Crossed-beam reaction of carbon atoms with hydrocarbon molecules. II. Chemical dynamics of \( n \text{-C}_4 \text{H}_3 \) formation from reaction of \( \text{C}^{(3P)} \) with methylacetylene, \( \text{CH}_3\text{CCH} (X^1A_1) \)

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The reaction between ground-state carbon atoms, \( \text{C}^{(3P)} \), and methylacetylene, \( \text{CH}_3\text{CCH} (X^1A_1) \), was studied at average collision energies of 20.4 and 33.2 kJ mol\(^{-1}\) using the crossed molecular beams technique. Product angular distributions and time-of-flight spectra of \( \text{C}_3\text{H}_3 \) at \( m/e = 51 \) were recorded. Forward-convolution fitting of the data yields weakly polarized center-of-mass angular flux distributions isotropic at lower, but forward scattered with respect to the carbon beam at a higher collision energy. The translational energy flux distributions peak at 30–60 kJ mol\(^{-1}\) and show an average fractional translational energy release of 22%–30%. The maximum energy release as well as the angular distributions are consistent with the formation of the \( n \text{-C}_3\text{H}_3 \) radical in its electronic ground state. Reaction dynamics inferred from these distributions indicate that the carbon atom attacks the \( \pi \)-orbitals of the methylacetylene molecule via a loose, reactant like transition state located at the centrifugal barrier. The initially formed triplet 1-methylpropendiylidene complex rotates in a plane almost perpendicular to the total angular momentum vector around the \( B\text{C}-\text{axes} \) and undergoes [2,3]-hydrogen migration to triplet 1-methylpropargylene. Within 1–2 ps, the complex decomposes via \( \text{C}–\text{H} \) bond cleavage to \( n\text{-C}_3\text{H}_1 \) and atomic hydrogen. The exit transition state is found to be tight and located at least 30–60 kJ mol\(^{-1}\) above the products. The explicit identification of the \( n\text{-C}_3\text{H}_3 \) radical under single collision conditions represents a further example of a carbon–hydrogen exchange in reactions of ground state carbon atoms with unsaturated hydrocarbons. This channel opens a versatile pathway to synthesize extremely reactive hydrocarbon radicals relevant to combustion processes as well as interstellar chemistry. © 1996 American Institute of Physics. [S0021-9606(96)00739-8]

I. INTRODUCTION

The interstellar medium (ISM) consists of gas and sub \( \mu \text{m} \) sized grain particles with averaged number densities of 1 H atom cm\(^{-3}\) and \( 10^{-11} \) grains cm\(^{-3}\). Its chemical composition is dominated by hydrogen and helium (H:He\( \approx 1:0.1 \)), whereas the biogenic elements oxygen, carbon, and nitrogen contribute \( \approx 0.001 \) relative to atomic hydrogen.\textsuperscript{1,2} Comprising approximately 99% neutrals and 1% ions, interstellar radicals, atoms, and molecules are not distributed homogeneously, but primarily localized in interstellar clouds as well as outflow of carbon stars.\textsuperscript{1,2} Diffuse (hot) clouds hold number densities \( n \) up to 100 molecules cm\(^{-3}\) and mean translational temperatures \( T \) of about 100 K, whereas in dense (cold, dark, molecular) clouds typical scenarios range between \( n = 10^2–10^6 \) cm\(^{-3}\) and \( T = 10–40 \) K. Molecules in the outflow of carbon stars contribute only a minor amount, but temperatures can rise up to 4000 K,\textsuperscript{3} and a more complex chemistry is expected as compared to interstellar clouds.

Since the average kinetic energy of the interstellar species is confined to typically 0.8 kJ mol\(^{-1}\) (diffuse clouds) and 0.08 kJ mol\(^{-1}\) (dark clouds), gas phase reactions under thermodynamic equilibrium conditions must have little or no barriers and involve only two body collisions. Ternary encounters occur only once in a few \( 10^9 \) years, and can be excluded considering mean interstellar cloud lifetimes of \( 10^6 \) years.\textsuperscript{4} The first chemical equilibrium models of interstellar chemistry satisfy these criteria and focus on ion-molecule reactions, radiative associations, as well as dissociative recombination between cations and electrons to advance interstellar chemistry.\textsuperscript{5,6} This approach, however, involves reaction chains with subsequent collisions, and often cannot reproduce observed structural isomer ratios as well as number densities for example of \( \text{C}_3\text{H}_7 \) and \( \text{C}_3\text{H}_2 \).\textsuperscript{7} The inclusion of alternative, one step, exothermic neutral–neutral reactions into chemical models of the circumstellar envelope surrounding the carbon star IRC+10216 and the dark cloud TMC-1 occurred only gradually.\textsuperscript{8–16} However, the \textit{ad hoc} postulation of spin conservation and simple thermochemistry clearly demonstrate the urgency of systematic laboratory examinations probing detailed chemical dynamics and reaction products of neutral–neutral encounters.

Very recently, these studies were initiated investigating exothermic atom-molecule reactions of atomic carbon in its \( ^3P_J \) electronic ground state with unsaturated hydrocarbons...
via the crossed beam technique as a potential source of carbon hydride and the propargyl radical.\(^\text{17}\)

\[
C(3\,P_{\text{j}}) + C_2H_2(X^1\Sigma_g^-) \rightarrow \text{1}e(?) - C_3H + H(2\,S_{1/2}),
\]

(1)

\[
C(3\,P_{\text{j}}) + C_2H_4(X^1A_g^-) \rightarrow C_3H_3(X^2B_2) + H(2\,S_{1/2}).
\]

(2)

The explicit identification of this carbon–hydrogen exchange channel opens a versatile synthetic pathway to carbon bearing species. Analogous to Eq. (1), reaction of \(C(3\,P_{\text{j}})\) with methylacetylene, \(CH_3CCH\), is expected to yield hitherto unobserved interstellar \(C_4H_3\) isomer(s)

\[
C(3\,P_{\text{j}}) + CH_3CCH(X^1A_1) \rightarrow C_4H_3 + H.
\]

(3)

Its prospective methylacetylene precursor and atomic carbon have been widely observed in the molecular clouds OMC-1 \(^\text{18}\) and TMC-1 \(^\text{19}\) with fractional abundances relative to hydrogen between \(4 \times 10^{-9}\) and \(6.3 \times 10^{-9}\). Likewise, methylacetylene \(^\text{20–22}\) as well as \(C_4H_3\) isomers are included in a photochemical model of Titan, Jupiter, and Saturn.\(^\text{23–24}\)

The authors postulate \(C_4H_3\) formation via three body recombination

\[
H + C_3H_2 + M \rightarrow M + C_4H_3,
\]

(4)

although cosmic ray produced carbon atoms survive the reducing atmospheres\(^\text{25}\) and might react via Eq. (3).\(^\text{26}\)

