Crossed-beam reaction of carbon atoms with hydrocarbon molecules. V. Chemical dynamics of $n$-$\text{C}_4\text{H}_3$ formation from reaction of $\text{C}(^3P_j)$ with allene, $\text{H}_2\text{CCCH}_2(X^1A_1)$

R. I. Kaiser$^a$\textsuperscript{a)}

University of California, Department of Chemistry, Berkeley, California 94720, and Academia Sinica, Institute of Atomic and Molecular Sciences, 1, Section 4, Roosevelt Road, Taipei, 106, Taiwan, Republic of China, and Department of Physics, Technical University Chemnitz-Zwickau, 09107 Chemnitz, Germany

A. M. Mebel$^b$

Academia Sinica, Institute of Atomic and Molecular Sciences, 1, Section 4, Roosevelt Road, Taipei, 106, Taiwan, Republic of China and Department of Chemistry, Tankang University, Tansui 25137, Taiwan, Republic of China

A. H. H. Chang$^c$ and S. H. Lin$^d$

Academia Sinica, Institute of Atomic and Molecular Sciences, 1, Section 4, Roosevelt Road, Taipei, 106, Taiwan, Republic of China

Y. T. Lee$^e$

University of California, Department of Chemistry, Berkeley, California 94720, and Academia Sinica, Institute of Atomic and Molecular Sciences, 1, Section 4, Roosevelt Road, Taipei, 106, Taiwan, Republic of China

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The crossed molecular beams technique was employed to investigate the reaction between ground state carbon atoms, $\text{C}(^3P_j)$, and allene, $\text{H}_2\text{CCCH}_2(X^1A_1)$, at two averaged collision energies of 19.6 and 38.8 kJ mol$^{-1}$. Product angular distributions and time-of-flight spectra of $\text{C}_4\text{H}_3$ 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 maximum translational energy release and the angular distributions combined with ab initio and RRKM calculations are consistent with the formation of the $n$-$\text{C}_4\text{H}_3$ radical in its electronic ground state. The channel to the $i$-$\text{C}_4\text{H}_3$ isomer contributes less than 1.5%. Reaction dynamics inferred from the experimental data indicate that the carbon atom attacks the $\pi$-orbitals of the allenic carbon–carbon double bond barrierless via a loose, reactant-like transition state located at the centrifugal barrier. The initially formed cyclopropylidene derivative rotates in a plane almost perpendicular to the total angular momentum vector around its C-axis and undergoes ring opening to triplet butatriene. At higher collision energy, the butatriene complex decomposes within 0.6 ps via hydrogen emission to form the $n$-$\text{C}_4\text{H}_3$ isomer and atomic hydrogen through an exit transition state located 9.2 kJ mol$^{-1}$ above the products. The explicit identification of the $n$-$\text{C}_4\text{H}_3$ 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 barrierless route to synthesize extremely reactive hydrocarbon radicals in combustion processes, interstellar chemistry, and hydrocarbon-rich atmospheres of Jupiter, Saturn, Titan, and as well as Triton.

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I. INTRODUCTION

The chemical reactivity and formation of distinct structural isomers of hydrocarbon radicals is of major importance in combustion chemistry,\textsuperscript{1} chemical processes in hydrocarbon-rich planetary atmospheres,\textsuperscript{2} and outflow of dying carbon stars as well as interstellar clouds and hot molecular cores.\textsuperscript{3} In oxygen-deficit combustion flames, for example, only $i/n$-$\text{C}_4\text{H}_3$ isomers are expected to play a crucial role in formation of the first aromatic ring, the phenyl radical $\text{C}_6\text{H}_5$, via the three body reaction $i/n$-$\text{C}_4\text{H}_3$+$\text{C}_2\text{H}_2$+$\text{M}$→$\text{C}_6\text{H}_5$+$\text{M}$. Here, $\text{M}$ represents the third body collision partner, $i$- and $n$-the iso and normal $\text{C}_4\text{H}_3$ isomers, respectively.\textsuperscript{4} On the other hand, cyclic $\text{C}_4\text{H}_3$ isomers are expected not to form aromatic species. In addition, $\text{C}_4\text{H}_3$ isomers together with other hydrocarbon radicals are likely to be formed in extraterrestrial environments such as cold, molecular clouds and planetary atmospheres of Jupiter, Saturn, Uranus, and Neptune as well as the moons Titan and Triton.$^5$ Recent support is based on the observation of the carbon–hydrogen exchange channel in crossed-beam reactions of atomic carbon $C(^3P_j)$ with unsaturated hydrocarbons, cf. reactions (1)–(5).$^6$
C(3P_j) + C_2H_2(X^1Σ^+_g) → C_3H(X^2Π_{1/2}) + H^2S_{1/2},
\rightarrow c-C_3H(X^2B_2) + H^2S_{1/2}, \quad (1)
C(3P_j) + C_2H_4(X^1A_g) → C_3H_3(X^2B_2) + H^2S_{1/2}, \quad (2)
C(3P_j) + CH_3CCH(X^1A_1) → C_4H_3(X^2A^*) + H^2S_{1/2}, \quad (3)
C(3P_j) + C_3H_3(X^1A^*) → C_4H_3(X^2B_2^2A^*) + H^2S_{1/2}, \quad (4)
C(3P_j) + C_3H_3(X^2B_2) → C_4H_3(X^1Σ^+_g) + H^2S_{1/2}. \quad (5)

In this paper, we elucidate the intimate chemical dynamics of the atom-neutral reaction of C(3P_j) with a second C_3H_4 isomer, allene H_2CCCH_2(X^1A_1) under single collision conditions at two collision energies of 19.6 kJ mol\(^{-1}\) and 38.8 kJ mol\(^{-1}\). Our findings are compared with the reaction of C(3P_j) with methylacetylene, CH_3CCH(X^1A_1) studied earlier. Energy-dependent, triply differential cross sections are derived from the experimental data and then combined with state-of-the-art \textit{ab initio} and RRKM calculations to reveal unprecedented information on poorly explored triplet C_3H_4 and doublet C_4H_3 potential energy surfaces (PESs). These findings expose likely reaction pathways to hitherto unobserved extraterrestrial C_3H_4 isomer(s) and unravel potential synthetic routes to these radicals in combustion flame chemistry.

