation in Premixed Methane and Ethane Flames. *Combust. Sci. Technol.* **1996**, *116–117*, 211–287.
- (9) Lindstedt, R. P.; Skevis, G. Benene Formation Chemistry in Premixed 1,3-Butadiene Flames. *Symp. (Int.) Combust.* **1996**, *26*, 703–709.
- (10) Wu, C. H.; Kern, R. D. Shock-Tube Study of Allene Pyrolysis. *J. Phys. Chem. A* **1987**, *91*, 6291–6296.
- (11) Leung, K. M.; Lindstedt, R. P. Detailed Kinetic Modeling of C<sub>1</sub>–C<sub>3</sub> Alkane Diffusion Flames. *Combust. Flame* **1995**, *102*, 129–160.
- (12) Golan, A.; Ahmed, M.; Mebel, A. M.; Kaiser, R. I. A VUV Photoionization Study of the Multichannel Reaction of Phenyl Radicals with 1,3-Butadiene under Combustion Relevant Conditions. *Phys. Chem. Chem. Phys.* **2013**, *15*, 341–347.
- (13) Gu, X.; Zhang, F.; Kaiser, R. I. A Crossed Molecular Beam Study of the Phenyl Radical Reaction with 1,3-Butadiene and its Deuterated Isotopologues. *J. Phys. Chem. A* **2009**, *113*, 998–1006.
- (14) 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. USA* **2011**, *108*, 452–457.
- (15) 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.
- (16) Li, Y.; Liu, H.-L.; Zhou, Z.-J.; Huang, X.-R.; Sun, C.-C. Reaction Mechanism of CH + C<sub>3</sub>H<sub>6</sub>: A Theoretical Study. *J. Phys. Chem. A* **2010**, *114*, 9496–9506.
- (17) Loison, J.-C.; Bergeat, A. Rate Constants and the H Atom Branching Ratio of the Reactions of the Methylidyne CH(X<sup>2</sup>Π) Radical with C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>4</sub> (Methylacetylene and Allene), C<sub>3</sub>H<sub>6</sub> (Propene) and C<sub>4</sub>H<sub>8</sub> (Trans-Butene). *Phys. Chem. Chem. Phys.* **2009**, *11*, 655–664.
- (18) Mebel, A. M.; Kaiser, R. I. Formation of Resonantly Stabilised Free Radicals via the Reactions of Atomic Carbon, Dicarbon, and Tricarbon with Unsaturated Hydrocarbons: Theory and Crossed Molecular Beams Experiments. *Int. Rev. Phys. Chem.* **2015**, *34*, 461–514.
- (19) Miller, J. L. Theoretical Study of the Straight-Chain C<sub>4</sub>H<sub>7</sub> Radical Isomers and Their Dissociation and Isomerization Transition States. *J. Phys. Chem. A* **2004**, *108*, 2268–2277.
- (20) Morales, S. B.; Bennett, C. J.; Le Picard, S. D.; Canosa, A.; Sims, I. R.; Sun, B. J.; Chen, P. H.; Chang, A. H. H.; Kislov, V. V.; Mebel, A. M.; Gu, X.; Zhang, F.; Maksyutenko, P.; Kaiser, R. I. A Crossed Molecular Beam, Low-Temperature Kinetics, and Theoretical Investigation of the Reaction of the Cyano Radical (CN) with 1, 3-Butadiene (C<sub>4</sub>H<sub>6</sub>). A Route to Complex Nitrogen-Bearing Molecules in Low-Temperature Extraterrestrial Environments. *Astrophys. J.* **2011**, *742*, 26.
- (21) Sun, B. J.; Huang, C. H.; Chen, S. Y.; Chen, S. H.; Kaiser, R. I.; Chang, A. H. H. Theoretical Study on Reaction Mechanism of Ground-State Cyano Radical with 1,3-Butadiene: Prospect of Pyridine Formation. *J. Phys. Chem. A* **2014**, *118*, 7715–7724.
- (22) Trevitt, A. J.; Prendergast, M. B.; Goulay, F.; Savee, J. D.; Osborn, D. L.; Taatjes, C. A.; Leone, S. R. Product Branching Fractions of the CH + Propene Reaction from Synchrotron

Photoionization Mass Spectrometry. *J. Phys. Chem. A* **2013**, *117*, 6450–6457.