Besides its potential interstellar relevance, a scavenged \(C_4H_3\) isomer in acetylene/oxygen flames\(^\text{26}\) is expected to play a significant role in formation of the first aromatic ring in sooting combustion flames. Wang \textit{et al.} postulated a stepwise ring growth initiated by Eq. (5) or (6) to the phenyl radical or benzene\(^\text{27}\)

\[
n-C_3H_3 + C_2H_2 + M \rightarrow C_4H_3 + M,
\]

(5)

\[
n-C_4H_3 + C_2H_2 \rightarrow C_6H_4 + H,
\]

(6)

whereas Walsh outlined \(i-C_4H_3\) reacts with only a minor entrance barrier as well.\(^\text{28}\)

However, no reliable information is available on the mechanism of \(C_4H_3\) radical formation. Miller \textit{et al.} suggested pathways via Eqs. (7)–(10),\(^\text{29}\) followed by interconversion of \(i/n-C_4H_3\) \[Eq. (11)]

\[
C_3H_3 + CH_2 \rightarrow n-C_4H_3 + H,
\]

(7)

\[
l-C_3H_3 + CH \rightarrow i/n-C_4H_3 + H,
\]

(8)

\[
CH_2=CHCCH + OH \rightarrow H_2O + i/n-C_4H_3,
\]

(9)

\[
CH_2=CHCCH + H \rightarrow H_2 + i/n-C_4H_3,
\]

(10)

\[
i-C_4H_3 + H \rightarrow C_6H_4 \rightarrow n-C_4H_3 + H.
\]

(11)

Alternatively, acetylene dimerization [Eq. (12)],\(^\text{30–31}\) recombination with \(C_2H\) [Eq. (13)],\(^\text{32}\) and thermal decomposition of vinylacetylene intermediates [Eq. (14)]\(^\text{33–35}\) might yield \(C_4H_3\)

\[
2C_2H_2 \rightarrow H + i-C_4H_3,
\]

(12)

\[
C_2H + C_2H_2 \rightarrow i-C_4H_3,
\]

(13)

\[
CH_2=CHCCH \rightarrow i/n-C_4H_3 + H.
\]

(14)

Although atomic carbon is only a minor species in oxidative flames, it is assumed to contribute significantly to combustion chemistry.\(^\text{36}\) and the carbon–hydrogen exchange channel [Eq. (3)] could synthesize several \(C_4H_3\) isomers as well as advance diamond synthesis in methylacetylene flames.\(^\text{37}\)

However, despite the potential astrochemical and combustion relevance, the experimental as well as theoretical characterization of the \(C_4H_3\) PES is far from being complete. Fig. 1.\(^\text{n-C_4H_3 (1a/b) holds the global minimum on the doublet C_4H_3 PES (\(\Delta H = 486 \pm 3\) kJmol\(^{-1}\))\(^\text{28,38–39}\) followed by a 40±1 kJmol\(^{-1}\) less stable isomer (2) (\(\Delta H = 526 \pm 4\) kJmol\(^{-1}\)).\(^\text{28,38}\) The structure of \(n-C_4H_3\) has not yet been resolved. Gay \textit{et al.} calculated a bent, \(\alpha\)-ethylnvinyl carbon skeleton, whereas ESR studies in an argon matrix at 4 K support a linear structure with \(2B_2\) electronic ground state of the butatrienyl radical.\(^\text{40–41}\)

Very recently, high level \(ab\) \(\text{ini-tio}\) calculations at the SCF-CISD(6-311G**) level depict a quasilinear structure (1\(a\)) and an interconversion barrier between both bent \(C_4H_3\) conformations (1\(b\)) of only 3 kJmol\(^{-1}\).\(^\text{42}\) Since the \(C_4H_3\) isomers are extremely reactive, isolation is restricted to a low temperature matrix (\(n-C_4H_3\)) or trapping as an 1,3,3,5-trimetalated cyclic species (\(M_1\) as well as 1,3,3,5,7-trimetalated chain isomer (\(M_2\)).\(^\text{43–44}\)

In this paper, we investigate the detailed chemical dynamics of the atom-neutral reaction of \(C(3\,P_{\text{j}})\) with methylacetylene, \(CH_3CCH(X^1A_1)\) under single collision conditions at collision energies of 20.4 and 33.2 kJmol\(^{-1}\) as provided in crossed molecular beam experiments. The insights into the reaction dynamics disclose precise information on the hitherto unexplored triplet \(C_4H_3\) and doublet \(C_4H_3\) potential energy surface (PES) under well-defined collision energies, and potential exit channel(s) to \(C_4H_3\) isomers.

**II. EXPERIMENTAL SETUP AND DATA ANALYSIS**

Owing to the high reactivity of prospective open shell products, reactions must be performed under single collision conditions to identify the primary reaction products. These requirements are achieved here using a universal crossed molecular beam apparatus described in Ref. 45 in detail. A pulsed supersonic carbon beam was generated via laser ablation of graphite at 266 nm.\(^\text{46}\) The 30 Hz, 35–40 mJ output of a Spectra Physics GCR-270-30 Nd:YAG laser is focused onto a rotating carbon rod. Ablated carbon atoms are seeded onto neon or helium released by a Proch–Trickl pulsed valve operating at 60 Hz, 80 \(\mu\)s pulses, and 4 atm backing pressure. A four slot chopper wheel mounted 40 mm after the ablation zone selects a 9.0 Torr backing pressure pass through skimmers, and cross at 90° in the interaction region of the scattering.


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chamber. Reactively scattered products were detected in the plane of the beams using a rotatable detector consisting of a Brink-type electron-impact ionizer, quadrupole mass filter, and a Daly ion detector at different laboratory angles in 5.0° steps between 5.0° and 60.0° with respect to the carbon beam. The velocity distribution of the products was recorded using the time-of-flight technique choosing a channel width of 7.5 ms. Counting times ranged from 0.5–4 h.

FIG. 1. Structures of low lying \( \text{C}_4 \text{H}_3 \) isomers as well as metalated radicals M1 and M2. A linear isomer of Eq. (4), analogous to the \( \text{c/1} \)–\( \text{C}_3 \text{H} \) isomer pair, has not been investigated. Since \( \text{c/1} \) and \( \text{1} \)–\( \text{C}_3 \text{H} \) differ only by 8±4 kJ mol\(^{-1}\), the linear isomer (5) holds approximately \( \Delta H = 560 \text{ kJ mol}^{-1} \). Other enthalpies of formations for the isomers are (1) 486, (2) 526, (3) 541, (4) 553, (6) 572, (7) 604, (8) 613, (9) 660, and (10) 766 kJ mol\(^{-1}\).

chamber, Reactively scattered products were detected in the plane of the beams using a rotatable detector consisting of a Brink-type electron-impact ionizer, quadrupole mass filter, and a Daly ion detector at different laboratory angles in 5.0° steps between 5.0° and 60.0° with respect to the carbon beam. The velocity distribution of the products was recorded using the time-of-flight (TOF) technique choosing a channel width of 7.5 ms. Counting times ranged from 0.5–4 h.