**II. EXPERIMENTAL SETUP**

The experiments were performed under single collision conditions using a universal crossed molecular beams apparatus described in Ref. 7 in detail. A pulsed supersonic carbon beam was generated via laser ablation of graphite at 266 nm.\(^8\) The 30 Hz, 40 mJ output of a Spectra Physics GCR-270-30 Nd:YAG laser was focused onto a rotating carbon rod, and the ablated carbon atoms were seeded into 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 selected a 9.0 \(\mu\)s segment of the seeded carbon beam. Table I summarizes the experimental beam conditions. The carbon beam and a pulsed allene beam hold at 660±5 Torr backing pressure passed through skimmers and crossed at 90° in the interaction region of the scattering chamber. The reactively scattered products were detected in the plane defined by both beams using a rotatable detector consisting of a Brink-type electron-impact ionizer,\(^9\) quadrupole mass filter, and a Daly ion detector at laboratory angles in 2.5° and 5.0° steps between 10.0° 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 \(\mu\)s. Information on the chemical dynamics of the reaction was gained by fitting the TOF spectra and the product angular distribution in the laboratory frame (LAB) using a forward-convolution routine.\(^10\) This approach initially assumes an angular flux distribution \(T(θ)\) and the translational energy flux distribution \(P(E_{T})\) in the center-of-mass system (CM). Laboratory TOF spectra and the laboratory angular distributions were then calculated from these \(T(θ)\) and \(P(E_{T})\) averaged over the apparatus and beam functions. Best TOF and laboratory angular distributions were archived by iteratively refining adjustable \(T(θ)\) and \(P(E_{T})\) parameters.

**III. \textit{AB INITIO} AND RRKM CALCULATIONS**

The geometries of the reactants, products, various intermediates, and transition states for the C(3P_j) + H_2CCCH_2 reaction were optimized using the hybrid density functional B3LYP method, i.e., Becke’s three-parameter nonlocal exchange functional\(^11\) with the nonlocal correlation functional of Lee, Yang, and Parr,\(^12\) and the 6-311G(d,p) basis set.\(^13\) Vibrational frequencies, calculated at the B3LYP/6-311G(d,p) level, were used for characterization of stationary points, zero-point energy (ZPE) correction, and for the RRKM calculations. All the stationary points were positively identified for minimum (number of imaginary frequencies \(\text{NIMAG}=0\)) or transition state (\(\text{NIMAG}=1\)). In some cases, geometries and frequencies were recalculated at the MP2/6-311G(d,p) and CCSD(T)/6-311G(d,p) level.\(^14\)

In order to obtain more reliable energies, we used the G2M(RCC,MP2)\(^15\) method, a modification of the Gaussian-2 [G2(MP2)] approach.\(^16\) The total energy in G2M(RCC,MP2) is calculated as follows:

\[
E[\text{G2M(RCC,MP2)}] = E[\text{RCCSD(T)/6-311G(d,p)}] + \Delta E(+3df2p) + \Delta E(\text{HLC}) + \text{ZPE}[\text{B3LYP/6-311G(d,p)}].
\]

where

\[
\Delta E(+3df2p) = E[\text{MP2/6-311+G(3df,2p)}] - E[\text{MP2/6-311G(d,p)}]
\]

and the empirical “higher level correction”

\[
\Delta E(\text{HLC}) = -5.25n_β - 0.19n_α.
\]
FIG. 1. Lower: Newton diagram for the reaction \( \text{C}(^3P_J) + \text{H}_2\text{CCCH}_2 \) at a collision energy of 19.6 kJ mol\(^{-1}\). The circle stands for the maximum center-of-mass recoil velocity of the \( \nu\text{-C}_4\text{H}_3 \) isomer assuming no energy channels into the internal degrees of freedom. Upper: Laboratory angular distribution of product channel at \( m/e = 51 \). Circles and \( 1\sigma \) error bars indicate experimental data, the solid lines the calculated distribution. 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. 3.

![Image of Newton diagram and laboratory angular distribution](image1.png)

FIG. 2. Lower: Newton diagram for the reaction \( \text{C}(^3P_J) + \text{H}_2\text{CCCH}_2 \) at a collision energy of 38.8 kJ mol\(^{-1}\). The circle stands for the maximum center-of-mass recoil velocity of the \( \nu\text{-C}_4\text{H}_3 \) isomer assuming no energy channels into the internal degrees of freedom. Upper: Laboratory angular distribution of product channel at \( m/e = 51 \). Circles and \( 1\sigma \) error bars indicate experimental data, the solid lines the calculated distribution. 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.

![Image of Newton diagram and laboratory angular distribution](image2.png)

FIG. 3. Time-of-flight data at \( m/e = 51 \) for indicated laboratory angles at a collision energy of 19.6 kJ mol\(^{-1}\). Open circles represent experimental data, the solid line the fit. TOF spectra have been normalized to the relative intensity at each angle.

![Image of time-of-flight data for 35.0° and 50.0°](image3.png)

FIG. 4. Time-of-flight data at \( m/e = 51 \) for indicated laboratory angles at a collision energy of 38.8 kJ mol\(^{-1}\). Open circles represent experimental data, the solid line the fit. TOF spectra have been normalized to the relative intensity at each angle.

![Image of time-of-flight data for 40.0°, 55.0°, 45.0°, and 60.0°](image4.png)
G2M(RCC, MP2) method gives the averaged absolute deviation of 4.8 kJ mol⁻¹ of calculated atomization energies from experiment for 32 first-row G2 test compounds. The GAUSSIAN 94,¹⁷ MOLPRO 96,¹⁸ and ACES-II¹⁹ programs were employed for the potential energy surface computations. In this paper, we present only those results necessary to understand our experimental data. All details are given in a forthcoming publication.²⁰

According to the quasi-equilibrium theory or RRKM theory,²¹ rate constant $k(E)$ at a collision energy $E$ for a unimolecular reaction $A^\# \rightarrow P$ can be expressed as

$$k(E) = \frac{\sigma}{\hbar} \frac{W^\#(E-E^\#)}{\rho(E)},$$

where $\sigma$ is the symmetry factor, $W^\#(E-E^\#)$ denotes the total number of states of the transition state (activated complex) $A^\#$ with the barrier $E^\#$, $\rho(E)$ represents the density of states of the energized reactant molecule $A^\#$, and $P$ is the product or products. The saddle point method²¹ was applied to evaluate $\rho(E)$ and $W(E)$. A simple scheme²² where the barrier along the reaction coordinate was assumed as an inverted parabola was applied to incorporate the tunneling corrections to the RRKM rate constants at the lower collision energy of 19.6 kJ mol⁻¹.