(23) Zhang, F.; Jones, B.; Maksyutenko, P.; Kaiser, R. I.; Chin, C.; Kislov, V. V.; Mebel, A. M. Formation of the Phenyl Radical- $[C_6H_5(X^2A_1)]$  under Single Collision Conditions: A Crossed Molecular Beam and Ab Initio Study. *J. Am. Chem. Soc.* **2010**, *132*, 2672–2683.

(24) 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.

(25) Huang, L. C. L.; Balucani, N.; Lee, Y. T.; Kaiser, R. I.; Osamura, Y. Crossed Beam Reaction of the Cyano Radical,  $CN(X^2\Sigma^+)$ , with Methylacetylene,  $CH_3CCH(X^1A_1)$ : Observation of Cyanopropyne,  $CH_3CCCN(X^1A_1)$ , and Cyanoallene,  $H_2CCCHCN(X^1A')$ . *J. Chem. Phys.* **1999**, *111*, 2857–2860.

(26) Balucani, N.; Asvany, O.; Kaiser, R. I.; Osamura, Y. Formation of Three  $C_4H_3N$  Isomers from the Reaction of  $CN(X^2\Sigma^+)$  with Allene,  $H_2CCCH_2(X^1A_1)$ , and Methylacetylene,  $CH_3CCH(X^1A_1)$ : A Combined Crossed Beam and Ab Initio Study. *J. Phys. Chem. A* **2002**, *106*, 4301–4311.

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

(28) Balucani, N.; Asvany, O.; Osamura, Y.; Huang, L. C. L.; Lee, Y. T.; Kaiser, R. I. Laboratory Investigation on the Formation of Unsaturated Nitriles in Titan's Atmosphere. *Planet. Space Sci.* **2000**, *48*, 447–462.

(29) Kaiser, R. I.; Stranges, D.; Lee, Y. T.; Suits, A. G. Neutral-Neutral Reactions in the Interstellar Medium. I. Formation of Carbon Hydride Radicals via Reaction of Carbon Atoms with Unsaturated Hydrocarbons. *Astrophys. J.* **1997**, *477*, 982–989.

(30) 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.

(31) Stahl, F.; Schleyer, P. vR.; Schaefer, H. F., III; Kaiser, R. I. Reactions of Ethynyl Radicals as a Source of  $C_4$  and  $C_5$  Hydrocarbons in Titan's Atmosphere. *Planet. Space Sci.* **2002**, *50*, 685–692.

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

(33) 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.

(34) Zhang, F.; Kaiser, R. I.; Kislov, V. V.; Mebel, A. M.; Golan, A.; Ahmed, M. A VUV Photoionization Study of the Formation of the Indene Molecule and its Isomers. *J. Phys. Chem. Lett.* **2011**, *2*, 1731–1735.

(35) Hidaka, Y.; Higashihara, T.; Ninomiya, N.; Masaoka, H.; Nakamura, T.; Kawano, H. Shock Tube and Modeling Study of 1,3-Butadiene Pyrolysis. *Int. J. Chem. Kinet.* **1996**, *28*, 137–151.

(36) Lockhart, J. P. A.; Goldsmith, C. F.; Randazzo, J. B.; Ruscic, B.; Tranter, R. S. An Experimental and Theoretical Study of the Thermal Decomposition of  $C_4H_6$  Isomers. *J. Phys. Chem. A* **2017**, *121*, 3827–3850.

(37) Lifshitz, A.; Tamburu, C.; Shashua, R. Decomposition of 2-Methylfuran. Experimental and Modeling Study. *J. Phys. Chem. A* **1997**, *101*, 1018–1029.

(38) Hidaka, Y.; Higashihara, T.; Ninomiya, N.; Oki, T.; Kawano, H. Thermal Isomerization and Decomposition of 1,2-Butadiene in Shock Waves. *Int. J. Chem. Kinet.* **1995**, *27*, 331–341.

(39) Hidaka, Y.; Higashihara, T.; Ninomiya, N.; Oshita, H.; Kawano, H. Thermal Isomerization and Decomposition of 2-Butyne in Shock Waves. *J. Phys. Chem. B* **1993**, *97*, 10977–10983.

(40) Goldaniga, A.; Faravelli, T.; Ranzi, E. The Kinetic Modeling of Soot Precursors in a Butadiene Flame. *Combust. Flame* **2000**, *122*, 350–358.