**TABLE I.** Experimental beam conditions and 1σ errors averaged over the experimental time: Most probable velocity \( v_0 \), speed ratio \( S \), most probable relative collision energy, \( E_{\text{coll}} \), center-of-mass angle, \( \theta_{\text{CM}} \), composition of the carbon beam, and flux factor \( f_v \).

<table>
<thead>
<tr>
<th>Beam</th>
<th>( v_0 ), m/s(^{-1} )</th>
<th>( S )</th>
<th>( E_{\text{coll}} ), kJ mol(^{-1} )</th>
<th>( \theta_{\text{CM}} )</th>
<th>( C_1 : C_2 : C_3 )</th>
<th>( f_v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2 \text{H}_2 \text{}/ \text{Ne} )</td>
<td>1950±40</td>
<td>3.9±0.3</td>
<td>20.4±1.0</td>
<td>53.5±1.5</td>
<td>1:0.6:0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 \text{}/ \text{He} )</td>
<td>2560±50</td>
<td>4.7±0.3</td>
<td>33.2±1.4</td>
<td>46.2±1.6</td>
<td>1:0.4:0.9</td>
<td>1.8±0.3</td>
</tr>
<tr>
<td>( \text{C}_3 \text{H}_4 )</td>
<td>790±30</td>
<td>7.7±0.5</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>
averaged over several angular scans. The velocity of the supersonic carbon beam was monitored frequently after 2–5 angles and minor velocity drifts corrected by adjusting the laser pulse delay within ±1.5 μs. A reference angle was chosen at 55° and 45°, respectively, to calibrate fluctuating carbon beam intensities and mass dial settings at the quadrupole controller.

Information on the reaction dynamics is gained by fitting the TOF spectra and the product angular distribution in the laboratory frame using a forward-convolution routine. This iterative approach initially guesses the angular flux distribution \( T(\theta) \) and the translational energy flux distribution \( P(E_T) \) in the center-of-mass system (CM) assuming mutual independence. Laboratory TOF spectra and the laboratory angular distributions were then calculated from these \( T(\theta) \) and \( P(E_T) \) averaged over a grid of Newton diagrams defining the velocity and angular spread of each beam, detector acceptance angle, and the ionizer length. Best TOF and laboratory angular distributions were archived by iteratively refining adjustable \( T(\theta) \) and \( P(E_T) \) parameters.

### III. RESULTS

#### A. Reactive scattering signal

Reactive scattering signal was only observed at \( m/e = 51 \), i.e., \( \text{C}_4\text{H}_3 \), cf. Figs. 2–5 and Table II. Reaction of carbon with methylacetylene dimers does not contribute the data, since the integrated \( m/e = 51 \) signal scales linearly with the \( \text{CH}_3\text{CCH} \) source backing pressure. TOF spectra recorded at \( m/e = 48–50 \) show identical patterns indicating the signal originates in cracking of the parent in the detector. Energetically accessible channels 2 and 3 to diacetylene (Table II), \( \text{C}_4\text{H}_2 \), are absent within detection limits of our system, and endothermic channels 3 and 4 could not be opened at relative collision energies up to 33.2 kJ mol\(^{-1}\) applied in our experiments. In addition, no radiative association to \( \text{C}_4\text{H}_4 \) isomers at \( m/e = 52 \) or higher masses were observed. Lower molecular weight products bearing two or three carbon atoms (exo-

![Fig. 2](image-url)

**FIG. 2.** Lower: Newton diagram for the reaction \( \text{C}^3\text{P}_1 + \text{CH}_3\text{CCH}(X^1\text{A}_1) \) at a collision energy of 20.4 kJ mol\(^{-1}\). The circles stand for the maximum center-of-mass recoil velocity. From outer to inner: \( n\text{-C}_4\text{H}_3 \), \( i\text{-C}_4\text{H}_3 \), \( i\text{-C}_4\text{H}_3 \) isomers (3)–(8), and \( \text{C}_4\text{H}_3 \) isomer (9). Upper: Laboratory angular distribution of product channel at \( m/e = 51 \). Circles and 1σ error bars indicate experimental data, the solid lines the calculated distribution for the upper and lower carbon beam velocity (Table I). C.M. designates the center-of-mass angle. The solid lines originating in the Newton diagram point to distinct laboratory angles whose TOFs are shown in Fig. 4.

![Fig. 3](image-url)

**FIG. 3.** Lower: Newton diagram for the reaction \( \text{C}^3\text{P}_1 + \text{CH}_3\text{CCH}(X^1\text{A}_1) \) at a collision energy of 33.2 kJ mol\(^{-1}\). The circles are corrected for difference in the relative collision energy. Upper: Laboratory angular distribution of product channel at \( m/e = 51 \). Circles and 1σ error bars indicate experimental data, the solid lines the calculated distribution for the upper and lower carbon beam velocity. The solid lines originating in the Newton diagram point to distinct laboratory angles whose TOFs are shown in Fig. 5.
thermic channels 6–12) could not be verified yet. Their detection suffers from the high background level via methylacetylene fragmentation in the ionizer. Upper limits of detection are blurred out due to the velocity spread of the carbon beam (Table I). However, the scattering range of the \( m/e = 51 \) signal was derived.

**B. Laboratory angular distributions (LAB) and TOF spectra**

Figures 2 and 3 display the most probable Newton diagrams of the title reaction as well as the laboratory angular (LAB) distributions of the \( \text{C}_4\text{H}_3 \) product at collision energies of 20.4 and 33.2 kJ mol\(^{-1}\), respectively. Both LAB distributions peak close to the CM angles at 53.5° and 46.2° and show a slightly forward peaking distribution at higher collision energy. This behavior suggests indirect reaction dynamics via a long-lived \( \text{C}_4\text{H}_3 \) complex with a lifetime exceeding (20.4 kJ mol\(^{-1}\)) or comparable to its rotational period (33.2 kJ mol\(^{-1}\), oscillating complex). Since the enthalpy of formation of low lying \( \text{C}_4\text{H}_3 \) isomers differs only by about 30–50 kJ mol\(^{-1}\), Fig. 1, the nature of the \( \text{C}_4\text{H}_3 \) solely based on limiting circles is not possible. The maximum scattering range of isomers (1)–(8) falls within 8°, and individual limit circles are blurred out due to the velocity spread of the carbon beam (Table I). However, the scattering range of the \( m/e = 51 \) product allows us to eliminate isomer (9) and the endothermic channel to isomer (10). Further, the large width of the laboratory angular distribution of at least 60° and the \( \text{C}_4\text{H}_3 + \text{H} \) product mass ratio of 51 indicates that the average translational energy release \( (E_T) \) is large and that the center-of-mass translational energy distributions \( P(E_T) \) peak well away from zero, cf. Sec. III C.

