Crossed-beam reaction of carbon atoms with hydrocarbon molecules. I. Chemical dynamics of the propargyl radical formation, C₃H₃ (X²B₂), from reaction of C(³P) with ethylene, C₂H₄(X¹Aᵩ)

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The reaction between ground-state carbon atoms, C(³P), and ethylene, C₂H₄(X¹Aᵩ), was studied at average collision energies of 17.1 and 38.3 kJmol⁻¹ using the crossed molecular beams technique. Product angular distributions and time-of-flight spectra of m/e=39 were recorded. Forward-convolution fitting of the results yields a maximum energy release as well as angular distributions consistent with the formation of the propargyl radical in its X²B₂ state. Reaction dynamics inferred from the experimental data indicate two microchannels, both initiated by attack of the carbon atom to the π-orbital of the ethylene molecule via a loose, reactant like transition state located at the centrifugal barrier. Following C₃ symmetry on the ground state 3A'' surface, the initially formed triplet cyclopropylidene complex rotates in a plane roughly perpendicular to the total angular momentum vector around its C-axis, undergoes ring opening to triplet allene, and decomposes via hydrogen emission through a tight transition state to the propargyl radical. The initial and final orbital angular momenta L and L' are weakly coupled and result in an isotropic center-of-mass angular distribution. A second microchannel arises from A-like rotations of the cyclopropylidene complex, followed by ring opening and H-atom elimination. In this case, a strong L·L' correlation leads to a forward-scattered center-of-mass angular distribution. The explicit identification of C₂H₄ under single collision conditions represents a single, one-step mechanism to build up hydrocarbon radicals. Our findings strongly demand incorporation of distinct product isomers of carbon atom-neutral reactions in reaction networks simulating chemistry in combustion processes, the interstellar medium, as well as in outflows of carbon stars, and open the search for the hitherto unobserved interstellar propargyl radical. © 1996 American Institute of Physics.

I. INTRODUCTION

The propargyl radical in its ²B₂ electronic ground state holds the global minimum on the C₂H₃ potential energy surface (PES) and has received considerable attention due to its potential importance in interstellar and planetary chemistry and contribution to combustion processes. High propargyl concentrations are predicted in oxygen rich hydrocarbon flames due to a partial delocalization of the unpaired B₂ electron and an inherent low reaction rate constant of k(295 K)=5×10⁻¹⁴ cm³ s⁻¹ with O₂. Current combustion models postulate that soot formation and synthesis of polycyclic aromatic hydrocarbons (PAHs) are strongly correlated and initiated by recombination of two C₂H₃ radicals to C₄H₆ isomers [k(295 K)=1.2×10⁻¹⁰ cm³ s⁻¹] followed by stepwise ring growth to larger PAHs. However, little is known on the synthesis of the propargyl radical in hydrocarbon flames. Adamson investigated the reaction of singlet methylene with acetylene, reaction (1), as a potential pathway, whereas a unimolecular decomposition of vibrationally excited singlet allene or methylacetylene, C₂H₃ via C–H bond rupture, is suggested as a propargyl source, reactions (2) and (3).

\[
\begin{align*}
\text{CH}_2(a^1A_1) + \text{C}_2\text{H}_2(X\ 1\Sigma_g^+) &\rightarrow \text{C}_3\text{H}_3(X\ 2\text{B}_2) + \text{H}(2\text{S}_{1/2}). \\
\text{C}_2\text{H}_4(X\ 1\text{A}_1) &\rightarrow \text{C}_3\text{H}_3(X\ 2\text{B}_2) + \text{H}(2\text{S}_{1/2}). \\
\text{CH}_3\text{CCH}(X\ 1\text{A}_1) &\rightarrow \text{C}_3\text{H}_3(X\ 2\text{B}_2) + \text{H}(2\text{S}_{1/2}).
\end{align*}
\]

Besides its relevance in combustion chemistry, the propargyl isomer is expected to exist in interstellar and planetary environments. Its potential ethylene precursor has been widely incorporated into photochemical models of the stratosphere of Jupiter, Saturn, Uranus, Neptune, and Titan, as well as into sophisticated ion-molecule networks of the jovian ionosphere. The very first detection of ethylene outside our solar system in circumstellar shells fueled Herbst et al. to include the reaction of C(³P) with C₂H₄ in a generic chemical model of the circumstellar envelope surrounding IRC+10216, postulating the existence of C₂H₃ products. Since the reaction network was based simply on spin-conservation and thermochemistry without investigation of the chemical dynamics, the explicit identification of any hitherto unobserved interstellar C₂H₃ isomer remains to be resolved, cf. Fig. 1.

Previous mechanistic information on the C/C₂H₄-system was derived from radioactive tracer studies of superthermal C(³P) and C(³D₂) recoil atom reactions with C₂H₄,C₂D₄,C₂H₃/O₂, as well as C₂H₃/Ne-mixtures under...
bulk conditions. Four product classes were identified: \( \text{C}_2 \text{H}_2 \) (class 1), \( \text{C}_5 \text{H}_x \) products (class 2), vinylacetylene (class 3), and allene/methylacetylene (class 4). Suprathermal \( ^{11}\text{C}(^1\text{D}) \) atoms add to the olefinic double bond to singlet cyclopropylidene (1, Fig. 2) followed by insertion between the previously joined carbon atoms to singlet allene (2). The vibrationally excited molecule could be stabilized via a third body collision, undergoes 1,3-hydrogen migration to methylnlacetylene (3) prior to its collisional deactivation, or is assumed to fragment to hydrogen and \( \text{C}_3 \text{H}_3 \) radicals. To a minor amount, hot \( ^{11}\text{C}(^1\text{D}) \) inserts in a C–H bond to singlet vinylcarbene (4). Intermediate (4) undergoes 1,2- or 2,3-H migration to singlet allene (2), or methylnlacetylene (3), respectively, before a third body deactivation takes place. Thermal \( ^{11}\text{C}(^1\text{D}) \) atoms, however, are found to add exclusively to the ethylene \( \pi \)-bond.

Suprathermal \( ^{11}\text{C}(^3\text{P}) \) inserts into \( \text{C}–\text{H} \) bonds yielding triplet vinylcarbene (5) and adds to olefinic double bonds to triplet cyclopropylidene (6). The yield of \( \text{C}–\text{H} \) insertion products is reduced with increasing thermalization of the hot \( ^{11}\text{C}(^3\text{P}) \) atoms. Both triplet intermediates (5) and (6) are postulated to lose H to form \( \text{C}_3 \text{H}_3 \) radicals with subsequent attack of a second ethylene molecule, producing 1-propynyl-5 (7) and 1,2-pentadienyl-5 (8). Internally excited (7) and (8) abstract hydrogen atoms yielding 1-propyne (9) and 1,2-pentadiene (10). Vinylacetylene is assumed to be generated via reaction of \( \text{C}_2 \text{H}_4 \) radicals with ethylene molecules. The diminished concentration of vinylacetylene and acetylene goes hand in hand with a decreasing internal excitation of triplet \( \text{C}_3 \text{H}_4 \) intermediates, suggesting \( \text{C}_2 \text{H}_2 \) as a fragmentation product via \( \text{C}_5 \text{C} \) bond rupture in (6) or indirectly via vinylidenecarbene (11) after ring cleavage of (6) and 1,2-H-migration. Postulated cyclopropylidene intermediates were trapped as dimethyl-spiranes (12) as reaction products of carbon recoils with 2-butene.