### IV. RESULTS

#### A. Reactive scattering signal

Reactive scattering signal was observed at $m/e = 51$, i.e., C₄H₃, cf. Figs. 1–4. TOF spectra were recorded at lower $m/e$ values 50–48 as well but show identical TOF patterns. This finding indicates that the signal at these $m/e$ ratios originates in cracking of the C₄H₃ parent in the ionizer and that channels 2–5 are absent under our experimental conditions, cf. Table II. In addition, no radiativeassociations to C₄H₄ ($m/e = 52$) could be detected, indicating that internally excited C₄H₄ collision complexes do not survive under single collision conditions employed in our experiments. Finally, no higher masses than $m/e = 51$ from reaction of C₂ and C₃ clusters were observed.

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

The most probable Newton diagrams of the title reaction as well as the laboratory angular (LAB) distributions of the C₄H₃ product are displayed in Figs. 1 and 2 at collision energies of 19.6 and 38.8 kJ mol⁻¹, respectively. At lower collision energy, the LAB distribution peaks close to the CM angle of 55.0°. As the collision energy rises, the LAB distribution shows a slightly forward peaking at 40.0° compared to the CM angle of 44.2°. This result hints to indirect reactive scattering dynamics through a long-lived C₄H₄ complex with a lifetime exceeding (19.6 kJ mol⁻¹) or comparable to its rotational period (38.8 kJ mol⁻¹, oscillating complex). Further, both LAB distributions are very broad and extend to at least 50.0° in the scattering plane. This order-of-magnitude together with the C₄H₃+H product mass ratio of 51 points out that the averaged translational energy release $\langle E_T \rangle$ in the products is large and that the center-of-mass translational energy distributions $P(E_T)$’s peak away from zero, cf. Sec. IV C.

#### C. Center-of-mass translational energy distributions, $P(E_T)$

Figures 5 and 6 present the best fits of the translational energy distributions $P(E_T)$ and angular distributions $T(\theta)$ of the title reaction in the center-of-mass frame. The LAB distributions and TOF data were fitted with a single $P(E_T)$ extending to a maximum translational energy release $E_{\text{max}}$ of 215 kJ mol⁻¹ and 240 kJ mol⁻¹ at lower and higher collision energy, respectively. These high energy cutoffs are accurate within 25 kJ mol⁻¹. If the energetics of distinct isomers are well separated, $E_{\text{max}}$ can be used to identify individual C₄H₃ isomers. The maximal translational energy release, i.e., the sum of the reaction exothermicity and relative collision energy, suggests the formation of the n-C₄H₃ isomer. Here, the theoretical calculations expect high energy cutoffs of the $P(E_T)$’s of $E_{\text{max}}(\text{theor.}=19.6 \text{kJ mol}^{-1})=199.5 \text{kJ mol}^{-1}$ and

### Table II. Thermochemistry of the reaction C(³P₂)+H₂CCCH₃(X ¹A₁).

<table>
<thead>
<tr>
<th>#</th>
<th>Exit channel</th>
<th>Reaction enthalpy at 0 K, ΔₑH(0 K), kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-C₄H₃(X ²Σ⁺) + H(²S, ¹S)</td>
<td>−179.9</td>
</tr>
<tr>
<td>2</td>
<td>HCCCCH(X ¹Σ⁺) + H₂(X ¹Σ⁺)</td>
<td>−450±12</td>
</tr>
<tr>
<td>3</td>
<td>HCCCCH(X ¹Σ⁺) + 2H(²S, ¹S)</td>
<td>−18±5</td>
</tr>
<tr>
<td>4</td>
<td>C₄H(X ²Σ⁺) + H₂(X ¹Σ⁺) + H(²S, ¹S)</td>
<td>+72±10</td>
</tr>
<tr>
<td>5</td>
<td>C₄H(X ¹Σ⁺) + 2H₂(X ¹Σ⁺)</td>
<td>+62±15</td>
</tr>
</tbody>
</table>
collision energy, respectively. $E_{\text{max}}$ (theor. $= 38.8 \text{ kJ mol}^{-1}$) $= 218.7 \text{ kJ mol}^{-1}$, are both in good agreement with our experimental data. The formation of the $46.9 \text{ kJ mol}^{-1}$ less stable $i$-$C_4H_3$ can be excluded as a major contribution, since the maximum energy release is restricted to 153.9 and 173.1 kJ mol$^{-1}$ at higher and lower collision energy. However, minor contributions might prevail, cf. discussion in Sec. V. Furthermore, both $P(\varepsilon_j)$'s peak away from zero as expected from the LAB distributions and depict a broad plateau between 30 and 50 kJ mol$^{-1}$. The fraction of energy channeling into translation of the products is quite large, i.e., $33 \pm 3$ and $30 \pm 2\%$ at higher and lower collision energy, respectively.

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

At lower collision energy, $T(\theta)$ is isotropic and symmetric around $\pi/2$, cf. Fig. 5. This implies that either the lifetime of the decomposing $C_6H_4$ complex is longer than its rotational period $\tau$, or that two hydrogen atoms of the $C_6H_4$ intermediate can be interconverted through a rotational axis. In this case, the light H-atom could be emitted in $\theta$ and $\pi-\theta$ to result in the forward–backward symmetry of $T(\theta)$. However, as the collision energy rises, the center-of-mass angular distribution peaks forward with respect to the carbon beam (Fig. 6) suggesting a reduced lifetime of the fragmenting $C_6H_4$ complex as the collision energy rises (osculating complex): A complex 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 $2.1 \pm 0.2$, 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. V). 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 isotropic angular distribution at lower collision energy is the result of a poor coupling between the initial and final angular momentum vectors, $\mathbf{L}$ and $\mathbf{L'}$, respectively, as already observed in crossed-beams reaction (2)–(5). If we calculate the maximum impact parameter $b_{\text{max}}$ and the maximum orbital angular momentum $L_{\text{max}}$ within the orbiting limit as outlined in Ref. 5 $b_{\text{max}}$ yields $b_{\text{max}}(19.6 \text{ kJ mol}^{-1}) = 3.8 \AA$, $b_{\text{max}}(38.8 \text{ kJ mol}^{-1}) = 3.2 \AA$, $L_{\text{max}}(19.6 \text{ kJ mol}^{-1}) = 114\hbar$ and $L_{\text{max}}(38.8 \text{ kJ mol}^{-1}) = 132\hbar$. If we compare these numbers with the final orbital angular momentum $L'$ as derived from acceptable $ab$ initio exit impact parameters of decomposing triplet $C_6H_4$ isomers, cf. Sec. V, we find $L' < 0.17L'$. Therefore, a large fraction of the initial orbital angular momentum is routed into rotational excitation of $n$-$C_6H_3$.