**TABLE II. Thermochemistry of the reaction \( \text{C}(^3\text{P}_j) + \text{CH}_3\text{CCH} \rightarrow \text{X}_2 \).** Enthalpies of formations were taken from Refs. 28, 38, 39, 52, and 53. The symmetry of the \( n\text{-C}_4\text{H}_3 \) ground-state electronic wave function is omitted.

<table>
<thead>
<tr>
<th>#</th>
<th>Exit channel</th>
<th>Reaction enthalpy at 0 K, ( \Delta H ) (0 K), kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( n\text{-C}_4\text{H}_3(?) + \text{H}(^2\text{S}_1/2) )</td>
<td>(-194 \pm 1)</td>
</tr>
<tr>
<td>2</td>
<td>( \text{HCCCH}(X^1\Sigma^+)+\text{H}(X^1\Sigma^+) )</td>
<td>(-444 \pm 12)</td>
</tr>
<tr>
<td>3</td>
<td>( \text{HCCCH}(X^1\Sigma^+)+2\text{H}(^2\text{S}_1/2) )</td>
<td>(-12 \pm 12)</td>
</tr>
<tr>
<td>4</td>
<td>( \text{C}_4\text{H}(X^2\Sigma^+) + \text{H}_2(X^1\Sigma^+) )</td>
<td>(+78 \pm 10)</td>
</tr>
<tr>
<td>5</td>
<td>( \text{C}_4\text{H}(X^2\Sigma^+) + \text{CH}(X^2\Pi) )</td>
<td>(+68 \pm 15)</td>
</tr>
<tr>
<td>6</td>
<td>( \text{C}_4\text{H}(X^2\Sigma^+) + \text{CH}_2(X^2\Pi_1) )</td>
<td>(+35 \pm 12)</td>
</tr>
<tr>
<td>7</td>
<td>( \text{C}_4\text{H}(X^2\Sigma^+) + \text{CH}_2(X^2\Pi_2) )</td>
<td>(+35 \pm 12)</td>
</tr>
<tr>
<td>8</td>
<td>( \text{C}_4\text{H}(X^2\Pi_2) + \text{CH}_2(X^2\Pi_2) )</td>
<td>(-36 \pm 4)</td>
</tr>
<tr>
<td>9</td>
<td>( \text{C}_4\text{H}(X^2\Pi_2) + \text{CH}_2(X^2\Pi_1) )</td>
<td>(-28 \pm 4)</td>
</tr>
<tr>
<td>10</td>
<td>( \text{C}_4\text{H}(X^2\Pi_2) + \text{CH}_2(X^2\Pi_1) )</td>
<td>(-6 \pm 1)</td>
</tr>
<tr>
<td>11</td>
<td>( \text{C}_4\text{H}(X^2\Pi_1) + \text{CH}_2(X^2\Pi_1) )</td>
<td>(-30 \pm 6)</td>
</tr>
<tr>
<td>12</td>
<td>( \text{C}_4\text{H}(X^2\Pi_1) + \text{CH}_2(X^2\Pi_1) )</td>
<td>(-440 \pm 1)</td>
</tr>
</tbody>
</table>
C. Center-of-mass translational energy distributions, $P(E_T)$

Figures 6 and 7 present the translational energy distributions $P(E_T)$ and angular distributions $T(\theta)$ in the center-of-mass frame. Both LAB distributions and TOF data were fitted with a single $P(E_T)$ extending to a maximum translational energy release $E_{\text{max}}$ of 110–170 kJmol$^{-1}$ and 225–255 kJmol$^{-1}$, respectively. If the energetics of distinct isomers are well separated, $E_{\text{max}}$ can be used to identify individual C$_4$H$_3$ isomers. The maximal translational energy releases, i.e., the sum of the reaction exothermicity and relative collision energy, were already presented in Figs. 2 and 3 with a reasonable approximation of rotationally and vibrationally cold methylacetylene molecules prepared in the supersonic expansion. The production of the $n$–C$_4$H$_3$ isomer at 33.2 kJmol$^{-1}$ is evident by comparing the theoretical and experimental high energy cutoff of $P(E_T)$ with $E_{\text{max}}$ (exp.; 33.2 kJmol$^{-1}$)=225–255 kJmol$^{-1}$ vs $E_{\text{max}}$(theor.; 33.2 kJmol$^{-1}$)=226±7 kJmol$^{-1}$. Formation of the 40 kJmol$^{-1}$ less stable iso isomer can be rejected, since the maximum energy release is restricted to 186 kJmol$^{-1}$. Based entirely on the high energy cutoff, the reactive scattering product at lower collision energy is hard to identify, since all C$_4$H$_3$ isomers (2)–(6) fall within the $E_{\text{max}}$ range. Due to the internal excitation of the C$_4$H$_3$ product, even Eq. (1) cannot be ruled out, cf. Sec. III D.

Besides identification of structural isomers, the most probable translational energy yields the order-of-magnitude of the barrier height in the exit channel. Both $P(E_T)$'s peak away from zero as expected from the LAB distributions and depict a broad plateau between 30–60 kJmol$^{-1}$. A barrier is further implied by the large fraction of energy channeled into translational motion of the C$_4$H$_3$ and H products, i.e., 22±5% and 30±3% at lower and higher collision energy, respectively. These findings suggest a tight transition state with a significant change in electronic structure as the C$_4$H$_4$ complex decomposes.

D. Center-of-mass angular distributions, $T(\theta)$

At lower collision energy, $T(\theta)$ is isotropic and symmetric around $\pi/2$ implying that either the fragmenting C$_4$H$_4$ holds a lifetime longer than its rotational period $\tau_1$ or that the exit transition state is symmetric. With increasing collision energy, the center-of-mass angular distribution peaks forward with respect to the carbon beam. These findings indicate a reduced lifetime of the decomposing C$_4$H$_4$ complex and agrees with our suggested osculating complex: a com-
plex formation takes place, but the well depth along the reaction coordinate is too shallow to allow multiple rotations, and the complex decomposes with a random lifetime distribution before one full rotation elapses. Based on the intensity ratio of $T(\theta)$ at $\theta=0^\circ$ and $180^\circ$ of 1.7$\pm$0.1, the identification of the fragmenting complex enables us to use the rotational period of the complex as a molecular clock to estimate its lifetime (cf. Sec. IV D). To explain the forward-peaking, the carbon atom and the leaving hydrogen atom must further be situated on opposite sites of the rotation axis of the fragmenting complex.