Here, we investigate the detailed chemical dynamics of
the atom-neutral reaction of C(3P) with C2H4(X1A) under single collision conditions at relative collision energies of 17.1 and 38.3 kJ mol−1 as provided in crossed molecular beam experiments.77 The detailed information on the reaction dynamics disclose the nature of the triplet C3H4 PES, the formation of C3H3 isomers in interstellar environments and hydrocarbon flames, reaction intermediates postulated in bulk experiments, and offer a valuable comparison to the O(3P)+C2H4(X1A) reaction studied recently in our group.28

II. EXPERIMENT

The reactive scattering experiments are performed in a universal crossed molecular beam apparatus described in Ref. 29. A pulsed supersonic carbon beam was generated via laser ablation of graphite at 266 nm.30 The 50/30 Hz, 35–40 mJ output of a Spectra Physics GCR-270-50/30 Nd:YAG laser is focused onto a rotating carbon rod. Ablated carbon bulk experiments, and offer a valuable comparison to the laser is focused onto a rotating carbon rod. Ablated carbon mJ output of a Spectra Physics GCR-270-50/30 Nd:YAG zone selects a 9.0/7.5 four slot chopper wheel mounted 40 mm after the ablation experiment 1 or helium (99.999%, Bay Area Gas) (experiment 2) released by a Proch–Trickl pulsed valve operating at 100 Hz or 60 Hz, 80 μs pulses, and 4 atm backing pressure. A four slot chopper wheel mounted 40 mm after the ablation zone selects a 9.0/7.5 μs segment of the seeded carbon beam. Table I compiles the experimental beam conditions. The pulsed carbon beam and a continuous ethylene (99.999%, Matheson) beam with 584±10 Torr backing pressure pass through skimmers with apertures of 1.0 and 0.58 mm, and cross at 90° with divergences of 3.0° and 4.7° in the interaction region of the scattering chamber at relative collision energies of 17.1 and 38.3 kJ mol−1. The reactively scattered products were detected in the plane of the beams using a rotatable detector consisting of a Brink-type electron-impact ionizer,31 quadrupole mass filter, and a Daly ion detector32 at different laboratory angles between 5.0° and 60.0° with respect to the carbon beam in 2.5°–5.0° steps. The velocity distribution of the products was determined using the time-of-flight (TOF) technique33 choosing a channel width of 10 μs. Counting times ranged from 0.5–5 h, averaged over several angular scans. The velocity of the supersonic carbon beam was monitored frequently after taking the data for 2–4 angles and minor velocity drifts corrected by adjusting the laser pulse delay within ±1 μs.30 Reference angles were chosen at 35° and 47.5°, respectively, to calibrate fluctuating carbon beam intensities and mass dial settings at the quadrupole controller.

III. DATA ANALYSIS

A. Velocity and speed ratio of the parent beams

The velocity distribution of each supersonic parent beam is defined by

\[ N(v) = \frac{v}{v_0^2} \exp \left( -\frac{v_0 - v}{\alpha} \right) \]

with the velocity \( v_0 \), the speed ratio \( S \), and \( \alpha = m / 2RT \), mass of the molecule (atom) \( m \), the temperature of the beam \( T \) and the ideal gas constant \( R \). A transformation from the velocity to time domain yields

\[ N(t) = \frac{L^3}{r^2} \exp \left( -\frac{L}{\alpha t} \right) \]

where \( L \) is the neutral flight length. The most probable velocity and speed ratio are fitted after convolution over the ionizer length and the shutter function of the chopper wheel (Table I).

B. TOF spectra and laboratory angular distribution

Information on the velocity and angular distributions of products in the center-of-mass coordinate system was obtained by fitting the TOF spectra and the product angular distribution in the laboratory frame using a forward-convolution routine.34,35 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) which are assumed to be independent of each other. Since neither of the reactants is polarized, the cylindrical symmetry of the scattering process around the relative velocity vector in the CM-system restricts the angular dependence to \( \theta \), the scattering angle in the center-of-mass coordinate system measured from the direction of the carbon beam. The \( P(E_T) \) is chosen as a parameterized function

\[ P(E_T) = (E_T - B)^p \times (E_{av} - E_T)^q \]

The \( B \)-parameter is related to the exit barrier with \( B = 0 \) for a simple bond rupture without an exit-barrier. Peaking at a finite value \( E_p \) and for \( B \neq 0 \), the first argument in Eq. (6) governs the energy difference of \( E_p \) and the low energy tail where \( E_{av} \to 0 \), whereas the second argument describes a decaying function from \( E_p \) to the high energy tail. Likewise, \( T(\theta) \) is defined as a sum of up to five Legendre-polynomials \( P_i(\cos \theta) \) with coefficients \( a_i \)

<table>
<thead>
<tr>
<th>Beam</th>
<th>( v_0, \text{ms}^{-1} )</th>
<th>( S )</th>
<th>( E_{coll}, \text{kJ mol}^{-1} )</th>
<th>( \theta_{CM} )</th>
<th>( C_1 : C_2 : C_3 )</th>
<th>( f_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(3P)Ne</td>
<td>1850±30</td>
<td>4.5±0.3</td>
<td>17.1±0.7</td>
<td>45.3±0.8</td>
<td>1:0.6:1.8</td>
<td>1.0</td>
</tr>
<tr>
<td>C(3P)He</td>
<td>2900±80</td>
<td>4.0±0.2</td>
<td>38.3±2.1</td>
<td>34.1±1.6</td>
<td>1:0.2:0.3</td>
<td>5.6±1.1</td>
</tr>
<tr>
<td>C2H4</td>
<td>840±40</td>
<td>8.3±0.2</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

TABLE I. Experimental beam conditions and 1σ errors: Most probable velocity \( v_0 \), speed ratio \( S \), most probable relative collision energy with the ethylene molecules, \( E_{coll} \), center-of-mass angle, \( \theta_{CM} \), composition of the carbon beam, and flux factor \( f_o \), in relative units, cf. Sec. IV A.
Laboratory TOF spectra and the laboratory angular distribution (LAB) were calculated from the $T(\theta)$ and $P(E_T)$ distributions, and averaged over a grid of Newton diagrams defining the velocity and angular spread of each beam, detector acceptance angle, and the ionizer length. Best fits were obtained by iteratively refining the Legendre-coefficients and adjustable $P(E_T)$ parameters.

Collision energy dependent relative cross sections are computed by integrating $T(\theta)$ and $P(E_T)$:

$$
\sigma'(E) = \int_0^\infty \int_0^\pi \int_0^{2\pi} P(E_T)T(\theta) \sin \theta d\theta d\varphi dE_T .
$$

(8)

Since the product yield under single collision conditions follows Eq. (9) with the number density of the $i$th reactant $n_i$ and the relative velocity $v_r$, $\sigma'$ has to be scaled by the flux factor $f_v$ (Table I):

$$
dn_p/dt = \sigma \times n(C) \times n(C_2H_3) \times v_r = \sigma' \times f_v .
$$

(9)

IV. RESULTS AND ANALYSIS

A. Reactive scattering signal

Reactive scattering signal was only observed at $m/e = 39$, i.e., $C_3H_3$. TOF spectra of $m/e = 36–38$ were recorded at several laboratory angles, but depict identical patterns with decreasing intensity. Therefore, the signal at $m/e = 36–38$ originates in cracking of the $C_3H_3$ parent in the ionizer, and channel 6–15 are not observed within detection limits (Table II). In addition, no radiative association to $C_3H_4$ ($m/e = 40$) or higher masses were detected. Endothermic channels 12–16 could not be opened at relative collision energies up to 38.3 kJmol$^{-1}$ employed in the present experiments.

The detection of reactive scattering products $C_2H_2$, $C_2H$, and $C_2$ (channel 17–19) suffers from the inherent high background level at these masses arising from fragmentation of $C_2H_2$ in the detector. Attempts were made to identify these channels by replacing the continuous $C_2H_4$ source by a second pulsed valve with 0.25 mm nozzle diameter operating at 30 Hz with 1 atm backing pressure and increasing the pumping speed in the main chamber. Nevertheless, no reactive scattering signal was observed at $m/e = 26$, 25, 24, 16, or 15. Upper limits of 60% (channel 17) and 25% (channel 18) and 3% (channel 19) relative to $m/e = 39$ signal were derived.

B. Laboratory angular distribution (LAB) and TOF spectra

The most probable Newton diagrams of the reaction $C(3P) + C_2H_4(X^1A_1)$ $\rightarrow$ $C_3H_3 + H$ and the laboratory angular distributions of the $C_3H_3$ product are displayed in Figs. 3 and 4 at collision energies of 17.1 and 38.3 kJmol$^{-1}$, respectively; TOF spectra are presented in Figs. 5 and 6. Both LAB distributions are very broad, and products are spread at least over a range of 50$^\circ$ in the scattering plane suggesting a large average translational energy release. Comparison of this scattering range with limiting circles which correspond to the maximum energy release of different $C_3H_3$ isomers confine energetically accessible products to the propargyl, cyclopropen-1-yl, or propyn-1-yl isomer. Cyclopropen-2-yl can most likely be eliminated, since its observable range is restricted between $\sim$42–47$^\circ$ at lower, and $\sim$15–45$^\circ$ at higher collision energies. Reactive scattering signal, however, extends to at least 12.5–60.0$^\circ$ and 10–55$^\circ$, respectively. Contributions from the velocity spread of the carbon beam (Table I) can hardly account for this discrepancy. The allenyl isomer is energetically inaccessible at both collision energies and is excluded from the discussion.