E. Flux contour maps and total relative cross sections

Figures 7 and 8 depict the two and three dimensional center-of-mass flux contour plots $I(\theta,\alpha) = P(u) * T(\theta)$ for collision energies at 19.6 and 38.8 kJ mol$^{-1}$. As expected from the center-of-mass angular distributions, data at lower collision energy show a forward–backward symmetric flux profile. As the collision energy rises, a forward peaking on
the relative velocity vector is obvious. Integrating this flux distribution and correcting for the reactant flux as well as relative reactant velocity (cf. Table I), we find an integrated relative reactive scattering cross section ratio of $\sigma(19.6 \text{ kJ mol}^{-1})/\sigma(38.8 \text{ kJ mol}^{-1}) = 1.9 \pm 0.6$ within our error limits, i.e., a rising cross section as the collision energy drops. This result together with recent bulk experiments and our ab initio calculations, cf. Sec. V, suggest a barrierless, attractive long-range dispersion forces dominated reaction together with a loose, reactantlike entrance transition state located at the centrifugal barrier.

V. DISCUSSION

In this section, we present the results of our ab initio calculations and feasible reaction pathways to distinct C$_4$H$_3$ isomers via insertion of the electrophile carbon atoms into the allenic C–H bond, addition to two $\pi$-molecular orbitals located either at two distinct carbon atoms or at the central carbon atom, and possible intersystem crossing (ISC) to the singlet surface (Sec. V A). The observed CM angular and translational energy distributions are then compared in Sec. V B to those distributions expected from possible reaction pathways elucidated from our ab initio calculations. We illustrate that large impact parameters dominate the reactive scattering dynamics. The reaction proceeds mainly via addition of C($3P_f$) to the terminal carbon atoms of the allene molecule to a cyclopropylidene derivative C$_4$H$_4$ on the triplet surface. This intermediate ring opens to triplet butatriene, which emits an H-atom to form the $n$-C$_4$H$_3$. As the collision energy rises, low impact parameter trajectories might add C($3P_f$) to the central allenic carbon atom followed by ring closure to the cyclopropylidene derivative C$_4$H$_4$.

FIG. 8. Contour flux map for the reaction C($3P_f$)+H$_2$CCCH$_2$(X'1A$_1$) at a collision energy of 38.8 kJ mol$^{-1}$. (a) Three-dimensional map; (b) two-dimensional projection.

FIG. 9. Schematic representation of the lowest-energy pathways on the triplet C$_4$H$_4$ PES and structures of potentially involved collision complexes. Those structures designated with ‘‘i’’ indicate intermediates, those with ‘‘p’’ potential C$_4$H$_3$ isomers.

FIG. 9. Schematic representation of the lowest-energy pathways on the triplet C$_4$H$_4$ PES and structures of potentially involved collision complexes. Those structures designated with ‘‘i’’ indicate intermediates, those with ‘‘p’’ potential C$_4$H$_3$ isomers.
A. The C$_4$H$_4$ potential energy surface

1. Addition to the C=C double bond

The \textit{ab initio} calculations reveal that C(3$^P$) can add without entrance barrier to one allenic C=C double bond to form a triplet cyclopropylidene derivative $i_1$, Figs. 9–11. This isomer is stabilized by 265.3 kJ mol$^{-1}$ with respect to the reactants, belongs to the C$_s$ point group, and has a 3$^A_9$ electronic wave function. ($i_1$) ring opens with a barrier of 39.4 kJ mol$^{-1}$ to triplet butatriene ($i_2$; D$_2$; 3$^A_1$) which represents the global minimum of the triplet C$_4$H$_4$ potential energy surface ($\sim$PES) and is bound by 404.6 kJ mol$^{-1}$. In addition, $i_1$ could lose an H-atom to form the C$_4$H$_3$ isomer $p_3$(C$_s$, 2$^A_8$). The exit barrier of this process is only 5.9 kJ mol$^{-1}$ above the products. $i_2$ either emits an H-atom to form the n-C$_4$H$_3$ isomer $p_1$(C$_s$, 2$^A_8$) through a productlike transition state located only 9.2 kJ mol$^{-1}$ above $n$-C$_4$H$_3$ or depicts a 1,2-H migration to form C$_4$H$_4$ isomer $i_7$(C$_1$, 3$^A_9$). The barrier for this migration lies below the total available energy of our crossed-beam reactions. $i_7$ can fragment via C–H bond cleavage to three different C$_4$H$_3$ isomers, i.e., $p_1$, $p_2$(C$_s$, 2$^A_8$), and $p_7$(C$_1$, 3$^A_9$). The exit barriers of these pathways are 25.1 kJ mol$^{-1}$, 5.9 kJ mol$^{-1}$, and 0 kJ mol$^{-1}$. In addition, $i_7$ can undergo two successive H-atom migrations to $i_8$(C$_s$, 3$^A_9$) and $i_9$(C$_1$, 3$^A_9$) through barriers of 181.6 kJ mol$^{-1}$ and 186.2 kJ mol$^{-1}$. $i_8$ can fragment through H-atom emission to form $p_1$ or $p_2$, $i_9$ to $p_1$ and $p_8$. The barrier for fragmentation of $i_8$ are located 29.3 and 11.3 kJ mol$^{-1}$ above the products, of $i_9$ to $p_1$ 24.3 kJ mol$^{-1}$, and to $p_8$ 3.0 kJ mol$^{-1}$. Based on \textit{ab initio} calculations and our relative collision energies we can conclude that reaction to $p_7$ is too endothermic to occur. Finally, the \textit{ab initio} calculations showed that the transition state of the isomerization of $p_1$ to $p_2$ and vice versa is located 46.1 kJ mol$^{-1}$ above the reactants and hence energetically not accessible in our experiments at collision energies of 19.6 and 38.8 kJ mol$^{-1}$.