The weak polarization of all $T(\theta)$s can be explained solely based on total angular momentum conservation and angular momentum disposal.\textsuperscript{17,54,55} In terms of a classical treatment, the total angular momentum $\mathbf{J}$ is given by

$$ \mathbf{J}=\mathbf{L}+\mathbf{j}=\mathbf{L}'+\mathbf{j}', \quad (15) $$

with the initial and final orbital angular momentum $\mathbf{L}$ and $\mathbf{L}'$ perpendicular to the initial and final relative velocity vectors $\mathbf{v}$ and $\mathbf{v}'$, and $\mathbf{j}$ and $\mathbf{j}'$ the rotational angular momenta of reactants and products. Since bulk experiments indicate that the reaction of $\text{C}(^3P_j)$ with $\text{CH}_3\text{CCH}$ proceeds within orbiting limits\textsuperscript{56} and our relative cross sections rise with decreasing collision energy (Sec. III E), an upper limit of the impact parameter, $b_{\text{max}}$, is determined via the classical capture theory.\textsuperscript{56,57} Approximating the Lennard-Jones coefficient $C_6$ according to Hirschfelder et al.\textsuperscript{58} and using the ionization potentials $E_{\text{IC}(^3P_j)}=11.76$ eV, $E_{\text{IC\text{CH}_3}}=10.36$ eV, and polarizabilities $\alpha_{\text{IC}(^3P_j)}=1.76 \times 10^{-30}$ m$^3$, $\alpha_{\text{IC\text{CH}_3}}=6.18 \times 10^{-30}$ m$^3$\textsuperscript{52}, $b_{\text{max}}$ gives rise to $b_{\text{max}}(20.4 \text{ kJmol}^{-1})=3.8$ Å and $b_{\text{max}}(33.2 \text{ kJmol}^{-1})=3.2$ Å. The maximum orbital angular momentum yields $L_{\text{max}}(20.4 \text{ kJmol}^{-1})=116h$ and $L_{\text{max}}(33.2 \text{ kJmol}^{-1})=125h$. Since $\text{CH}_3\text{CCH}$ is produced in a supersonic expansion and $j$ peaks at $2\text{--}4h$ for typical rotational temperatures between 20 and 40 K, $j$ contributes less than 2.5% to the total angular momentum $\mathbf{J}$, and Eq. (15) reduces to

$$ \mathbf{L} \approx \mathbf{L}'+\mathbf{j}'. \quad (16) $$

To justify the weak $T(\theta)$ polarization, $\mathbf{L}$ and $\mathbf{L}'$ must be uncoupled with $\mathbf{j} \approx \mathbf{j}'$, and the initial orbital angular momentum becomes the final rotational angular momentum. This weak $\mathbf{L} \approx \mathbf{L}'$ correlation is a direct result of the inability of the departing H atom to carry significant orbital angular momentum. On the other hand, a strong $\mathbf{L} \approx \mathbf{L}'$ correlation would have indicated that the complex decomposed with $\mathbf{L}' \approx \mathbf{j}'$, but the expected $(\sin \theta)^{-1}$ shaped $T(\theta)$ at 20.4 kJmol$^{-1}$ is clearly not observed.

E. Flux contour maps and total relative cross sections

Figures 8 and 9 show center-of-mass flux contour maps $I(\theta,E_T) \sim T(\theta) \times P(E_T)$ for collision energies at 20.4 and 33.2 kJmol$^{-1}$. Data at lower collision energy depict a forward–backward symmetric flux profile as expected from the center-of-mass angular distribution. With increasing collision energy, the pronounced forward peaking on the relative velocity vector is evident. Integrating this flux distribution and correcting for the reactant flux as well as relative reactant velocity, we find a total, relative cross section ratio of $(20.4 \text{ kJmol}^{-1})/(33.2 \text{ kJmol}^{-1})=1.7 \pm 0.4$. This finding together with recent bulk experiments\textsuperscript{56} suggest a barrierless, attractive long-range dispersion forces dominating the C–H$_3$CCH interaction as well as a loose, reactant-like transition state located at the centrifugal barrier to the triplet C$_3$H$_4$ PES at about 3 Å.

F. Energy partition of total available energy

The identification of the $n$-C$_3$H$_3$ isomer allows us to estimate partition of the total available energy, $E_{\text{tot}}$, into product translation, $E_{\text{tr}} \propto (E_T)$. Even if the butatrienyl structure resembles only an inversion transition state, the 3 kJmol$^{-1}$ barrier can be easily overcome at experimental conditions applied here. The quasilinear n-C$_3$H$_3$ radical holds the rotational constants $A=10.17$ cm$^{-1}$, $B=0.139$ cm$^{-1}$, and $C=0.137$ cm$^{-1}$ and classify it as a highly prolate asymmetric top with asymmetry parameter $\kappa=-0.9996$, Fig. 10. Hence, we approximate the rotational levels to those of a rigid symmetric top\textsuperscript{17} using the rotational quantum number $J=116$ ($E_{\text{coll}}=20.4$ kJmol$^{-1}$) and $J=125$ ($E_{\text{coll}}=33.2$ kJmol$^{-1}$) cf. Sec. III D, and calculate the component of the rotational angular momentum about the principal axis $K$ with $K=0$ for no rotation about the figure axis, but perpendicular to it, and...
to two \( \pi \)-orbitals at one carbon atom. The observed CM angular and translational energy distributions are then compared to what is expected based on these channels. Pathways incompatible with experimental data are dismissed. Since no \( \text{C}_2 \text{H}_4 \) intermediate fulfills requirements for intersystem crossing,\(^\text{17}\) the discussion is restricted to the triplet surface. However, neither \textit{ab initio} nor experimental enthalpies of formations of triplet \( \text{C}_2 \text{H}_4 \) isomers are available, and their energetics are approximated based on corresponding triplet \( \text{C}_2 \text{H}_3 \) isomers.\(^\text{59-65}\)