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

The translational energy distributions in the center-of-mass-frame $P(E_T)$ are presented together with the center-of-mass angular distributions $T(\theta)$ in Figs. 7–8. Best fits of TOF spectra and LAB distributions were achieved with $P(E_T)$s extending to $E_{max} = 230$ and 255 kJmol$^{-1}$, respectively. The fits are relatively insensitive to the $q$-parameter (Sec. II B): Adding or cutting the high energy tail by ±20 kJmol$^{-1}$ did not affect the calculated data due to the limited signal to noise ratio and the unfavorable kinematic relation as well as the uncertainty in the velocity spread of the carbon beam. The magnitude of $E_{max}$ can be used to identify the nature of the product isomer if their energetics are well separated. Table III compiles the maximal translational energy release, i.e., the sum of the reaction exothermicity and relative collision energy, with the reasonable approximation of cold ethylene molecules in the supersonic expansion. The formation of the propargyl isomer is consistent with the ex-
experimentally determined high energy cutoff. Even within the error limits, the 100 kJ mol\(^{-1}\) less stable cyclopropenyl radical can be clearly dismissed (Fig. 1).

Besides identification of structural isomers, the most probable translational energy gives the order-of-magnitude of the barrier height in the exit channel. Both \(P(E_T)\)s show a broad plateau between 28–43 kJ mol\(^{-1}\), nearly independent of the collision energy. These data clearly indicate a significant geometry as well as electron density change from the \(C_3H_4\) complex to the products resulting in a repulsive bond rupture from a tight transition state. The existence of an exit potential energy barrier is further indicated by the large fraction of energy released into translational motion of the products, i.e., 31±3% and 42±3%, respectively.

**D. Center-of-mass angular distribution, \(T(\theta)\)**

Both \(T(\theta)\)s are weakly polarized and show an intensity ratio of \(T(\theta)\) at \(\theta=0^\circ\) to 180\(^\circ\) increasing from 1.7±0.1 to 2.0±0.1 as the collision energy rises. Since the total fraction \(f\) of forward-scattered signal with respect to the carbon beam slightly decreases from \(f(17.1 \text{ kJ mol}^{-1}) = 13\pm2\%\) to \(f(38.3 \text{ kJ mol}^{-1}) = 8\pm2\%\) with increasing collision energy, the shape of the \(T(\theta)\)s does not propose the existence of a conventional oscillating \(C_3H_4\) complex.\(^{40,41}\) The results rather suggest two microchannels: A forward-scattered contribution with a strong correlation of the initial and final orbital angular momenta \(L\) and \(L'\) perpendicular to the initial and final relative velocity vectors \(v\) and \(v'\) (microchannel 1) and an isotropic channel, possibly symmetric around \(\theta = \pi/2\) (microchannel 2), but governed by a weak \(L\) and \(L'\) coupling allowing any of the four hydrogen atoms to depart, if the exit barriers are close together. Two alternative scenarios might account for a potential forward–backward symmetry of the center-of-mass angular distribution of microchannel 2. First, the decomposing \(C_3H_4\) complex could hold a lifetime longer than its rotational period.\(^{39,41}\) Second, a symmetric transition state might result in a center-of-mass angular distribution symmetric
The reaction of C

reduces to Eq. \( j_n \) in mind that nuclear momenta. In terms of a classical treatment and bear-

approximated in terms of the classical capture theory to angular momentum disposal.40–41 The total angular momen-
tum is given by

\[
J = L + j + j_n = L' + j' + j'_n, \tag{10}
\]

with the rotational angular momenta of the reactants and products \( j \) and \( j' \), as well as \( j_n \) and \( j'_n \) the initial and final nuclear momenta. In terms of a classical treatment and bearing in mind that \( j_n \ll L, j_n \ll j, j'_n \ll L', \text{ and } j'_n \ll j' \), Eq. \( \text{(10)} \) reduces to Eq. \( \text{(11)} \)

\[
J = L + j = L' + j'. \tag{11}
\]

A further simplification is introduced by comparing the magnitude of \( L \) and \( j \). Since bulk experiments indicate that the reaction of \( C(2P) \) with olefins and alkynes proceeds within orbiting limits5 and our relative cross sections rise with decreasing collision energy (Sec. IV E), the maximum impact parameter \( b_{\text{max}} \) leading to a complex formation is approximated in terms of the classical capture theory to \( b_{\text{max}}(17.1 \text{ kJmol}^{-1}) = 3.7 \text{ Å} \) and \( b_{\text{max}}(38.3 \text{ kJmol}^{-1}) = 3.2 \text{ Å} \) (see Appendix A and Table IV). The maximum orbital an-
gular momentum \( L_{\text{max}} \) relates to \( b_{\text{max}} \) via

\[
L_{\text{max}} = \mu \, b_{\text{max}} v_r, \tag{12}
\]

where \( \mu \) is the reduced mass and \( v_r \), the relative velocity of the reactants: Thus \( L_{\text{max}}(17.1 \text{ kJmol}^{-1}) = 99\hbar \) and \( L_{\text{max}}(38.3 \text{ kJmol}^{-1}) = 128\hbar \). Since \( C_2H_4 \) is produced in a supersonic ex-
pansion and \( j \) peaks at only 3\hbar \) at a typical rotational temperature of 30 K, \( j \) contributes less than 3% to the total angular momentum, and \( J \) becomes the initial orbital angular momentum \( L \)

\[
L \approx J = L' + j'. \tag{13}
\]

Further, an upper limit of \( L' \) can be estimated by assuming a relative velocity of the recoiling products corresponding to the average translational energy release \( \langle E_T \rangle \), and choosing an acetylenic \( C=\text{C} \) bond length of 1.08 Å as the exit impact parameter to \( L'(17.1 \text{ kJmol}^{-1}) = 20\hbar \) and \( L'(38.3 \text{ kJmol}^{-1}) = 24\hbar \). Since \( L' \approx 0.2 \text{ L}, L \) and \( L' \) are not likely to be strongly coupled on average, resulting in weakly polarized \( T(\theta) \)s. This prevents us from classifying the decompos-
ing complex as prolate- or oblate-like solely based on \( T(\theta) \). In a prolate case, low \( M' \) values dominate, where \( M' \) de-
notes the projection of \( J \) on the decomposing complex' principal axis parallel to \( v' \), and the complex decomposes in the plane containing the relative velocity vector. An oblate de-
composition geometry directs large \( M' \) values, and a frag-
mentation parallel to \( J \). Therefore, a sharply peaked \( T(\theta) \) is

\[
\text{FIG. 5. Time-of-flight data at } m/e=39 \text{ for laboratory angle } 27.5, 37.5, 45.0, 47.5, 52.5, \text{ and } 60.0^\circ \text{ at a collision energy of } 17.1 \text{ kJmol}^{-1}. \text{ Open circles represent experimental data, the solid line the fit. TOF spectra have been normalized to the relative intensity at each angle.}
\]

\[
\text{FIG. 6. Time-of-flight data at } m/e=39 \text{ for laboratory angle } 15.0, 20.0, 25.0, 35.0, 45.0, \text{ and } 55.0^\circ \text{ at a collision energy of } 38.3 \text{ kJmol}^{-1}. \text{ Open circles represent experimental data, the solid line the fit. TOF spectra have been normalized to the relative intensity at each angle.}
\]
expected only if \( \mathbf{L} \) and \( \mathbf{L}' \) strongly correlated, i.e., parallel or antiparallel with \( j' \sim L' \), or if \( M' \) is zero. This weak \( \mathbf{L} \sim \mathbf{L}' \) correlation is a direct result of large impact parameters contributing to the complex formation and the inability of the departing H atom to carry significant orbital angular momentum supporting recent bulk experiments\(^{42}\) and our findings of a long-range term dominated interaction potential.

**E. Flux contour map and total relative cross section**

The center-of-mass flux contour maps \( I(\theta,E_T) \sim T(\theta) \times P(E_T) \) for both collision energies are shown in Figs. 9–10. As expected from discussed \( T(\theta) \)s, the product flux peaks in forward direction with respect to the carbon beam on the relative velocity vector. Integrating this flux distribution over \( \theta, \varphi, E_T \), and correcting for the reactant flux as well as relative reactant velocity, we find a total, relative cross section ratio of \( \sigma(17.1 \text{ kJmol}^{-1})/\sigma(38.3 \text{ kJmol}^{-1}) = 3.5 \pm 1.1 \). This ratio is most sensitive to the fragmentation applied for \( C_3 \), especially in the Ne seeded experiments where larger carbon clusters contribute \( \sim 80\% \) to the carbon number density (Table I). Lowering the fragmentation pattern of \( C_3 \) by 30\% reduces \( \sigma(17.1 \text{ kJmol}^{-1})/\sigma(38.3 \text{ kJmol}^{-1}) \) to 2.6\( \pm 0.9 \). Nevertheless, the drop in the cross section with increasing collision energy is consistent with recent bulk experiments.\(^{32}\) Clary *et al.* investigated reaction rate constants at 293 K of \( C(3P) \) atoms with alkynes as well as alkenes, indicating the reactions proceed fast \( (k=10^{10} \text{ cm}^3 \text{ s}^{-1}) \) without entrance barrier within orbiting limits, i.e., the \( C-C_2H_4 \) interaction is dominated by a barrier-less, attractive long-range intermolecular dispersion forces giving rise to a loose, reactant-like transition state located at the centrifugal barrier to the triplet \( C_2H_4 \) PES. Taking \( L_{\text{max}} \) from Table IV, and Eq. (A6), we calculate the lower limit of barrier locations to \( R_{\text{max}}(17.1 \text{ kJmol}^{-1})=3 \text{ Å} \) and \( R_{\text{max}}(38.3 \text{ kJmol}^{-1})=2.6 \text{ Å} \).