2. Addition to the central allenic carbon atom

C(3$^P$) could attack the central carbon atom of the allene molecule without entrance barrier to form a triplet C$_4$H$_4$ diradical $i_3$(C$_3$, 3$^B$) which is energetically favored by 192.9 kJ mol$^{-1}$ compared to C(3$^P$) + H$_2$CCCH$_2$. Here, each terminal allene carbon atom holds one unpaired electron. The fate of $i_3$ can be three-fold. First, the barrier to ring closure yielding $i_1$ is only 12.6 kJ mol$^{-1}$. Second, an H-atom migration combined with a ring closure can form C$_4$H$_3$ isomer $i_6$ through a tight transition state 65.7 kJ mol$^{-1}$ above $i_3$. $i_6$ is stabilized by 272.4 kJ mol$^{-1}$ with respect to the reactants, belongs to the C$_2$ point group, and shows a 2$^B$ electronic wave function. C–H bond rupture in $i_6$ can yield either C$_4$H$_3$ isomer $p_3$(C$_s$, 2$^A_8$) or $p_4$(C$_s$, 2$^A_8$) without exit barrier ex-
cept the reaction endothermicity. Likewise, $i6$ could ring open through a barrier of 50.6 kJ mol$^{-1}$ to $i7$. Third, $i3$ might show a ring closure to form $i4(C_2v, 3B_2)$ through a barrier of 145.2 kJ mol$^{-1}$. $i4$ either shows a barrierless C–H bond rupture to yield C$_4$H$_3$ isomer $p6(C_s, 2A')$ or ring opens to triplet C$_4$H$_4$ isomer $i5(C_1, 3A, \text{barrier}=40.1 \text{ kJ mol}^{-1})$ prior to C–H bond rupture to form C$_4$H$_3$ isomer $p5(C_1, 2A, \text{exit barrier}=7.1 \text{ kJ mol}^{-1})$.

3. Insertion into C–H bond

Despite a careful search, no transition states of a C($^3P_f$) insertion into the allenic C–H bond could be found. We started the saddle point optimization from the geometries with a CCH three-membered ring suggesting that the C–H bond of allene is broken and two new bonds, C–C and C–H with the attacking carbon atom are formed during the insertion process. This process would lead directly to $i7$. However, the energies of the initial structures are very high. Upon transition state optimization, the C–H bond of allene is restored, the system descends to the vicinity of $i3$ or $i1$, and the optimization does not converge to a saddle point. This indicates that the trajectories directly leading from C($^3P_f$)+H$_2$CCCH$_2$ to $i7$ require high energies and do not contain a first order hill top. The low-energy pathways from the reactants to $i7$ go through $i3$ and $i6$ or $i1$ and $i2$.

4. Intersystem crossing (ISC)

The triplet C$_4$H$_4$ isomer $i3$ fulfills the requirements for a potential intersystem crossing (ISC), cf. Figs. 12 and 13. Here, the two unpaired electrons are placed in $p_x$ and $p_z$ orbitals located on both terminal carbon atoms of the former allene molecule. In this case, orbital angular momentum and spin can be changed simultaneously: for the reaction from $i3$ to $i1-s$, this results in a $a \rightarrow b$ spin flip and $p_x \rightarrow p_z$ orbital angular momentum change. Thus the overall angular momentum is conserved, and both unpaired electrons are now in the plane containing four carbon atoms, ring closure to singlet C$_4$H$_4$ $i1-s$, $i3-s$ is 31.0 kJ mol$^{-1}$ less stable than the triplet isomer. A frequency analysis shows that $i3-s$ is not a local minimum, but a transition state to the singlet C$_4$H$_4$ isomer $i1-s$. $i1-s$ belongs to the $C_s$ point group, holds a fully symmetric $1A'$ electronic wave function, and is 315.9 kJ mol$^{-1}$ stabilized as compared to the reactants. It either undergoes H-atom migration via a 63.2 kJ mol$^{-1}$ barrier to form $i6-s(C_{2v}, 1A_1)$, or ring opens almost barrierless to singlet butatriene $i2-s(D_{2h}, 1A_g)$, or decomposes to form...
p3 and atomic hydrogen. i2-s represents the global minimum on the singlet C4H4 PES and is bound by 576.6 kJ mol\(^{-1}\) with respect to the reactants. Finally, i6-s can decompose via C–H cleavage either to p3 or p4, whereas i2-s could fragment to form the most stable C4H3 isomer p1. All C–H bond ruptures to p1, p3, and p3 are barrierless.

B. Reaction pathways on C4H4 potential energy surface

In this section, the observed chemical dynamics and energetics are compared to what is expected from our \textit{ab initio} pathways as discussed in the preceding paragraphs. Those channels not compatible with the experimental center-of-mass angular and translational energy distributions are dismissed. This approach ultimately identifies the remaining channel(s) as the only possible one(s). The high-energy cutoff of the \(P(E_T)\)'s as described in Sec. IV C strongly suggest the formation of the \(n\)-C4H3 isomer p1 and possibly i-C4H3 p2. Remaining C4H3 isomers such as p3 are at least 123.8 kJ mol\(^{-1}\) less stable than p1 and are expected to contribute only to a minor amount to the reactive scattering signal.

1. Pathways to \(n\)-C4H3
   a. In-plane approach toward the C=C bond. What are the underlying chemical dynamics to yield \(n\)-C4H3? Conserving the C–C–C–C plane as a plane, the singly occupied orbitals of \(\text{C}(^3P_j)\) could interact in-plane with the \(\pi\) orbital at the carbon–carbon double bond under \(C_s\) symmetry on the

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FIG. 13. Structures of potentially involved singlet C4H4 collision complexes and transition states (TS). Bond lengths are given in Angstroms, bond angles in degrees. Those structures designated with ‘’i’’ indicate intermediates.

FIG. 14. Approach geometries of \(\text{C}(^3P_j)\) toward the allene molecule and involved rotations. (a) in-plane approach toward the C=C bond; (b) out-of-plane approach to the C=C bond; (c) in-plane approach toward the central carbon atom.
surface to form $i_1$, cf. Fig. 14(a). This pathway supports a maximum orbital overlap to form two C–C–σ bonds in the cyclopropylidene substructure. Since $L \approx j^2$, the four carbon atoms rotate in a plane approximately perpendicular to $L$ around the $C$-axis of the prolate C$_2$H$_6$ isomer $i_1$ which has an asymmetry parameter $\kappa = -0.8736$. The consecutive ring opening conserves the rotational axis $C$ of the highly prolate triplet butatriene $i_2$, $\kappa = -0.999996$. Since this complex is excited to C-like rotations, the added carbon atom and both H-atoms located at terminal carbon atom are located on opposite sites of the rotation axis as required to explain the forward peaking $T(\theta)$ at higher collision energies. These findings give strong support of the osculating complex model as suggested in Sec. IV D: At lower collision energy, the lifetime of $i_2$ is longer than the rotational period around the $C$ axis; with increasing collision energy increases, the lifetime is reduced to less than one rotational period. Based on these results, a symmetric C$_2$H$_6$ complex in which H-atoms can be interconverted through a rotation axis to give rise to a symmetric $T(\theta)$ at lower collision energy can be dismissed: first, rotation of $i_2$ around the $C$ axis does interconvert any H-atoms. Second, hypothetical A-like rotations of $i_2$ around the $C_2$ axis could interconvert both H-atoms, but these rotations are energetically not accessible. Here, angular momentum conservation requires that $i_2$ is excited to $j(i_2) = 114h$ at a collision energy of 19.6 kJ mol$^{-1}$ using the ab initio rotational constants of $i_2$ of $A = 4.85151$ cm$^{-1}$ and $B = C = 0.12789$ cm$^{-1}$, and the asymmetric top approximation, about 63 000 kJ mol$^{-1}$ are needed to excite A-like rotations. Considering a maximum available internal energy of 424.8 kJ mol$^{-1}$, only less than 0.7% of $i_2$ populate A rotational states, and most of $i_2$ are excited to C-like rotations as deduced above. A final C–H bond rupture in $i_2$ yields the n-C$_2$H$_3$ isomer, rotating around its $C$-axis. We like to point out that our proposed chemical dynamics to form n-C$_2$H$_3$ through an initial addition to $i_1$, followed by ring opening to form $i_2$ and a final C–H bond rupture is consistent with large impact parameters leading to the reaction within orbiting limits. This overwhelming contribution of large impact parameters to the capture process up to 3.8 Å was already mentioned in Secs. IV D and E. Here, our relative cross sections increase as the collision energy drops, strongly indicating no entrance barrier to the reaction. This gains strong support from our ab initio calculations since despite a careful search no barrier could be found in the entrance channel to form $i_1$. Besides our in-plane approach, out-of-plane approach geometries exciting C-like rotations in $i_1$ are supported as well and open larger impact parameters for the reaction.