### A. \( \text{C}_4 \text{H}_4 \) potential energy surface

Addition of \( \text{C}(^3P_f) \) to two perpendicular \( \pi \)-orbitals at the methylacetylene \( \alpha \text{-C} \) atom (the neighboring carbon atom to the methyl group) yields triplet \( s\text{-cis}/\text{trans} \) 2-methylpropadienylidene (11)/(12), Fig. 11, whereas attack to the \( \beta \text{-C} \) atom forms triplet \( s\text{-trans}/\text{cis} \) 1-methylpropadienylidene (13)/(14). Since trans-propadienylidene is energetically favored by about 80 kJmol\(^{-1}\) as compared to the \textit{cis} isomer on the triplet \( \text{C}_4 \text{H}_4 \) surface, this difference is adapted to \textit{cis} (11)/(14) vs \textit{trans} (12)/(13) isomers. Further, we approximate identical enthalpies of formations of (11)/(14) \( (\Delta H = 815 \text{ kJmol}^{-1}) \) and (12)/(13) \( (\Delta H = 735 \text{ kJmol}^{-1}) \). (13)/(14) undergo [2,1]-H-migration to triplet 1-methylpropadienylidene (15), [2,3]-H-rearrangement to triplet 1-methylpropargylen (16), ring closure to triplet methylyclopentadienylidene (17), or \textit{direct} \textit{C–H} fragmentation to the linear \( \text{C}_4 \text{H}_3 \) isomer (5). Two remaining channels are energetically not accessible: H loss of the methyl group yields a \( 1,3,3\)\textit{-triradical} which—if it existed—suffers ring closure to a \textit{tri} or \textit{tetra} cycle which is less stable than the already closed channel to (10); the [1,2] methyl group migration to triplet 2-methylpropadienylidyn (19) is endothermic by 150 kJmol\(^{-1}\). Similar to (13)/(14), (11)/(12) might react via [2,3] or [2,1] CH\(_3\)-migration to (16) and (15), respectively. Besides addition to \( \alpha \text{-C} \)-atom, \( \text{C}(^3P_f) \) might add to both \( \alpha \text{-} \) and \( \beta \text{-C} \)-atoms of the methylacetylene molecule, generating methylyclopentadienylidene (17).

Furthermore, \( \text{C}(^3P_f) \) insertion into the acetylenic \textit{C–H} as well as the \textit{C–C} single bond might lead to triplet methylpropargylen (16), whereas insertion into the aliphatic \textit{C–H} bond of the methyl group forms a triplet carbene (20). The fate of (15)–(17) is governed by \textit{C–H} fragmentation and/or H-migration: (17) decomposes via \textit{C–H} bond rupture to (4) or (3), then rearranges to triplet methylycyclopentene (21), which is followed by H-loss to (3) or (6); the only energetically feasible fragmentation of (15) yields \( \text{C}_2 \text{H}_3 \) isomer (5), whereas (16) decomposes either to (5) or \( \text{n-C}_4 \text{H}_3 \) (1). Finally, (15) might rearrange via hydrogen migration to triplet vinylidenecarben (22).

The reaction pathway to the identified \( \text{n-C}_4 \text{H}_3 \) radical (Sec. III C) can only proceed via hydrogen loss from the \( \text{CH}_3 \) group of triplet 1-methylpropargylen (16). Here, the preference of the methyl \textit{H}-atom loss compared to the acetylenic \textit{C–H} bond cleavage even at higher collision energy correlates with the \( \sim 140 \text{ kJmol}^{-1} \) weaker aliphatic carbon-hydrogen bond energy and excludes decomposition of (16) to \( \text{C}_2 \text{H}_3 \) isomer (5). Additionally, the identification

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**FIG. 10.** Principal rotation axis of the butatrienyl radical. The \( C \)-axis is perpendicular to the paper plane.

\( K = J \) for a fast rotation about the principal axis, with a slow end-over-end one. Since no data on the \( K \)-distributions are available, we use the same procedure as applied for the \( \text{C}(^3P_f) + \text{C}_2 \text{H}_4 \) system\(^\text{17}\) and calculate first the rotational energy assuming \( K = 0 \) ("low \( K \) approximation"). This gives us the maximal vibrational energy release \( E_{\text{vib}} \) in the \( n\text{-C}_4 \text{H}_3 \) radical. Hereafter, the highest energetically accessible \( K \) states \( K_{\text{max}} \) are computed assuming \( E_{\text{vib}} = 0 \text{ kJmol}^{-1} \) to estimate an upper limit of the product rotational excitation as well as an order of magnitude of the lowest tilt angle \( \alpha_{\text{min}} \) of the \( n\text{-C}_4 \text{H}_3 \) principal inertial axis with respect to \( \mathbf{j} \) in terms of the classical vector model.\(^\text{17}\)

The low \( K \) approximation yields a nearly constant partitioning of total energy into rotational degrees of freedom at both collision energies, i.e., \( 21 \pm 2 \text{ kJmol}^{-1} (10 \pm 1\%) \) vs \( 26 \pm 3 \text{ kJmol}^{-1} (11 \pm 2\%) \). Further, the fraction of the maximum vibrational energy release stays constant within the error limits (68 \( \pm 20\% \) and 59 \( \pm 10\% \); 145 kJmol\(^{-1}\) at lower and 133 kJmol\(^{-1}\) at higher collision energy) and might suggest a lifetime long enough to randomize the energy into the vibrational modes of the \( \text{C}_4 \text{H}_4 \) complex. Finally, even in the limit of zero vibrational excitation of the \( n\text{-C}_4 \text{H}_3 \) product and a maximum \( K \) value, the principal axis is tilted \( 73^\circ - 76^\circ \) with respect to \( \mathbf{j} \) and clearly demonstrates a predominant end-over-end-rotation of the \( n\text{-C}_4 \text{H}_3 \) radical.

### IV. DISCUSSION

In this section, we outline feasible reaction pathways on the triplet \( \text{C}_2 \text{H}_4 \) PES to produce \( \text{C}_3 \text{H}_3 \) isomers (1)–(6) via insertion of the electrophile carbon atoms into the \textit{C–H} and \textit{C–C} bonds of methylacetylene, addition to two \( \pi \)-molecular orbitals at both distinct carbon atoms, and, finally, addition
FIG. 11. (a) Schematic representation of the lowest energy pathways on the triplet C₄H₄ PES and structures of potentially involved collision complexes. Triplet methylenecyclopropene and vinylacetylene are not included, since their singlet-triplet gaps have not been investigated yet. (b) Additional structures for possible intermediates and products relevant to the discussion. Three potential electronic structures of propargylene are presented: 1,3-diradical (16a) and carben-like structures (16b/c). Isomers (11)–(14) are named with respect to atoms/groups at the former acetylenic triple bond.
of Eq. (16) as the decomposing complex eliminates the possibility the symmetric $T(\theta)$ originates from a symmetric complex (Sec. III D), since rotation around any principal axis cannot fulfill this requirement. The remaining question to be solved is the reaction pathway to (16). Insertion of $C(3P_j)$ into the acetylenic C–H bond can be rejected, since only a narrow range of impact parameters between 1.19 and 2.24 Å would contribute to reactive scattering signal. The overwhelming contribution of large impact parameters to the capture process up to 3.8 Å was already mentioned in Sec. III D and III E. Additionally, no evidence of insertion was found in the crossed beam reaction of $C(3P_j)$ with unsubstituted acetylene indicating that the symmetry-forbidden insertion into the acetylenic C–H bond involves a barrier of at least 33.2 kJmol$^{-1}$. Insertion into the C–C single bond can be excluded as well: The forward peaking center of mass angular distribution requires the inserted carbon atom and the leaving hydrogen to be located on opposite sides of the rotation axis of fragmenting (16). However, this condition is not satisfied. In addition, hot atom tracer experiments of $^{11}C(3P_j)$ with $C_2H_6$ and even strained cyclobutane rings show a screening of the C–C bond by hydrogen atoms, and only insertion into C–H bonds is observed. Therefore, any insertion process can be excluded from the discussion.