Simple capture calculations yield a cross section proportional to \( E_{\text{col}}^{-1/3} \) and \( [\sigma(17.1 \text{ kJmol}^{-1})/\sigma(38.3 \text{ kJmol}^{-1})]_{\text{capture}} = 1.3 \pm 0.1 \). This treatment assumes the reaction proceeds with unit efficiency after barrier-crossing and under absence of steric effects. However, at higher relative collision energies the orbiting radii become comparable or smaller than the van der Waals radii. Since the capture assumption is based solely on a long-range \( C_6 \) attraction, this approximation breaks down, and the structure of the molecule becomes important. Alternatively, the presence of a second reaction channel might contribute to this deviation. Equation (14) outlines this alternative for \( j \) exit channels with cross sections \( \sigma_j \) at two collision energies \( E_1 \) and \( E_2 \):

\[
\frac{\sigma(E_1)}{\sigma(E_2)} = \frac{\sum_{j=1}^{N} \sigma_j(E_1)}{\sum_{j=1}^{N} \sigma_j(E_2)}
\]

The framework of the capture theory cannot supply information on how many exit channels are involved and yields only a total cross section, here \( \sigma(E_1) \) and \( \sigma(E_2) \). Assuming a constant opacity function and an ideal, long range-term dominated potential, both sides in Eq. (14) are identical only if we find all \( \sigma_i(E_1) \) and \( \sigma_i(E_2) \) or if only one channel is involved \((j=1)\). Therefore, our data might suggest the existence of at least a second channel leading to products with \( \frac{m}{e} \) ratios different from 39. Its relative cross section must increase with rising collision energy to reduce the right hand side of Eq. (14).

F. Energy partition of total available energy

The total available energy, \( E_{\text{tot}} \), channels into product translation, \( E_u \), rotation, \( E_{\text{rot}} \), and vibration, \( E_{\text{vib}} \). \( E_u \) can be obtained from the \( P(E_T)s \) and, hence, equals \( E_T \), cf. Sec. IV C. Since the reaction products in the crossed beam experiment were identified as atomic hydrogen and the propargyl radical, the rotational energy is confined to the \( \text{C}_3\text{H}_3 \) isomer. The rotational constants \( A=9.6081 \text{ cm}^{-1} \), \( B=0.31757 \text{ cm}^{-1} \), and \( C=0.30765 \text{ cm}^{-1} \) classify this radical as a highly prolate asymmetric top with asymmetry parameter \( \kappa=-0.9978 \). Its energy levels follow therefore in good approximation those of a symmetric top

\[
E = h\pi \left[ BJ(J+1) + (A-B)K^2 \right].
\]  

(15)

\( J \) denotes the rotational quantum number of 79 \((E_{\text{coll}}=17.1 \text{ kJ mol}^{-1})\) and \( \sim 104 \) \((E_{\text{coll}}=38.3 \text{ kJ mol}^{-1})\) since the total angular momentum is conserved. \( K \) indicates the component of the rotational angular momentum about the principal axis, with \( K=0 \) for no rotation about the figure axis, but perpendicular to it, and \( K\approx J \) for a fast rotation about the principal axis, with a slow end-over-end one.

Since no explicit information on the \( K \)-distribution is available, an exact solution of this problem is unrealistic. Here, we calculate first the rotational energy for \( K=0 \), and, therefore, the maximal vibrational energy release \( E_{\text{vib}} \) in the propargyl product. This approach is referred to as “low \( K \) approximation.” Second, we assume the forward-peaking microchannel 1 corresponds to rotations of the propargyl radical around its \( C_2 \) axis. Finally, the highest energetically accessible \( K \) states, \( K_{\text{max}} \), are computed assuming no vibrational excitation of the \( \text{C}_3\text{H}_3 \). This gives us the upper limit of the average product rotational excitation and an order of magnitude of the lowest tilt angle \( \alpha_{\text{min}} \) of the propargyl \( C_2 \) axis with respect to \( j' \) in terms of the classical vector model to

\[
\alpha_{\text{min}} = \arccos(K_{\text{max}}/j').
\]  

(16)

As evident from Table V, the low \( K \) approximation yields an increasing channeling of total energy into rotational degrees of freedom as the collision energy rises. The reduced fraction of vibrational energy from 59% to 43% indicating an incomplete energy randomization before the \( \text{C}_4\text{H}_3 \) complex decomposes, cf. Sec. V E. In case of zero vibrational excitation of the propargyl radical and upper \( K \) limit, the \( C_2 \) principal axis tilts about 68° on average with respect to \( j \) and clearly indicates a dominant end-over-end-rotation of the \( \text{C}_3\text{H}_3 \) radical. Even the assumption that microchannel 1 contributes solely to rotations around the propargyl figure axis is consistent with the energy conservation (Table V) as well as with a decreasing fraction of vibrational energy, in this case from 24% to 8%, as the relative collision energy rises.

V. DISCUSSION

The crossed beam method allows insight into the dynamics of the reaction and reveals unprecedented information on the reaction intermediate. In the following discussion, we outline all theoretically feasible reaction pathways on the \( \text{C}_3\text{H}_3 \) PES\(^{43-58}\) to the propargyl radical without imposing any dynamic or energetic constraints (Sec. V B). Thereafter, the observed dynamics and energetics are compared to what is expected based on these ad-hoc pathways. Channels not compatible with the experimental results are eliminated. This approach ultimately identifies the remaining channel as the only possible one.

TABLE III. Comparison of the maximal available translational energy release, \( E_{\text{tot \text{ theor}}} \), of the reaction \( \text{C}(^1\Pi)+\text{C}_2\text{H}_3(X^1\Delta)\rightarrow\text{C}_2\text{H}_4+\text{H}(^2S_{2}) \) for different \( \text{C}_3\text{H}_3 \) isomers with experimental data, \( E_{\text{tot \text{ exp}}} \).

<table>
<thead>
<tr>
<th>( E_{\text{coll}}, \text{kJ mol}^{-1} )</th>
<th>( \text{Propargyl} )</th>
<th>( \text{Cyclopropen-1-yl} )</th>
<th>( E_{\text{tot \text{ theor}}} ), kJ mol(^{-1} )</th>
<th>( \text{Propyn-1-yl} )</th>
<th>( \text{Cyclopropen-2-yl} )</th>
<th>( \text{Allenyl} )</th>
<th>( E_{\text{tot \text{ exp}}} ), kJ mol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.1</td>
<td>232±9</td>
<td>132±34</td>
<td>85±9</td>
<td>1±9</td>
<td>⋯</td>
<td>230±30</td>
<td></td>
</tr>
<tr>
<td>38.3</td>
<td>253±10</td>
<td>153±35</td>
<td>106±10</td>
<td>20±10</td>
<td>⋯</td>
<td>255±25</td>
<td></td>
</tr>
</tbody>
</table>

TABLE IV. Maximum impact parameter \( b_{\text{max}} \), maximum initial orbital angular momentum, \( L_{\text{max}} \), and capture cross sections \( \sigma \) at two relative collision energies \( E_{\text{coll}} \) employed in the present experiments. Cross sections \( \sigma \) are calculated for no \( \{P(b)=1\} \), one \( \{P(b)=2/3\} \), and two \( \{P(b)=1/3\} \) repulsing surfaces of the split triplet manifold.

<table>
<thead>
<tr>
<th>( E_{\text{coll}}, \text{kJ mol}^{-1} )</th>
<th>( b_{\text{max}}, \text{Å} )</th>
<th>( L_{\text{max}}, h )</th>
<th>( \sigma, \text{Å}^2 {P(b)=1} )</th>
<th>( \sigma, \text{Å}^2 {P(b)=2/3} )</th>
<th>( \sigma, \text{Å}^2 {P(b)=1/3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.1</td>
<td>3.7</td>
<td>99</td>
<td>42</td>
<td>28</td>
<td>14</td>
</tr>
<tr>
<td>38.3</td>
<td>3.2</td>
<td>128</td>
<td>32</td>
<td>21</td>
<td>11</td>
</tr>
</tbody>
</table>
FIG. 9. Contour flux map distribution for the reaction \( \text{C}_2\text{H}_4 + \text{C}_2\text{H}_4(\text{X}^1\text{A}_e) \) at a collision energy of 17.1 kJ mol\(^{-1}\).