In addition to $i_2$, the complexes $i_7$, $i_8$, and/or $i_9$ can go through H-atom emission to form $p_1 + H$ as well. Our experimental data alone cannot identify the decomposing complex, and we employ RRKM calculations to tackle this problem. The rate equations for the title reaction were derived according to Fig. 15 and solved with the rate constants computed by the RRKM theory. As a result, the concentration of each species present in the reaction mechanism was obtained as a function of time. The concentration of the products at $t \rightarrow \infty$ were then taken to calculate the branching ratios. 26

Table III shows the calculated rate constants with and without tunneling corrections for each elementary step in Fig. 15, and the additional $k_{14}$ and $k_{15}$ for the reaction $i_3 \rightarrow i_4$ and $i_1 \rightarrow p_3$, respectively. The rate equations derived from Fig. 15 were solved for two cases that $P$ is from $i_2$, $i_7$, $i_8$, and $i_9$ are distinguishable and nondistinguishable. Our ab initio calculations show no entrance barriers for the atomic carbon attack of the allene molecule. Moreover, the RRKM theory can be applied only for unimolecular reactions. Therefore, at the present stage we cannot calculate the branching ratio for the attack of the C–C bond (pathway $i_2$ to $i_1$) versus the central carbon atom (pathway $i_2$ to $i_1$). To circumvent this problem, the resulting branching ratios for $p_1$ and $p_2$ were expressed as a function of $i_1$ and $i_3$ initial concentrations which were not known. The computed branching ratios listed in Tables IV, V, and VI were obtained by plugging in the assumed composition between the initial concentrations of $i_1$ and $i_3$ in steps of 0.1. At both collision energies, it is evident that more than 96.7% of the n-C$_2$H$_3$ isomer is formed through decomposition of $i_2$. The results of these calculations indicate that successive H-atom migrations from $i_2$ to $i_7$, $i_8$, and $i_9$ play no role in the chemical dynamics of the reaction of atomic carbon with allene molecules.

b. Out-of-plane approach toward the C–C bond. Besides in-plane approach geometries, we have to take out-of-plane attack of C($^3P_g$) to the C–C bond conserving C$_3$ symmetry as well. As evident from Fig. 14(b), these trajectories excite predominantly A-like rotations in Eq. (1) and—after a subsequent ring opening—in $i_2$ as well. A final C–H bond fission leads ultimately to n-C$_2$H$_3$ isomers in A rotational states. However, detailed energy and angular momentum conservation considerations in the previous section already excluded A-like rotations of $i_2$ intermediate as well as n-C$_2$H$_3$ product isomer since they cannot be covered energetically. Hence, we conclude that these approach geometries very likely play no contribution in the chemical dynamics of the title reaction.

c. In-plane and out-of-plane approaches toward the cen-
and 145.2 kJ mol\(^{-1}\) for reactions \(i3\rightarrow i6\) and \(i3\rightarrow i4\), formation of \(i1\) should dominate these processes due to the lowest barrier. This is in strong agreement with our results since \(i4\) would yield only the \(C_2H_3\) isomers \(p5\) and \(p6\). \(i6\) could rearrange to \(i7\) which loses an H-atom to form \(n-C_4H_3\). However, angular momentum conservation dictates that \(i7\) is excited to \(C\)-like rotations, but the incorporated carbon atom and the leaving H-atom are located on the same site of the rotation axis and cannot account for the forward peaked center-of-mass angular distribution at higher collision energy. Hence, the reaction sequence \(i3\rightarrow i6\rightarrow i7\rightarrow p1\) can be excluded from the discussion as well. Based on our experimental data alone, we cannot quantify the contribution of the \(i3\rightarrow i1\) sequence to yield \(p1\). As discussed above, however, large impact parameters should dominate the chemical dynamics. The attack of \(C(3\,P)\) to the central allenic C atom involves only small impact parameters less than 0.65 Å. Therefore we conclude that this microchannel should contribute to a minor extent compared to addition of atomic carbon to the \(C=C\) bond of allene. Since our data suggest the reaction proceeds within orbiting limits, the contribution of trajectories with a smaller impact parameter—and hence the contribution of microchannel \(i3\rightarrow i1\)—should decrease as the collision energy rises.