Remaining pathways to (16) involve triplet $C_4H_3$ intermediates (11)–(14). Using the concept of regioselectivity of electrophilic radical attacks on substituted olefines and extending it to alkynes, we can eliminate further collision complexes. The framework predicts the radical attack to be directed at the carbon center which holds the highest spin density. Since partial delocalization of the methyl $\pi$-group orbitals increases the spin density on the $\beta$-C-atom at the expense of the $\alpha$-position, $C(3P_j)$ attacks preferentially at the $\beta$-C. Additionally, the sterical hindrance of the CH$_3$ group reduces the cone of acceptance at the $\alpha$-C-atom and the range of reactive impact parameters. Both effects together direct the electrophilic carbon addition to (13)/(14). Even if (11) and (12) were formed to a minor extent, rearrangement to (16) would involve a CH$_3$-group ($m=15$) migration which is unfavorable compared to rearrangement of the light H atom to (16) via (12)/(13). Similar arguments eliminate a simultaneous attack of $C(3P_j)$ to $\alpha$- and $\beta$-C-atom with maximum impact parameters of about 0.6 Å to (17). Both prevailing pathways to (16) via (13) and (14) cannot be discriminated based on our experimental data. The chemical dynamics to alternative $C_4H_3$ isomers at lower collision energy involve isomers (13)–(15), (17), or (20). The last one can be ruled out, since insertion of $C(3P_j)$ into the aliphatic C–H bond does not play a role. Results of crossed beam experiments $C(3P_j) + CH_4$ at relative collision energies up to 40 kJmol$^{-1}$ show no reactive scattering signal of insertion into the aliphatic C–H bond. Therefore—if (2) contributes—hydrogen loss of triplet vinylacetylene (22) represents the only open channel.

**B. Rotation axis of the triplet 1-methylpropargylene complex**

Conserving the C-C-C-C-plane as a plane of symmetry, the singly occupied $p_x$ and $p_y$ orbitals of the carbon atom might add to the $\pi_\alpha$ and $\pi_\beta$-orbitals under $C_3$ symmetry on the $^3A''$ surface to form isomers (13)/(14), Fig. 12. This pathway supports a maximum orbital overlap to the C-C-$\sigma$- and C-C-$\pi$-bond via interaction of $p_z$ with $\pi_\alpha$ as well as $p_z$ with $\pi_\beta$-orbitals. Oblique approach geometries are supported as well and open larger impact parameters for the reaction as discussed in Sec. III E. Since $L \approx J$, the four carbon atoms rotate in a plane approximately perpendicular to $L$ around the $C$-axis of the prolate 1-methylpropendiylidene. The consecutive hydrogen shift to 1-methylpropargylene conserves either the symmetry plane [assuming $C_1$ symmetry of (16b) or (16c), Fig. 12] or follows $C_1$ symmetry (geometry (16a)). Since the adduct still rotates around the $C$-axis, the added carbon atom in the C4 position and the methyl hydrogens are located on opposite sides of the rotation axis as required to explain the forward-peaking $C_3H_4$ product with respect to the carbon beam. This almost in-plane rotation yields extremely low $K$ values as well as a minor $J$ component about the

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**FIG. 12.** Approach geometry of the carbon atom toward the methylacetylene molecule conserving $C_3$ symmetry and induced rotation around the $B$-axis.
figure axis of the 1-methylpropargylene and can be related to
dominating low K states populated in the n-C4H3 product
(Sec. III F).

An alternative C(3Pj) trajectory under C1 symmetry on the
'A' surface might induce rotations about the A, B, and C
axes of 1-methylpropadienyldiene and—after H migration—of 1-methylpropargylene, but does not support a max-
imum overlap of both perpendicular p*- with p-orbitals. Fur-
thermore, a freely rotating CH3 group in (16) undermines
A-like rotations, since its hydrogen atoms rotate to the same
side as the incorporated carbon atom. Hence, the required
forward-peaked T(θ) cannot be supplied.

C. Lifetime of the triplet 1-methylpropargylene
complex

The rotational period of the 1-methylpropargylene com-
plex can act as a clock in the molecular beam experiment and
can be used to estimate the lifetime τ of the decomposing
complex at a relative collision energy of 33.2 kJmol−1. The
osculating model relates the intensity ratio of T(θ) at both
doles to τ via Eq. (17)

\[ I(180°)/I(0°) = \exp\left(-\frac{t_{rot}}{2\tau}\right), \]

where \( t_{rot} \) represents the rotational period with:

\[ t_{rot} = 2\pi I_i/L_{max}. \]  

\( I_i \) represents the moment of inertia of the complex rotating
around the i-axis, and \( L_{max} \) the maximum orbital angular
momentum. Using the \textit{ab initio} geometries of propargylene
and a C–CH3 distance in (16) of 1.47 Å, we can estimate the
rotational period of the methylpropargylene complex: around
the A axis we find \( t_{rot}(A)=0.01–0.02 \) ps, and around the
B/C axis we obtain \( t_{rot}(B,C)=1–2 \) ps. Plugging in all data
in Eq. (17) yields a lifetime of the triplet
1-methylpropargylene complex equal to one rotational pe-
riod. The absolute value of \( \tau \) depends dramatically on the
rotation axis, i.e., B, C vs A. Since reactions with a collision
time \(<0.1 \) ps follow direct scattering dynamics, the \( T(θ) \) at
33.2 kJmol−1 relative collision energy should be strongly
forward peaked, if the complex rotated around the A-axis.
Our data show only a moderate peaked center-of-mass angular
distribution at 33.2 kJmol−1 and an isotropic one at 22.4
kJmol−1. Therefore, rotation about the A axis can be elim-
nated as already suggested in Sec. IV B, and end-over-end
rotation around the B- or C-axis of (16) takes place. Due to
the optimal orbital overlap (Sec. IV B), C-like rotations
should dominate. Compared to the forward peaked \( T(θ) \) as
found in the crossed beam reaction C(3Pj)+C2H2→C2H+H
at a relative collision energy of 8.8 kJmol−1, the enhanced
complex lifetime is a direct consequence of the additional 9
vibrational modes of the CH3 group. A similar behavior con-
tributes to the increased lifetime of the triplet 1-methylallene
complex [crossed beam reaction C(3Pj)+C2H6
→C2H5+→C3H5+ (Ref. 69)] vs triplet allene [crossed beam
reaction C(3Pj)+C2H4→C3H4→C3H3+H (Ref. 69)].