(41) Senosiain, J. P.; Miller, J. A. The Reaction of  $n$ - and  $i$ - $C_4H_5$  Radicals with Acetylene. *J. Phys. Chem. A* **2007**, *111*, 3740–3747.

(42) Miller, J. A.; Pilling, M. J.; Troe, J. Unravelling Combustion Mechanisms through a Quantitative Understanding of Elementary Reactions. *Proc. Combust. Inst.* **2005**, *30*, 43–88.

(43) Zheng, X. L.; Lu, T. F.; Law, C. K. Experimental Counterflow Ignition Temperatures and Reaction Mechanisms of 1,3-Butadiene. *Proc. Combust. Inst.* **2007**, *31*, 367–375.

(44) Dagaut, P.; Cathonnet, M. The Oxidation of 1,3-Butadiene: Experimental Results and Kinetic Modeling. *Combust. Sci. Technol.* **1998**, *140*, 225–257.

(45) Miller, J. A.; Melius, C. F. Kinetic and Thermodynamic Issues in the Formation of Aromatic Compounds in Flames of Aliphatic Fuels. *Combust. Flame* **1992**, *91*, 21–39.

(46) Lamprecht, A.; Atakan, B.; Kohse-Höör, K. Fuel-Rich Propene and Acetylene Flames: a Comparison of Their Flame Chemistries. *Combust. Flame* **2000**, *122*, 483–491.

(47) Tsang, W. Chemical Kinetic Data Base for Combustion Chemistry Part V. Propene. *J. Phys. Chem. Ref. Data* **1991**, *20*, 221–273.

(48) Hansen, N.; Klippenstein, S. J.; Taatjes, C. A.; Miller, J. A.; Wang, J.; Cool, T. A.; Yang, B.; Yang, R.; Wei, L.; Huang, C.; Wang, J.; Qi, F.; Law, M. E.; Westmoreland, P. R. Identification and Chemistry of  $C_4H_3$  and  $C_4H_5$  Isomers in Fuel-Rich Flames. *J. Phys. Chem. A* **2006**, *110*, 3670–3678.

(49) Schenk, M.; Hansen, N.; Vieker, H.; Beyer, A.; Götzhäuser, A.; Kohse-Höinghaus, K. PAH Formation and Soot Morphology in Flames of  $C_4$  Fuels. *Proc. Combust. Inst.* **2015**, *35*, 1761–1769.

(50) Wang, H.; Frenklach, M. Calculations of Rate Coefficients for the Chemically Activated Reactions of Acetylene with Vinylidene and Aromatic Radicals. *J. Phys. Chem. C* **1994**, *98*, 11465–11489.

(51) Nawdiyal, A.; Hansen, N.; Zeuch, T.; Seidel, L.; Mauss, F. Experimental and Modelling Study of Speciation and Benzene Formation Pathways in Premixed 1-Hexene Flames. *Proc. Combust. Inst.* **2015**, *35*, 325–332.

(52) Wang, H.; Frenklach, M. A Detailed Kinetic Modeling Study of Aromatics Formation in Laminar Premixed Acetylene and Ethylene Flames. *Combust. Flame* **1997**, *110*, 173–221.

(53) 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  $C(^3P_1)$  with Allene,  $H_2CCCH_2(X^1A_1)$ . *J. Chem. Phys.* **1999**, *110*, 10330–10344.

(54) Stahl, F.; Von Ragué Schleyer, P.; Bettinger, H. F.; Kaiser, R. I.; Lee, Y. T.; Schaefer, H. F., III. Reaction of the Ethynyl Radical,  $C_2H$ , with Methylacetylene,  $CH_3CCH$ , under Single Collision Conditions: Implications for Astrochemistry. *J. Chem. Phys.* **2001**, *114*, 3476–3487.

(55) Ribeiro, J. M.; Mebel, A. M. Reaction Mechanism and Product Branching Ratios of the  $CH + C_3H_6$  Reaction: A Theoretical Study. *J. Phys. Chem. A* **2016**, *120*, 1800–1812.

(56) 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.

(57) Gu, X.; Kaiser, R. I. Reaction Dynamics of Phenyl Radicals in Extreme Environments: a Crossed Molecular Beam Study. *Acc. Chem. Res.* **2009**, *42*, 290–302.