<table>
<thead>
<tr>
<th>(i1,i3)</th>
<th>(i2\rightarrow p1)</th>
<th>(i7\rightarrow p1)</th>
<th>(i8\rightarrow p1)</th>
<th>(i9\rightarrow p1)</th>
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<td>3.42</td>
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<td>0.33</td>
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<td>2.58</td>
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<table>
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<th>(i2\rightarrow p1)</th>
<th>(i7\rightarrow p1)</th>
<th>(i8\rightarrow p1)</th>
<th>(i9\rightarrow p1)</th>
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<td>160 (144)</td>
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<tr>
<td>(1, 0)</td>
<td>73 (68)</td>
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</table>

\(^{a}i3\rightarrow i4.\)

\(^{b}i1\rightarrow p3.\)
2. Pathways to i-C_4H_3

The center-of-mass translational energy distributions cannot rule out minor contributions of the i-C_4H_3 isomer p2. Based on our ab initio calculations, p2 can be synthesized through C–H bond rupture of C_4H_3 intermediate i7. i7 itself is either formed through ring opening of i6 or H-atom shift in i2. As already discussed above, trajectories with large impact parameters should dominate the chemical dynamics. Therefore the reaction sequence i3 → i6 → i7 should be only of minor importance, and i7 is likely to be formed predominantly through H-atom migration from i2 rotating around its C axis, cf. Sec. V B 1. Alternatively, decomposition of i8 can lead to p2 + H as well. Based on our experimental data, we cannot quantify the contribution of the i-versus n-C_4H_3 isomer. As evident from Table VI, the computed ratios of the n-C_4H_3 isomer is more than 98.4%, and n-C_4H_3 dominates the chemical dynamics of the title reaction.

C. Possible contributions from the singlet C_4H_4 potential energy surface

As discussed in Sec. V A 4, the C_4H_4 isomer i3 fulfills requirements for ISC to form eventually i1-s on the singlet C_4H_4 surface. The shape of the center-of-mass translational energy distribution helps to unravel the contribution of the singlet surface. Both P(E")'s peak at around 30–50 kJ mol^{-1} indicating a tight exit transition state from the decomposing C_4H_3 intermediate to the products. However, our ab initio calculations depict no exit barrier to form p1, p3, or p4 + H. Hence, our P(E")'s are expected to peak at 0 kJ mol^{-1} in strong contrast to our findings. In addition, a minor barrier of only 0.8 kJ mol^{-1} favors a ring opening of i1-s to i2-s. A-, B-, as well as C-like rotations of i2-s are expected to show a symmetric center-of-mass angular distributions at both lower and higher collision energies since each rotation interconverts the hydrogen atoms, and H departs with equal probability into θ and θ-π result in a T(θ) symmetric around π/2. Hence, only i1-s and i6-s remain. A detailed analysis of the rotational axes and taking into account that the leaving H and incorporated C atom must be placed on different sides of the rotational axis shows that only i1-s excited to A to form p3, and i6-s excited to B-like rotations to yield p4 can fulfill this requirement. If we consider energy conservation and calculate the energy necessary to excite A-like rotations in i1-s employing the rigid rotor approximation, we find that these rotations are only accessible for 5% of the intermediates. In addition, formation of p3 and/or p4 expects to show a high-energy cutoffs in the P(E")'s between 60 and 80 kJ mol^{-1}, in strong disagreement with our data. Based on these arguments, we conclude that if ISC provides reactive scattering signal of the title reaction, this contribution is likely small.

D. Lifetime of the decomposing complex

The rotational period of the decomposing C_4H_3 isomers i2 acts as a clock in the molecular beam experiment and can be utilized to estimate the lifetime t of the fragmenting complex at a relative collision energy of 38.8 kJ mol^{-1}. The oscillating model relates the intensity ratio of T(θ) at both poles to t via Eq. (10):

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

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

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

Iᵣ represents the moment of inertia of the complex rotating around the i-axis, and L_{max} the maximum orbital angular momentum. Using our ab initio geometries we yield rotational periods of the complexes and plug in all data in Eq. (10). We calculate lifetimes of i2 rotating around the A, B, and C axes to \( \tau(A) = 0.017 \) ps, \( \tau(B) = \tau(C) = 0.66 \) ps. Accounting for the uncertainties in the center-of-mass angular distribution, these data are within 10%–20%. As evident, the magnitude of \( \tau \) depends strongly on the rotation axis, i.e., B, C vs A. Since reactions with a collision times <0.1 ps follow direct scattering dynamics and expect to show almost zero intensity at large angles of the center-of-mass angular distribution, the T(θ) at our higher collision energy is expected to be strongly forward peaked, if the complex rotated around the A axis. This is clearly not observed in the experiment. Hence a rotation about the A axis of all complexes can be excluded as already suggested in the previous paragraphs, and the end-over-end rotation dominates.

E. Comparison with the reaction C(3Pj) + CH_3CCH

The reaction between ground state carbon atoms, C(3Pj), and methylacetylene, CH_3CCH (X'1A1), was studied recently at averaged collision energies of 20.4 and 33.2 kJ mol^{-1} using the crossed molecular beams technique. The reaction dynamics indicate that the carbon atom attacks the σ-orbitals of the methylacetylene molecule via a loose, reactantlike transition state located at the centrifugal barrier. The initially formed triplet 1-methylpropenylidene complex rotates in a plane almost perpendicular to the total angular momentum vector around the B/C-axes and undergoes [2,3]-hydrogen migration to triplet 1-methylpropargylene. Within 1–2 ps, the complex decomposes via C–H bond cleavage to n-C_4H_3 and atomic hydrogen.

Compared to the reaction of C(3Pj) with H_2CCCH_2, data at higher collision energies of both C_3H_4 isomers show identical laboratory angular distribution and TOF spectra. Likewise, the center-of-mass angular as well as translational distributions are identical within the error limits. Finally, the fragmentation pattern and intensity of the integrated TOFs at m/e = 51, 50, and 49 are the same, i.e., 0.5(m/e = 51):1.0(m/e = 50):0.25(m/e = 49). However, at lower collision energies, the lab and center-of-mass distributions differ significantly. In addition, the fragmentation ratios of at m/e = 51, 50, and 49 of the C(3Pj) + H_2CCCH_2 reaction are identical to those obtained at higher collision energy within the error limits. This pattern is expected, since at both collision energies the n-C_4H_3 isomer is formed. But data of the reaction of atomic carbon with methylacetylene yield (m/e = 51):(m/e = 50):(m/e = 49) = 0.3:1.0:0.5. This sug-
gests that at lower collision, the reaction of carbon with methylacetylene and allene forms distinct isomers. Based on the high-energy cutoff of the center-of-mass translational energy distribution of the reaction of carbon with allene, the authors postulated the formation of a higher-energy isomer possibly a cyclic isomer, however, without an explicit identification.\textsuperscript{27} The postulation of a higher-energy isomer gains additional support if we consider the averaged fraction of energy channeling into the translational degrees of freedom. At collision energies between 19.6 and 45.0 kJ mol\textsuperscript{-1}, our data reveal that the reaction of atomic carbon with all unsaturated hydrocarbons containing three carbon atoms such as propylene C\textsubscript{3}H\textsubscript{6}, allene H\textsubscript{2}CCCH\textsubscript{2}, and methylacetylene CH\textsubscript{3}CCH except the latter at lower collision energies brings 30\%–35\% of the total available energy into kinetic energy of the product—almost independent on the collision energy and the reaction product. High level \textit{ab initio} calculations on the C/CH\textsubscript{3}CCH together with variational RRKM calculations are underway to resolve the outstanding question of the C\textsubscript{4}H\textsubscript{3} isomer formed at lower collision energy.