D. Exit transition state

The partitioning of the total available energy into the transla-
tional, rotational, and vibrational degrees of freedom of
the n-C4H3 radical as well as the collision energy depen-
dent \( P(E_T) \) shape reveal information on the exit transition
state. The framework of an ideal RRKM system requires that
exit channel interactions, i.e., the coupling between the re-
action coordinate (translation) and internal motion beyond the
critical configuration, must be small. This condition is only
fulfilled in loose transition states, implying the reverse reac-
tion of H+n-C4H3 to 1-methylpropargylene holds no en-
trance barrier. As shown in Sec. III C, the exit transition state
is located at least 30–60 kJmol−1 above the products,
indicating that the C–H bond rupture in triplet
1-methylpropargylene does not follow the patterns of an
ideal RRKM system with a loose transition state. On the
other hand, Marcus’ tight transition state theory quantifies a
rising fraction of total available energy into vibration with
increasing collision energy, if the decomposing triplet C4H3
complex has many degrees of freedom. Both \( P(E_T) \)'s clearly
underline a tight transition state, but within our error limits,
a complete energy randomization cannot be proved or dis-
proved. These deviations from the loose transition state are
based on dynamical effects during the separation of frag-
ments into products together with a significant geometry
change from the triplet 1-methylpropargylene complex. Comparing the bond orders (BO) of n-C4H3, Fig. 1 (1a/b)
with those of methylpropargylene, Fig. 11 (16a–c), supports
this approach: In the case of a propargylene-like, 1-3 di-
riangular (16a), the C–C bond orders change from two times 2.5
and 1.0 to an acetylenic (BO=3), olefinic (BO=2) and
shifted aliphatic C–C bond (BO=1). If (16) exists as a tri-
plet carbene (16b/c), the conversion of the C–C single bond
located at the carbene center to a partially delocalized C=C
bond increases the bond strength by ~250 kJmol−1. Finally,
an isotropic \( T(θ) \) distribution as compared to the forward
peaked distribution seen in the reaction
\[ C(3Pj)+C2H2→C2H+H \]  
(Ref. 16) implies the additional modes of the CH3 group induce the long-lived complex behavior and that the energy randomization in the collision complex might be complete.

E. Alternative isomers at lower collision energy

Based on our experimental results, any of the pathways
to C3H3 isomers (2)–(6) might show additional contributions
at lower collision energy. The electron density change of
each triplet C3H3 complex fragmenting to (3)–(6) suggest a
tight transition state as expected from the center of mass
translational energy distribution. Since the relative collision
energy increases by only 10 kJmol−1, formation of only one
isomer of (2)–(6) with no n-C4H3 formation is hard to ex-
plain. The isotropic center-of-mass angular distribution might
open a potential two channel fit of n-C4H3 and a sec-
ond C3H3 isomer as well. However, neither transition state
frequencies are available, and the experimental data alone
cannot resolve this question.
V. IMPLICATIONS TO INTERSTELLAR CHEMISTRY AND COMBUSTION PROCESSES

The crossed beam setup represents a versatile tool to study reaction products as well as chemical dynamics of neutral–neutral reactions relevant to combustion processes and interstellar chemistry under well-defined reactant conditions. Here, the explicit identification of the $n$-C$_4$H$_3$ radical under single collision conditions depicts a third example of the carbon–hydrogen exchange channel in the reaction of C$(^3P_j)$ with unsaturated hydrocarbons studied recently in our lab.\textsuperscript{17}

\begin{align}
C(^3P_j) + C_2H_2(X^1Σ^+g) & → C_2H + H(^2S_{1/2}), \quad (19) \\
C(^3P_j) + C_2H_4(X^1A_1) & → 1-C_3H_3(^2B_2) + H(^2S_{1/2}). \quad (20)
\end{align}

This reaction class presents an alternative to ion-molecule reactions to synthesize carbon-chain molecules in the interstellar medium\textsuperscript{7,17} and strictly excludes the formation of any C$_3$H$_2$ isomer via

\begin{equation}
C(^3P_j) + C_3H_4 → C_2H_2 + 2H, \quad (21)
\end{equation}

as postulated based on thermochemistry and spin conservation\textsuperscript{14} underlining the need of systematic laboratory studies to establish a well-defined data base for neutral–neutral reaction products. A rising cross section with decreasing translation energy underlines the potential contribution of these processes in interstellar clouds and should encourage astronomers to search for lighthiero undetected C$_3$H$_2$ isomers perhaps among unidentified microwave transitions in the spectrum toward the extended ridge of OMC-1. Since deuterated methylacetylenes (CH$_3$CCD and CH$_3$DCCH) were identified in OMC-1 and TMC-1, formation of partially deuterated C$_2$H$_2$D is expected to take place as well. Terrestrial based microwave spectra of C$_2$H$_2$ radicals could be simply recorded during RF discharges of CH$_3$CCCH/He/CO-mixtures.

Likewise, the identification of the $n$-C$_4$H$_3$ radical under single collision conditions as well as via trapping experiments in oxygen rich hydrocarbon flames\textsuperscript{26} validates inclusion of hydrocarbon radicals even in oxidative flames. Further investigations of C$(^3P_j)$ reactions with unsaturated hydrocarbons are in progress and will supply a new set of reactions as well as products to be incorporated into combustion models.

VI. CONCLUSIONS

The reaction between ground state carbon atoms, C$(^3P_j)$, and methylacetylene, CH$_3$CCH, was studied at average collision energies of 20.4 and 33.2 kJmol$^{-1}$ using the crossed molecular beam technique. The carbon atom attacks the $τ$-orbitals of the CH$_3$CCH molecule via a loose, reactant like transition state located at the centrifugal barrier. The highest symmetric approach follows $C_1$ symmetry on the ground state $^3A_1^\prime$ surface. The initially formed 1-methylpropendiyldene complex rotates in a plane almost perpendicular to the total angular momentum vector $J$ around its $C_3$-axis and undergoes hydrogen migration to 1-methylpropargylene. Within 1–2 ps, the complex decomposes via hydrogen emission to $n$-C$_3$H$_3$. The exit transition state is found to be tight and located at least 30–60 kJmol$^{-1}$ above the products. The explicit identification of the $n$-C$_3$H$_3$ radical under single collision represents a further example of a carbon–hydrogen exchange in reactions of ground-state carbon atoms with unsaturated hydrocarbons. This channel opens a versatile pathway to synthesize extremely reactive hydrocarbon radicals relevant to combustion processes as well as interstellar chemistry.

\textit{Note added in proof.} The assignment of the symmetry of the electronic wave function for C$_2$ is molecules follows the convention that the molecular plane is defined as the mirror plane, e.g., C$_3$H$_3(^2B_2)$ instead of C$_3$H$_3(^2B_1)$.

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