FIG. 10. Contour flux map distribution for the reaction \( \text{C}^3\text{P}_j + \text{C}_2\text{H}_4(\text{X}^1\text{A}_e) \) at a collision energy of 38.3 kJ mol\(^{-1}\).

A. \text{C}_3\text{H}_4 \textit{ab initio} potential energy surface

We investigate two mechanisms, the addition of \( \text{C}^3\text{P}_j \) to the ethylenic \( \pi \)-bond vs insertion into the olefinic C–H bond, as well as the fate of the initially formed triplet \( \text{C}_3\text{H}_4 \) intermediates. Addition of \( \text{C}^3\text{P}_j \) to the ethylene \( \pi \)-bond yields cyclopropyldiene, Fig. 11, followed by ring opening to allene, or 1,2-hydrogen migration to cyclopropene. A 1,3-diradical tricarbon chain holds no local minimum on the triplet \( \text{C}_3\text{H}_4 \) PES. Triplet-allene fragments via C–H bond cleavage to the propargyl radical or undergoes 1,2-H-migration to triplet \( \text{trans} \) vinylmethylenes or 1,3-H-migration to triplet methylacetylene, which subsequently yields propargyl \( \text{or propyn-1-yl} \) via C–H bond rupture. Triplet cyclopropene either decomposes to cyclopropen-1-yl/cyclopropen-2-yl radicals, or ring opens to vinylmethylene. This might fragment to the propargyl radical. C–H bond rupture in cyclopropyldiene may yield cyclopropen-2-yl. Finally, insertion of \( \text{C}^3\text{P}_j \) into the olefinic C–H bond leads to vinylmethylene.

The rigorous identification of the propargyl radical alone eliminates all exit channels to competing \( \text{C}_3\text{H}_4 \) isomers. The participation of a cyclopropene complex can be ruled out as well. A potential barrier connecting cyclopropyldiene with cyclopropene is located at least 120 kJ mol\(^{-1}\) above the transition state to allene. If a triplet cyclopropyldiene complex is initially formed, the reaction proceeds via the lowest energy pathway, in our case to allene. In this framework, the large potential energy difference of both transition states and the participation of only one isomer at \( m/e=39 \) is consistent with the TOFs and both LAB distributions, cf. Secs. IV A–IV D. The four remaining pathways differ by the migration of a H atom before the final bond rupture, but cannot be reduced further by investigating solely the \( \text{C}_3\text{H}_4 \) PES. However, hydrogen rearrangement prior to decomposition might be involved to certain extend.

B. Rotation axis of decomposing \( \text{C}_3\text{H}_4 \) complexes

The rotational motions of the prevailing \( \text{C}_3\text{H}_4 \) complexes are very interesting and help to explain the shapes of both \( T(\theta) \)s, if the distributions for distinct rotations are compared to what is found experimentally. We point out that the initial trajectory of the carbon atom prior to capture is unimportant in the frame of the capture theory, since the potential energy is assumed to depend only on the \( C_p \) parameter. But steric effects and attractive chemical forces come into play if the capture radius is in the order of the bond lengths, so that certain approach geometries and rotations might be favored. Based on this, we identify allowed rotations in each \( \text{C}_3\text{H}_4 \) intermediate, elucidate trajectories under highest possible symmetry of \( \text{C}^3\text{P}_j \) toward \( \text{C}_2\text{H}_4 \) which excite these rotations, and discuss the range of contributing impact parameters. Finally, we demonstrate that the title reaction proceeds via addition to the ethylene \( \pi \)-bond yielding cyclopropyldiene, followed by ring opening to allene and decomposition to propargyl and atomic hydrogen.

\textbf{1. Triplet allene complex}

Maintaining the C–C–C plane as a plane of symmetry, the carbon atom might add to the \( \text{C}_3\text{H}_4 \) molecular plane conserving \( C_s \) symmetry (Fig. 12). This pathway does not force...
perpendicular approaches towards the C=C bond, but permits rather in-plane trajectories skewed with respect to the perpendicular vector. Since \( \mathbf{L} \approx \mathbf{j} \), the three heavy atoms rotate in a plane roughly perpendicular to \( \mathbf{L} \) around the \( \mathbf{C} \)-axis of the prolate cyclopentadiene adduct. The successive ring opening to triplet allene conserves \( \mathbf{C}_5 \) symmetry and converts the previously out-of-plane \( \mathbf{H} \)-atoms into the symmetry plane. This scenario opens larger impact parameters than typical \( \mathbf{C}_2 \mathbf{H}_4 \) bond dimensions of \( r(\mathbf{C}=\mathbf{C})=1.325 \ \text{Å} \), and \( r(\mathbf{C}-\mathbf{H})=1.076 \ \text{Å} \) compared to the large \( \mathbf{b} \)-dominated opacity function with \( b_{\mathbf{max}}=3.7 \) and \( 3.2 \ \text{Å} \) (Secs. IV D and IV E). In addition, the nearly in-plane rotation about the \( \mathbf{C} \)-axis gives rise to extremely low \( K \) values and, therefore, a negligible \( \mathbf{J} \) component about the \( \mathbf{C}_2 \) figure axis of the triplet allene. This rotation axis could be associated with preferentially low \( K \) states populated in the propargyl product. Therefore, our results suggest that \( \mathbf{C} \)-like rotations of the triplet allene complex contribute predominantly to the isotropic microchannel 2, and that any of the four hydrogen atoms \( \mathbf{H}1-\mathbf{H}4 \) departs with almost equal probability to yield a weak \( \mathbf{L} \)-\( \mathbf{L}' \) correlation. Alternatively, a long-lived complex behavior was suggested in Sec. IV D, but can likely be dismissed: The rising collision energy should reduce the lifetime of the triplet allene complex and would have resulted in a more forward scattered fraction which was not verified in our experiments.

In addition, a parallel approach of \( \mathbf{C}(3\mathbf{P}) \) with respect to the ethylene plane under \( \mathbf{C}_2 \) symmetry induces rotations around the cyclopentadiene \( \mathbf{A} \)-axis, Figs. 12 and 13. Ring opening yields triplet allene. The rotation period \( \tau_{\text{rot}} \) of the complex around its \( \mathbf{A} \)-axis helps us to elucidate the effect of these trajectories on the \( T(\theta) \) function. Investigating a rotation around the \( i \)-axis, \( \tau_{\text{rot}} \) is calculated via Eq. (17)

\[
\tau_{\text{rot}} = 2\pi I_i / L_{\text{max}}
\]

with the moment of inertia \( I_i \) in respect to the \( i \)-axis and the maximum angular momentum \( L_{\text{max}} \). Table 7 compiles the calculated rotational periods around the \( A, B, \) and \( C \)-axis of the triplet allene complex. The rotational period depends strongly on the rotational axis \( A \) vs \( C \) and varies between 0.04 and 0.57 ps. Reactions with collision times <0.1 ps follow direct reactive scattering dynamics with almost zero intensity at \( \theta=180^\circ \). Based on this and a strong \( \mathbf{L} \)-\( \mathbf{L}' \) correlation, only \( \mathbf{A} \)-like rotations and \( \mathbf{H}2-\mathbf{H}3-\mathbf{C}1 \) bond ruptures should contribute to the forward-peaked microchannel 1. This conclusion is consistent with the partition of energy into the rotational degrees of freedom and the total conservation of energy (Table V), calculated for a dominant end-over-end rotation of propargyl (microchannel 2) and contributions of \( 8\% \sim 14\% \) \( A \)-like rotations (microchannel 1). However, a rapid inversion of triplet allene via a planar, \( D_{2h} \) transition state (Fig. 13) could induce a symmetric exit transition state as well as \( T(\theta) \) and could contradict our findings. Although the inversion barrier height ranges about 25 kJmol\(^{-1} \), well below the total available energy, the transition state would rotate fast about its principal axis with \( K=J \). This increases the inversion barrier to at least 420 kJmol\(^{-1} \), well above the total available energy. Bulk experiments support our conclusion of dominating \( C \)-rotations. The typical time between two collisions of the initially formed \( \mathbf{C}_2 \mathbf{H}_4 \) complex in \( ^1\mathbf{C} \) tracer studies and a second bath molecule are on the order of 1 ps at 100 Torr neat ethylene. A lifetime at least one order of magnitude less cannot account for detected \( \mathbf{C}5 \) compounds.