F. Comparison with the reaction O(\(3P_j\)) + H\textsubscript{2}CCCH\textsubscript{2}

The reaction of O(\(3P_j\)) with allene was studied recently at a collision energy of 33.5 kJ mol\textsuperscript{-1}.\textsuperscript{28} Three reaction channels were found. First, trajectories with small impact parameters are governed by an attack of O(3\(P_j\)) to the central allenic carbon atom form a triplet diradical which undergoes intersystem crossing to the singlet surface. The entrance barrier to this center addition is found to be less than 33.5 kJ mol\textsuperscript{-1}. A ring closure leads to cyclopropanone which fragments directly through C–H bond rupture to form H\textsubscript{2}C\textsubscript{v}C–COH (channel 2) or undergoes H-atom migration to yield triplet acrolein. The authors suggest a consecutive ISC to singlet acrolein followed by a C–C bond rupture to yield C\textsubscript{2}H\textsubscript{3} and HCO. The differences in the chemical dynamics to the C(\(3P_j\)) allene reaction are the direct consequence of the potential energy surface. Here, an open triplet diradical as an addition product of C(3\(P_j\)) to the terminal carbon atom holds no local minimum on the triplet C\textsubscript{4}H\textsubscript{4} PES as shown in our \textit{ab initio} calculations, but undergoes ring closure with a ring opening to triplet butatriene. Likewise, our title reaction has no entrance barrier, whereas the analogous O(\(3P_j\)) reaction has an entrance barrier of at least 33.5 kJ mol\textsuperscript{-1}. Hence, the latter reaction does not proceed within orbiting limits, and a larger fraction of smaller impact parameters is expected to lead to reaction.

\begin{center}
\textbf{FIG. 16.} Double potential energy well of the \(n\)-C\textsubscript{4}H\textsubscript{3} isomer and its linear transition state. Bond lengths are given in Angstroms, bond angles in degrees.
\end{center}
such as those approaches where the oxygen atom attacks the central carbon atom of the allene molecule.

VI. IMPLICATIONS TO INTERSTELLAR CHEMISTRY AND COMBUSTION PROCESSES

The identification of the \( n-C_4H_3 \) isomer under single collision conditions is of importance to chemical reaction networks modeling the temporal development of chemistry in molecular clouds, hot molecular cores, outflow of carbon stars, and hydrocarbon-rich planetary atmospheres. Hitherto, information on distinct structural isomers as reaction products were lacking and hence could not be included in these schemes. The present study underlines this importance, since \( C(3P_{1}) + CH_2CCH \) leads to a second, probably cyclic \( C_4H_3 \) isomer at lower, but to \( n-C_4H_3 \) at higher collision energies, whereas \( C(3P_{1}) + H_2CCCH_2 \) forms \( n-C_4H_3 \) at lower as well as higher collision energies. In addition, the barrierless nature of the reactions of atomic carbon with allene and methylacetylene demonstrates explicitly that these processes are of potential importance in even coldest interstellar clouds such as TMC-1 with typical translational temperatures of 10 K. Methylacetylene, \( CH_2CCH \), has been widely observed toward dark, molecular clouds such as OMC-1 and TMC-1 in high fractional abundances between \((4-6) \times 10^{-9} \text{ cm}^{-3}\) through microwave spectroscopy. A second \( C_2H_2 \) isomer, allene (\( H_2CCCH_2 \)), holds no permanent electric dipole moment and hence shows no rotational spectrum. Although \( H_2CCCH_2 \) should be detectable via infrared spectroscopy in the circumstellar shell of, e.g., the carbon star IRC+10216, this isomer has escaped any astronomical identification so far. Despite this failure, the allene isomer is strongly expected to be present.

Moreover, terrestrial based microwave spectra of \( C_4H_3 \) radicals should be recorded and transitions sought in interstellar environments. Here, especially the situation of the \( n-C_4H_3 \) is extremely interesting: the ground state is a bent structure \( p_1 \), cf. Fig. 16, whereas the linear butatrienyl structure represents a transition state between two bent states, located only 255 cm\(^{-1}\) above the \( n-C_4H_3 \), cf. Fig. 16. Since coldest molecular clouds have averaged translational temperatures of about 10 K—about 7 cm\(^{-1}\)—\( n-C_4H_3 \) must be bent. The transition state is energetically not accessible. In hotter interstellar environments such as hot molecular cores with averaged translational temperatures of 200–300 K—about 140–210 cm\(^{-1}\)—\( C_4H_3 \) radicals populating translational energies in the long tail of the Maxwell–Boltzmann distribution could overcome the barrier, cf. Fig. 16, and these radicals should be quasi-linear. Radicals with lower kinetic energies must be bent. Therefore, the microwave spectrum of the \( n-C_4H_3 \) radical depends strongly on the temperature of the interstellar environments. Vice versa, recording these microwave spectra could serve as a probe to sample the temperature in these environments. Likewise, the assignment of the \( n-C_4H_3 \) radical under our single collision conditions as well as via trapping experiments in oxygen-rich hydrocarbon flames supports inclusion of \( C_4H_3 \) hydrocarbon radicals even in oxidative hydrocarbon flames.

VII. CONCLUSIONS

The reaction between ground state carbon atoms, \( C(3P_{1}) \), and allene, \( H_2CCCH_2 \), was studied at averaged collision energies of 19.6 and 38.8 KJ mol\(^{-1}\) using the crossed molecular beam technique. The carbon atom attacks the \( \pi \) orbitals of the allene molecule barrierless via a loose, reactantlike transition state located at the centrifugal barrier. The initially formed cyclopropyldiene derivative rotates in a plane almost perpendicular to the total angular momentum vector \( J \) around its \( C \) axis and undergoes ring opening to triplet butatriene. Within 0.6 ps, the complex decomposes via hydrogen emission to the \( n-C_4H_3 \) isomer through a tight exit transition state. As the collision energy increases, the approach geometries with smaller impact parameter very likely show in enhanced contribution leading to a barrierless attack of \( C(3P_{1}) \) to the central carbon atom in the allene molecule. The explicit identification of the \( n-C_4H_3 \) 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, interstellar chemistry, and chemical modification of hydrocarbon-rich atmospheres of Jupiter, Saturn, Titan, as well as Triton.

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