(58) Kaiser, R. I.; Parker, D. S. N.; Mebel, A. M. Reaction Dynamics in Astrochemistry: Low-Temperature Pathways to Polycyclic Aromatic Hydrocarbons in the Interstellar Medium. *Annu. Rev. Phys. Chem.* **2015**, *66*, 43–67.

(59) Gu, X.; Kaiser, R. I.; Mebel, A. M. Chemistry of Energetically Activated Cumulenes—from Allene ( $H_2CCCH_2$ ) to Hexapentaene ( $H_2CCCCCH_2$ ). *ChemPhysChem* **2008**, *9*, 350–369.

(60) Kaiser, R. I.; Hahndorf, I.; Huang, L. C. L.; Lee, Y. T.; Bettinger, H. F.; Schleyer, P. V. R.; Schaefer, H. F., III; Schreiner, P. R. Crossed Beams Reaction of Atomic Carbon,  $C(^3P_1)$ , with  $d_6$ -



- benzene,  $C_6D_6$  ( $X^1A_{1g}$ ): Observation of the Per-Deutero-1,2-Didehydro-Cycloheptatrienyl Radical,  $C_7D_5$  ( $X^2B_2$ ). *J. Chem. Phys.* **1999**, *110*, 6091–6094.
- (61) Kaiser, R. I.; Stranges, D.; Bevsek, H. M.; Lee, Y. T.; Suits, A. G. Crossed-Beam Reaction of Carbon Atoms with Hydrocarbon Molecules. IV. Chemical Dynamics of Methylpropargyl Radical Formation,  $C_4H_5$ , from Reaction of  $C(^3P_j)$  with Propylene,  $C_3H_6$  ( $X^1A$ ). *J. Chem. Phys.* **1997**, *106*, 4945–4953.
- (62) Kaiser, R. I.; Lee, Y. T.; Suits, A. G. Crossed Beam Reaction of  $C(^3P_j)$  with  $C_2H_2(^1\Sigma_g^+)$ : Observation of Tricarbon-Hydride  $C_3H$ . *J. Chem. Phys.* **1995**, *103*, 23.
- (63) Ngugen, T. L.; Mebel, A. M.; Kaiser, R. I. A Theoretical Investigation of the Triplet Carbon Atom  $C(^3P)$  plus Vinyl Radical  $C_2H_3(^2A')$  Reaction and Thermochemistry of  $C_3H_n$  ( $n = 1-4$ ) Species. *J. Phys. Chem. A* **2001**, *105*, 3284–3299.
- (64) Kaiser, R. I.; Chiong, C. C.; Asvany, O.; Lee, Y. T.; Stahl, F.; Von Ragué Schleyer, P.; Schaefer, H. F., III Chemical Dynamics of D1-Methyldiacetylene ( $CH_3CCCCD$ ;  $X^1A_1$ ) and D1-Ethynyllallene ( $H_2CCCH(C_2D)$ ;  $X^1A'$ ) Formation from Reaction of  $C_2D(X^2\Sigma^+)$  with Methylacetylene,  $CH_3CCH$  ( $X^1A_1$ ). *J. Chem. Phys.* **2001**, *114*, 3488–3496.
- (65) Marcelino, N.; Cernicharo, J.; Agúndez, M.; Roueff, E.; Gerin, M.; Martín-Pintado, J.; Mauersberger, R.; Thum, C. Discovery of Interstellar Propylene ( $CH_2CHCH_3$ ): Missing Links in Interstellar Gas-Phase Chemistry. *Astrophys. J.* **2007**, *665*, L127–L130.
- (66) Kaiser, R. I. Experimental Investigation on the Formation of Carbon-Bearing Molecules in the Interstellar Medium via Neutral–Neutral Reactions. *Chem. Rev.* **2002**, *102*, 1309–1358.
- (67) Thomas, A. M.; Zhao, L.; He, C.; Galimova, G. R.; Mebel, A. M.; Kaiser, R. I. Directed Gas-Phase Synthesis of Triafulvene under Single-Collision Conditions. *Angew. Chem., Int. Ed.* **2019**, *58*, 2–10.
- (68) Kaiser, R. I.; Gu, X.; Zhang, F.; Maksyutenko, P. Crossed Beam Reactions of Methylidyne [ $CH(X^2\Pi)$ ] with D2-Acetylene [ $C_2D_2(X^1\Sigma_g^+)$ ] and of D1-Methylidyne [ $CD(X^2\Pi)$ ] with Acetylene [ $C_2H_2(X^1\Sigma_g^+)$ ]. *Phys. Chem. Chem. Phys.* **2012**, *14*, 575–588.