Finally, we discuss the potential contribution of \( B \)-type rotations of the triplet allene complex (Fig. 13). \( B \)-transitions can be excited by \( \mathbf{C} \)-atom trajectories following \( \mathbf{C}_1 \) symmetry and give rise to a symmetric exit transition state, since \( \mathbf{H}2 \) and \( \mathbf{H}3 \) as well as \( \mathbf{H}4 \) and \( \mathbf{H}1 \) can depart from either end, cf. Sec. IV D. Therefore, the strongly forward scattered microchannel 2 can be dismissed. Based only on the experimentally found \( T(\theta) \), a symmetric transition state might explain microchannel 2. Compared to reactions conserving \( \mathbf{C}_2 \) symmetry, however, encounters without any symmetry element show a reduced overlap of the \( p \)-type orbitals of the \( \mathbf{C} \)-atom with the \( \pi \)-molecular orbital of the ethylene molecule, and should be energetically less favorable.

### 2. Triplet cis/trans vinylcarbene complex

A pathway to triplet \( \text{cis/trans} \) vinylcarbene follows either 1,2-H-migration in triplet allene or a direct insertion of \( \mathbf{C}(3\mathbf{P}) \) into a \( \mathbf{C}--\mathbf{H} \) bond of ethylene. Figure 13 displays the principal rotational axis with the embodied carbon atom designated as \( \mathbf{C}2 \) and \( \mathbf{C}3 \), respectively. As evident, only a

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**TABLE VI. Principal moments of inertia \( I_i \), in amu Å\(^2 \), rotational constants in MHz, and asymmetry parameters \( \kappa \) of triplet \( \mathbf{C}_2 \mathbf{H}_4 \) complexes (TS: transition state) calculated from geometries in Refs. 43–55.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>( I_A )</th>
<th>( I_B )</th>
<th>( I_C )</th>
<th>( A )</th>
<th>( B )</th>
<th>( C )</th>
<th>( \kappa )</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{trans-vinylcarbene}</td>
<td>8.8629</td>
<td>44.6369</td>
<td>53.4998</td>
<td>57022</td>
<td>11322</td>
<td>9446</td>
<td>-0.92</td>
</tr>
<tr>
<td>\text{cis-vinylcarbene}</td>
<td>7.3813</td>
<td>47.2273</td>
<td>54.6086</td>
<td>68468</td>
<td>10701</td>
<td>9254</td>
<td>-0.95</td>
</tr>
<tr>
<td>allene</td>
<td>5.3910</td>
<td>51.8501</td>
<td>57.2411</td>
<td>93746</td>
<td>9747</td>
<td>8829</td>
<td>-0.98</td>
</tr>
<tr>
<td>allene (TS)</td>
<td>3.3489</td>
<td>58.3671</td>
<td>61.7160</td>
<td>150911</td>
<td>8658</td>
<td>8188</td>
<td>-0.99</td>
</tr>
<tr>
<td>methylacetylene</td>
<td>4.7216</td>
<td>45.5987</td>
<td>50.3203</td>
<td>107037</td>
<td>11083</td>
<td>10043</td>
<td>-0.98</td>
</tr>
</tbody>
</table>

**TABLE VII. Rotational periods \( \tau_{\text{rot}} \) of triplet allene calculated for rotations about the \( A, B, \) and \( C \)-axis at collision energy \( E_{\text{coll}} \). \( L_{\text{max}} \) denotes the maximum impact parameter.**

<table>
<thead>
<tr>
<th>( E_{\text{coll}} ) kJmol(^{-1} )</th>
<th>( I )</th>
<th>( L_{\text{max}} ) Å ( \cdot ) ps</th>
<th>( \tau_{\text{rot}}(A), \text{ps} )</th>
<th>( \tau_{\text{rot}}(B), \text{ps} )</th>
<th>( \tau_{\text{rot}}(C), \text{ps} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.1</td>
<td>1.7</td>
<td>99</td>
<td>0.05</td>
<td>0.52</td>
<td>0.57</td>
</tr>
<tr>
<td>38.3</td>
<td>2.0</td>
<td>128</td>
<td>0.04</td>
<td>0.40</td>
<td>0.44</td>
</tr>
</tbody>
</table>
H2/C2 bond rupture in vinylcarbene yields the propargyl radical. Since any of the four hydrogen atoms is required to depart equally likely under weak L and L′ coupling to account for the isotropy of microchannel 2 (Sec. IV C), a contribution of a cis/trans vinylcarbene intermediate to microchannel 2 can be likely ruled out. Further, only A-like rotations could give rise to microchannel one. The vinylcarbene complex rotating around the B/C axis must hold lifetimes of at least 0.4–0.3 ps to induce any forward-scattering, but the strongly forward-scattered T(θ) at higher collision energy requires collision times <0.1 ps to account for a strong L-L′ correlation.61 These rotations around the A-axis are induced, if C(3Pj) inserts via a perpendicular pathway into the C–H bond of the ethylene molecule. This trajectory, however, seems unlikely, since only a narrow range of impact parameters between 0.66 and 1.2 Å contributes to reactive scattering signal. The overwhelming contribution of large impact parameters up to 3.7 Å was already validated. Likewise, this insertion resembles a symmetry forbidden reaction, and an entrance barrier larger than our maximum collision energy of 38.3 kJmol⁻¹ is expected. Our interpretation correlates with ¹¹C(³Pj) and even ¹¹C(³Dj) add to the π-bond, but only suprathermal C-atoms in both spin states insert into the C–H bond. The only remaining pathway to A-like rotations in vinylcarbene involves a [3,2]-H-shift in triplet allene, rotating around its A-axis. Since the forward-peaking demands collision times

![Diagram](image_url)

**FIG. 11.** Schematic representation of the lowest energy pathways on the triplet C₂H₆ PES and structure of potentially involved collision complexes. Enthalpies of formation, electronic states, and were taken from Refs. 43–58: Cyclopropylidene (1): 501 kJmol⁻¹, ²B₁, ²C₂; allene (2/2): 405 kJmol⁻¹, ³A₂, ³C₂; cyclopropene (3): −720 kJmol⁻¹; propargyl (4): 557 kJmol⁻¹, ³B₂, ³C₂; cis vinylcarbene (5): 408 kJmol⁻¹, ³A₂, ³C₂; trans vinylcarbene (6): 409 kJmol⁻¹, ³A₂, ³C₂; methylenecyclopropane (7): −630 kJmol⁻¹; propyn-1-yl (8): 704 kJmol⁻¹, ³E, ³D₃; cyclopropen-1-yl (9): 657 kJmol⁻¹, ³E, ³D₃; cyclopropen-2-yl (10): 790 kJmol⁻¹, ³A₂, ³C₂; ? No information available.

![Diagram](image_url)

**FIG. 12.** Approach geometries of the carbon atom toward the ethylene molecule conserving C₃ symmetry and induced rotations. Upper: Perpendicular approach; lower: Parallel approach.
<0.1 ps, a hydrogen migration can most likely be excluded. Even a fast [1,2]-H-rearrangement from vinylidene to acetylene takes more than 0.2 ps.\textsuperscript{62}

3. Triplet methylacetylene complex

The triplet allene-methylacetylene rearrangement involves a symmetry-allowed [1,3]-H-shift\textsuperscript{60} similar to Sec. V B. The height of this barrier, however, ranges well above any conceivable one arising from [1,2]-H-migration. Considering that the lower energy pathway is closed, [1,3]-H-migration cannot take place either.

C. Surface splitting

The symmetry of the total wave function has to be conserved during the title reaction and is assumed to be separable into an electronic and spin part. Since we are dealing with light carbon atoms and the spin–orbit coupling constant increases with the fourth power of the nuclear charge, this simplification is justified. Interacting under highest possible $C_s$ symmetry, the $P$-term of the carbon atom splits into the irreducible representations $A''+A'''+A'$. The $C_2H_4$ symmetry reduces to $A'$. The total electronic wave function is gained via the direct product of the reactant’s wave function

$$\langle A''+A'''+A' \rangle \times A' = 2A''+A'. \quad (18)$$

The $B_2$ ground state of the propargyl radical reduces to $A''$ in $C_s$ symmetry ($C$-like rotations of the triplet allene complex) and the $S$ state of hydrogen atom to $A'$$\quad \langle A'' \times A' \rangle = A'' \quad (19)$

The ground state electronic wave functions of all triplet complexes and transition states involved in the elucidated reaction pathway, i.e., cyclopropylidene and allene, belonging to the $A''$ representation. Therefore, reactants, collision complexes, and products correlate on the $A''$ ground state surface under $C_s$ symmetry via excitation of $C$-like rotations. If the carbon atom approaches slightly off-axis, the $C_s$ symmetry reduces to $C_1$ and the electronic wave function to $A$. Likewise, $A$-rotations of the decomposing triplet allene complex do not conserve the symmetry plane in the final carbon-hydrogen bond rupture, and the symmetry of the electronic wave func-
tion is reduced to $^3A$. Finally, we point out that the opacity function $P(b)$ might be different for the $^3A$ (microchannel 1) and $^3A''$ surface (microchannel 2). This could account for the deviation of the relative energy dependent cross sections from the simple capture picture as well.

**D. Exit transition state**

The collision energy dependent $P(E_T)$ shape and their average translational energy releases, $\langle E_T \rangle$ reveal the chemical dynamics between the moment of the triple allene complex formation and the final separation into products. As shown in Sec. IV C, both $P(E_T)s$ peak at 28–43 kJmol$^{-1}$ and indicate that the C–H bond rupture in triplet allene does not resemble a system with a loose transition state. This finding and the lack of intensity in both $P(E_T)s$ below 3 and 12 kJmol$^{-1}$ suggest instead a tight transition state, and should go hand in hand with a significant geometry change from the triplet allene complex to the propargyl radical. As evident from Fig. 14, this requirement is fulfilled. Predominantly, the C2–C3-bond length in the propargyl radical is reduced by 0.141 Å, corresponding to a bond order increase from 1.5 to 3, and the C1–C2–C3 bond angle widens by 52.7°. The order of magnitude of the exit barrier is consistent when comparing the rotational period of the triplet allene complex with typical ISC timescales: Even the largest known ISC rate constants between $10^{10}$ to $10^{11}$ s$^{-1}$ for polycyclic aromats containing heavy atoms, e.g., bromonaphthalene, are at least one order of magnitude too low.$^{65}$

An alternative ISC mechanism follows a rotation of two perpendicular $\pi$-electron systems each filled with one electron.$^{66-67}$ In the case of triplet cyclopropylidene as well as allene, the first electron occupies a $\pi$-type orbital, the second one a nonbonding orbital with $\sigma$-symmetry. Therefore, this pathway cannot contribute to ISC in the title reaction. Summarized, our findings indicate ISC should not play an important role and strongly correlate with $^{11}$C($^3P_j$)|$^1D_2$) tracer experiments in C$_2$H$_4$ systems: allene molecules are solely the reaction product of C($^1D_2$) with a single ethylene molecule. C($^3P_j$) yields triplet C$_2$H$_4$ which fragments or reacts with a second C$_2$H$_4$ molecule.

**E. Possible contributions from the singlet C$_3$H$_4$ surface**

The experimental results strongly indicate that the title reaction proceeds on the ground-state triplet surface. However, we will also investigate the singlet PES for completeness. Here, intersystem crossing (ISC) might occur if the spin–orbit coupling operator acts as a perturbation capable of mixing the triplet wave function ($^3B_2$ in cyclopropylidene, $^3A_2$ in allene) with the final singlet wave function ($^1A_1$ in cyclopropylidene and allene; reduced via $C_{2v}$ symmetry). Since the operators transform as rotations, they span the irreducible representations $A_2$, $B_1$, and $B_2$. Hence, the $a^3B_2$ state of cyclopropylidene is mixed via a $B_2$ spin–orbit operator with $X^1A_1$ and the allene $a^3A_2$ state via a $A_2$ operator to its electronic ground state. This direct product approach however, yields no information on the magnitude of the spin–orbit interaction. Since no heavy atom is present in our complexes and the spin–orbit coupling constant rises with the fourth power of the atomic number, the ISC crossing is too slow compared to the lifetime $\tau$ of the C$_3$H$_4$ complex. This conclusion is consistent when comparing the rotational period of the triplet allene complex with typical ISC timescales: Even the largest known ISC rate constants between $10^{10}$ to $10^{11}$ s$^{-1}$ for polycyclic aromats containing heavy atoms, e.g., bromonaphthalene, are at least one order of magnitude too low.$^{65}$

An alternative ISC mechanism follows a rotation of two perpendicular $\pi$-electron systems each filled with one electron.$^{66-67}$ In the case of triplet cyclopropylidene as well as allene, the first electron occupies a $\pi$-type orbital, the second one a nonbonding orbital with $\sigma$-symmetry. Therefore, this pathway cannot contribute to ISC in the title reaction. Summarized, our findings indicate ISC should not play an important role and strongly correlate with $^{11}$C($^3P_j$)|$^1D_2$) tracer experiments in C$_2$H$_4$ systems: allene molecules are solely the reaction product of C($^1D_2$) with a single ethylene molecule. C($^3P_j$) yields triplet C$_2$H$_4$ which fragments or reacts with a second C$_2$H$_4$ molecule.

**F. Comparison with the reaction O($^3P_j$)+C$_2$H$_4$**

The dynamics of the reaction O($^3P_j$) with C$_2$H$_4$ were recently studied in our lab.$^{28}$ and two major channels were detected. The oxygen–hydrogen exchange channel yields H+CH$_3$O on the $^3A''$ surface via a short lived triplet 1,3 CH$_3$CH$_2$O diradical undergoing C–H bond rupture. Alternatively, the C$_2$H$_4$O complex undergoes ISC, followed by 1,2-hydrogen migration to acetaldyhyde and C–C bond rupture to CH$_3$ and HCO. The different dynamical behavior as compared to C($^3P_j$)+C$_2$H$_4$ is solely the effect of a stable triplet 1,3-diradical on the C$_2$H$_4$O PES and a successive ISC via rotation of both perpendicular $\pi$-electron systems to a deep potential well. These dynamics increase the lifetime of the complex and open up the channel of H-migration to acetaldyhyde. A triplet, 1,3 CH$_2$CH$_2$C diradical, however, holds no

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**FIG. 14.** Equilibrium geometries of triplet allene and the propargyl radical.

Refs. 36–37.
local minimum on the $C_2H_4$ PES and collapses to cyclopropylidene. ISC, successive ring opening to allene, and 1,2-H-migration to singlet methylacetylene are closed, and no $CH_3$-loss can occur.

G. Undetected channels

The dynamics of the title reaction account for the unobserved exothermic exit channels (Table II). First, all singlet channels 6, 8, and 9 to $C_2H_2$-isomers as well as to $CH_4$, # 19, are closed, since the reaction proceeds via spin conservation on the triplet surface. Reactions (10) and (11) to triplet cyclopropenylidene and vinylidenecarbone must proceed via cyclopropylidene and allene, respectively. Channel 10 is a symmetry-forbidden, 4 center-4 electron elimination (retro-addition of $H_2$ to the C=C in triplet cyclopropenylidene), whereas # 11 involves a symmetry forbidden, 3 center-4 electron elimination (retro cheletop reaction of $H_2$ with vinylidenecarbone). Both pathways are expected to involve a symmetry imposed barrier: lower barrier limits of 82 kJmol$^{-1}$ (# 10) and 103 kJmol$^{-1}$ (# 11) are reasonable for this class of symmetry forbidden reactions.$^{58}$ Reaction to triplet propargylene (# 7) must pass triplet allene, but geometrical constraints hinder this pathway. Further, elimination of a $CH_2$ group (# 18) remains unobserved, and the 1,3-H-migration to triplet methylacetylene is likely prevented in the triplet allene complex.

Channel 17 remains the only additional pathway. However, a direct fragmentation of cyclopropylidene or allene to $C_2H_2$ is not feasible. The elimination must proceed via a cyclopropenylidene ring cleavage [retrocycloaddition of $C_2H_5(X^2B_2)$ to $H_2CC$, vinylcarbene ($X^1A_1$)] or a C1-C2 bond cleavage in allene to $CH_2(X^2B_2) + H_2CC$ ($X^1A_1$). Since vinylcarbene ranges $\sim$180 kJmol$^{-1}$ higher in energy than acetylene and the 1,2-H-migration to $C_2H_2$ involves a barrier of about 11 kJmol$^{-1}$, the transition state is placed about 30 kJmol$^{-1}$ above the reactants. Hence, channel 18 could only be opened at the higher collision energy of 38.3 kJmol$^{-1}$ and might explain the deviation of the experimentally determined cross-section ratio from the theoretical one, cf. Sec. IV E as well as the diminishing acetylene yield in $^{13}C$ tracer experiments with increasing thermalization.