- (69) Zhang, F.; Maksyutenko, P.; Kaiser, R. I. Chemical Dynamics of the  $CH(X^2\Pi) + C_2H_4(X^1A_{1g})$ ,  $CH(X^2\Pi) + C_2D_4(X^1A_{1g})$ , and  $CD(X^2\Pi) + C_2H_4(X^1A_{1g})$  Reactions Studied under Single Collision Conditions. *Phys. Chem. Chem. Phys.* **2012**, *14*, 529–537.
- (70) 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  $C_3H + H_2$  Channels. *Phys. Chem. Chem. Phys.* **2011**, *13*, 240–252.
- (71) Brink, G. O. Electron Bombardment Molecular Beam Detector. *Rev. Sci. Instrum.* **1966**, *37*, 857–860.
- (72) Daly, N. R. Scintillation Type Mass Spectrometer Ion Detector. *Rev. Sci. Instrum.* **1960**, *31*, 264–267.
- (73) Vernon, M. F. *Molecular Beam Scattering*. Ph.D. Dissertation, University of California at Berkeley: California, 1983.
- (74) Weiss, P. S. *The Reaction Dynamics of Electronically Excited Alkali Atoms with Simple Molecules*. Ph.D. Dissertation, University of California at Berkeley: California, 1985.
- (75) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; John Wiley & Sons, Ltd.: New York, NY, 1972.
- (76) Eyring, H.; Lin, S. H.; Lin, S. M. *Basic Chemical Kinetics*; John Wiley & Sons, Inc.: New York, 1980.
- (77) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Oxford University Press: Oxford, U.K., 1990.
- (78) He, C.; Zhao, L.; Thomas, A. M.; Morozov, A. N.; Mebel, A. M.; Kaiser, R. I. Elucidating the Chemical Dynamics of the Elementary Reactions of the 1-Propynyl Radical ( $CH_3CC$ ;  $X^2A_1$ ) with Methylacetylene ( $H_3CCCH$ ;  $X^1A_1$ ) and Allene ( $H_2CCCH_2$ ;  $X^1A_1$ ). *J. Phys. Chem. A* **2019**, *123*, 5446–5462.
- (79) 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.
- (80) Levine, R. D.; Bernstein, R. B.; Lee, Y. T. Molecular Reaction Dynamics and Chemical Reactivity. *Phys. Today* **1988**, *41*, 90–92.
- (81) Herschbach, D. R. Reactive Collisions in Crossed Molecular Beams. *Discuss. Faraday Soc.* **1962**, *33*, 149–161.
- (82) Ribeiro, J. M.; Mebel, A. M. Reaction Mechanism and Product Branching Ratios of the  $CH + C_3H_4$  Reactions: a Theoretical Study. *Phys. Chem. Chem. Phys.* **2017**, *19*, 14543–14554.
- (83) Goulay, F.; Trevitt, A. J.; Meloni, G.; Selby, T. M.; Osborn, D. L.; Taatjes, C. A.; Vereecken, L.; Leone, S. R. Cyclic versus Linear Isomers Produced by Reaction of the Methylidyne Radical ( $CH$ ) with Small Unsaturated Hydrocarbons. *J. Am. Chem. Soc.* **2009**, *131*, 993–1005.
- (84) Trevitt, A. J.; Goulay, F. Insights into Gas-phase Reaction Mechanisms of Small Carbon Radicals using Isomer-resolved Product Detection. *Phys. Chem. Chem. Phys.* **2016**, *18*, 5867–5882.
- (85) Prosen, E. J.; Maron, F. W.; Rossini, F. D. Heats of Combustion, Formation, and Isomerization of ten  $C_4$  Hydrocarbons. *J. Res. Natl. Bur. Stand.* **1951**, *46*, 106–112.
- (86) Wiberg, K. B.; Fenoglio, R. A. Heats of Formation of  $C_4H_6$  Hydrocarbons. *J. Am. Chem. Soc.* **1968**, *90*, 3395–3397.