VI. IMPLICATIONS TO INTERSTELLAR CHEMISTRY AND COMBUSTION PROCESSES

The explicit identification of the $C_3H_3$ propargyl isomer in the crossed beam reaction $C(3P_j)$ with $C_2H_2$ portrays a further example of the dominant carbon–hydrogen exchange channel in the reaction of neutral carbon atoms with unsaturated hydrocarbons.$^{63}$ This pathway was elucidated recently based on molecular beams studies of reaction (20)

$$C(3P_j) + C_2H_2(X^1Σ_g^+) \rightarrow C_3H_3 + H,$$

and presents an alternative, one-step approach to build up carbon bearing molecules in interstellar environments and hydrocarbon flames. Competing ion-molecule reactions (21–23), for example,

$$C_2H_4 + C^+ \rightarrow C_3H_3^+ + H,$$

$$→ C_3H_3^+ + H_2,$$

$$\rightarrow C_3H_3 + H_2,$$

hold higher rate constants with $k(C^+ + C_2H_4; 293 K)$— $\left(1.2 \pm 0.1\right) \times 10^{-9}$ cm$^3$ s$^{-1}$ as compared to the atom-neutral reaction $k(C + C_2H_4; 293 K)$— $\left(2.0 \pm 0.1\right) \times 10^{-10}$ cm$^3$ s$^{-1}$, but modeling of high and low ionization phases in dark interstellar clouds yielded neutral carbon fractional abundances of about $10^{-5}$ and $10^{-7}$ vs C$^+$ data of $-3\times10^{-8}$ and $3\times10^{-9}$, respectively.$^{69}$ White and Sandell$^{70}$ confirmed these calculations and observed neutral carbon fractional abundances between $3.0 \times 10^{-5}$ and $5.0 \times 10^{-7}$ toward OMC-1. These data clearly undermine the order-of-magnitude advantage for the rate of ion-molecule reactions as compared to atom-molecule reactions. Most important, however, synthesis of carbon-hydride radicals via atom-neutral reaction proceeds in one step, eliminating the need for successive binary encounters. Lowest applied translational energies of $\sim17.1$ kJmol$^{-1}$ in our experiments are equivalent to about 1500 K and are easily accessible in the outflow of carbon stars with temperatures up to 4000 K. In addition, a verified rising re-active cross sections with decreasing collision energy identifies this reaction class as a potentially important means to form complex hydrocarbons even for dark and diffuse interstellar clouds, but extrapolation to typical temperatures of 10–100 K depends on the absence of small entrance barriers. Our findings, however, strongly encourage astronomical search for the hitherto unobserved propargyl isomer and hydrocarbon radicals as potential C–H exchange channels of atom-neutral reactions, e.g.,

$$C(3P_j) + HCCCH \rightarrow C_3H_3 + H.$$ (24)

In particular, methylacetylene has been widely observed toward the Orion ridge and TMC-1. These clouds serve as ideal targets to identify potential $C_3H_3$-isomers, perhaps among unidentified microwave transitions in the spectrum toward OMC-1.

VII. CONCLUSIONS

The reaction between ground state carbon atoms, C$^1(3P_j)$, and ethylene, $C_2H_4(X^1A_1)$, was studied at average collision energies of 17.1 and 38.3 kJmol$^{-1}$ using the crossed molecular beam technique. Our results suggest two microchannels, both initiated via an attack of the carbon atom to the π-orbital of the $C_2H_4$ molecule via a loose, reactant like transition state located at the centrifugal barrier. One microchannel follows the highest symmetric C-atom approach via $C^1_s$ symmetry on the ground state $\Lambda^3\Pi$ surface and contributes to an isotropic center-of-mass angular distribution. Initially, the cyclopropylened conditions rotates in a plane roughly perpendicular to J around its C-axis and undergoes ring opening to allene prior to decomposition to the propargyl radical in its $X^2B_2$ state. A second microchannel contributes $\sim$10% of the scattering signal. Here, the A-like rotations of the cyclopropylened adduct, ring opening to triplet allene, and a
strong \( \mathbf{L} \cdot \mathbf{L}' \) correlation give rise to a forward-peaking \( T(\theta) \). Both exit transition states are found to be tight and located at least 30–40 \( \text{kJmol}^{-1} \) above the products.

This mechanism is consistent with \(^{11}\text{C}(3P_g)\)-tracer studies under bulk conditions. The postulated triplet cyclopropyldiene complex was trapped as a spiroane, and an assumed \( \text{C}_3\text{H}_3 \) intermediate yielded 1-propenyl-5 and 1,2-pentadieny1-5 products. The acetylene production can be explained by assuming a second, but in our experiments undetected channel of the allene complex decomposing to vinylidene and triplet carbene.

The explicit identification of \( \text{C}_3\text{H}_3 \) under single collision represents a second example of a carbon–hydrogen exchange in reactions of ground-state carbon with unsaturated hydrocarbons. This versatile concept represents an alternative pathway to build up unsaturated hydrocarbons chains in combustion processes and in the interstellar medium.

Note added in proof. The assignment of the symmetry of the electronic wave function for \( \text{C}_2\text{v} \) molecules follows the convention that the molecular plane is defined as the mirror plane, e.g., \( \text{C}_3\text{H}_3(\Sigma^1\Delta_2) \) instead of \( \text{C}_3\text{H}_3(\Sigma^2\Delta_1) \).

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APPENDIX

The total energy of the system \( E_T \) [Eq. (A1)] is the sum of the kinetic energy of the reactants \( (A2) \) with the reduced mass \( \mu \) at distance \( R \) and the effective potential \( V_{\text{eff}}(R) \) as a sum of a repulsive centrifugal potential \( V_{\text{cen}}(R) \) Eq. (A3) and an attractive intermolecular dispersion term \( V_{\text{disp}}(R) \) with the Lennard-Jones-coefficient \( C_6 \) [Eq. (A4)]

\[
E_T = E_{\text{kin}}(R) + V_{\text{eff}}(R) = E_{\text{kin}}(R) + V_{\text{cen}}(R) + V_{\text{disp}}(R), \tag{A1}
\]

\[
E_{\text{kin}} = \frac{1}{2} \mu \dot{R}^2, \tag{A2}
\]

\[
V_{\text{cen}}(R) = \frac{E_pb^2}{R^2}, \tag{A3}
\]

\[
V_{\text{disp}}(R) = -\frac{C_6}{R^6}. \tag{A4}
\]

The effective potential holds a maximum at \( R=R_{\text{max}} \) [Eq. (A5)] giving rise to the barrier location at \( R_{\text{max}} \) [Eq. (A6)]; if the reactant approaches within \( R_{\text{max}} \), chemical forces take over.

\[
\left. \frac{dV_{\text{eff}}(R)}{dR} \right|_{R=R_{\text{max}}} = 0, \tag{A5}
\]

\[
R_{\text{max}} = \left( 6 \mu C_6 / L^2 \right)^{1/4}. \tag{A6}
\]

Consequently, the remaining kinetic energy at \( R=R_{\text{max}} \) has to fulfill the condition for reaction

\[
\frac{1}{2} \mu \dot{R}^2 = \left[ E_T - \frac{E_pb^2}{R^2} + C_6 \right]_{R=R_{\text{max}}} \geq 0, \tag{A7}
\]

yielding the maximum impact parameter \( b_{\text{max}} \)

\[
b_{\text{max}} = \left( \frac{L_{\text{max}}^2}{2 \mu E} \right)^{1/2}. \tag{A8}
\]

This treatment assumes the reaction proceeds with unit efficiency after barrier-crossing and under absence of steric effects. The Lennard-Jones coefficient \( C_6 \) is approximated according to Hirschfelder et al.\(^7\) to

\[
C_6 = \frac{3}{2} \left( \frac{E_cE_{C_2H_4}}{E_c+E_{C_2H_4}} \right) a_c a_{C_2H_4}, \tag{A9}
\]

with the ionization potentials \( E_i \) for \( i=\text{C}(3P_g) \), and \( E_{C_2H_4}(\Sigma^1\Delta_2) \), and the polarizabilities \( a_c \). Using \( a_{C(3P)} = 1.76 \times 10^{-30} \text{ m}^4 \), \( a_{C_2H_4} = 4.25 \times 10^{-30} \text{ m}^4 \), \( E_c(\text{C}_3\text{H}_3) = 11.76 \), \( E_{C_2H_4} = 10.5 \text{ eV} \), the maximum impact parameter \( b_{\text{max}} \) calculates to \( b_{\text{max}} \) (17.1 \text{ kJmol}^{-1})=3.7 \text{ Å} and \( b_{\text{max}} \) (38.3 \text{ kJmol}^{-1})=3.2 \text{ Å} (Table II).

5. P. R. Westmoreland, A. M. Dean, J. B. Howard, and J. P. Longwell, J. Phys. Chem. 93, 8171 (1989), and references therein.
A deviation of this long-lived complex outcome occurs, if a long-lived complex decomposes with oblate symmetry and energy conservation excludes states with high $M'$ values ($M'$: Projection of the total angular momentum vector $J$ on the relative velocity vector of the departing fragments, $v$). In this scenario, the $T(\theta)$ maximum shifts from 90° to an intermediate position.

Care has to be taken to classify symmetry allowed and forbidden reactions in open shell triplet biradicals.

See Ref. 59. In closed shell molecules, 1-3-H-migrations are symmetry forbidden.


