The Hidden Path to the Resonance-Stabilized Fulvenallenyl Radical (C7H5) via the Bimolecular Reaction of Tricarbon (C3, X1Σg+) with 1,3-Butadiene (C4H6; X1Ag)

Iakov A. Medvedkov,1 Alexander M. Mebel,2\* Zhenghai Yang,1 Shane J. Goettl,1 Ralf I. Kaiser1\*

1 Department of Chemistry, University of Hawai‘i at Manoa, Honolulu, HI 96822, USA

2 Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, USA

AUTHOR INFORMATION

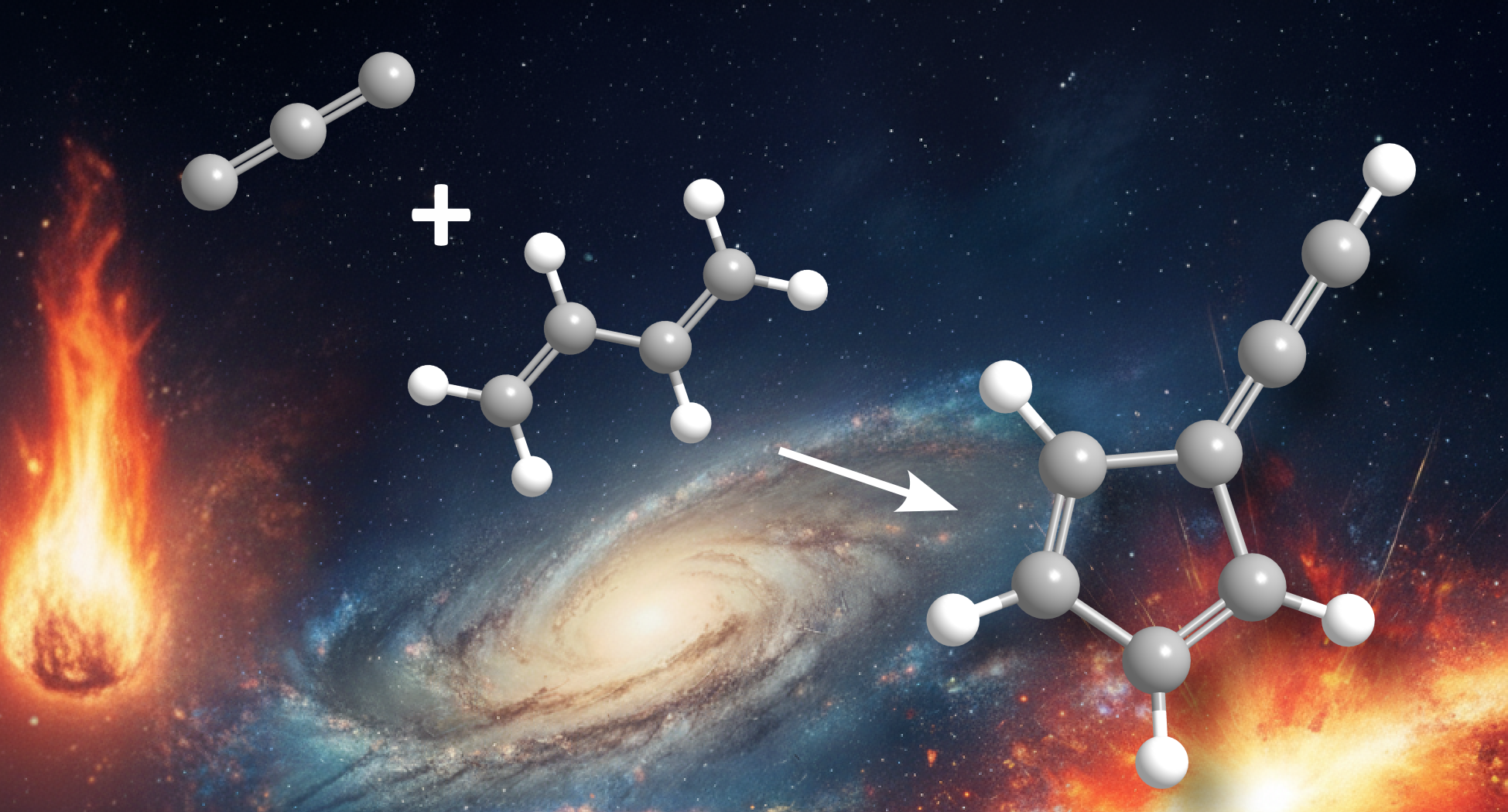
Corresponding Author

\* Corresponding to: ralfk@hawaii.edu; [mebela@fiu.edu](mailto:mebela@fiu.edu)

ABSTRACT

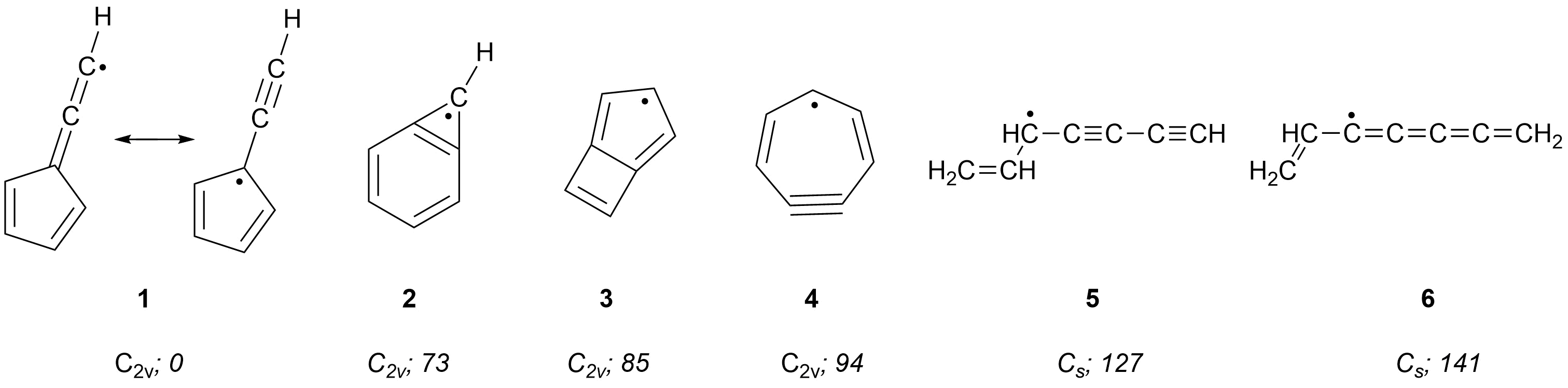
We report a novel bimolecular pathway forming resonance-stabilized C7H5 radicals *via* the gas-phase reaction of tricarbon (C3, X1Σg+) with 1,3-butadiene (C4H6, X1Ag). Crossed molecular beam experiments combined with high-level electronic structure and statistical calculations, we reveal a rich potential energy surface. The reaction proceeds *via* C3 to a double bond , overcoming 30 kJ mol–1 barrier, followed by ring opening and hydrogen atom loss, yielding predominantly acyclic 1-heptene-4,6-diyn-3-yl (**p2**). Other channels yield **p3** (1,3,4,5,6-heptapentaen-3-yl) and the fulvenallenyl radical (**p1**) with similar branching ratios of about 8%. Due to its energy threshold, this reaction occurs in high-temperature environments like flames and carbon star envelopes, but is suppressed in colder regions such as molecular clouds and Titan’s atmosphere. These findings invite further exploration into the role of small carbon clusters in shaping the molecular complexity of our universe – from the flicker of a flame to the death of a star.

**TOC GRAPHICS**

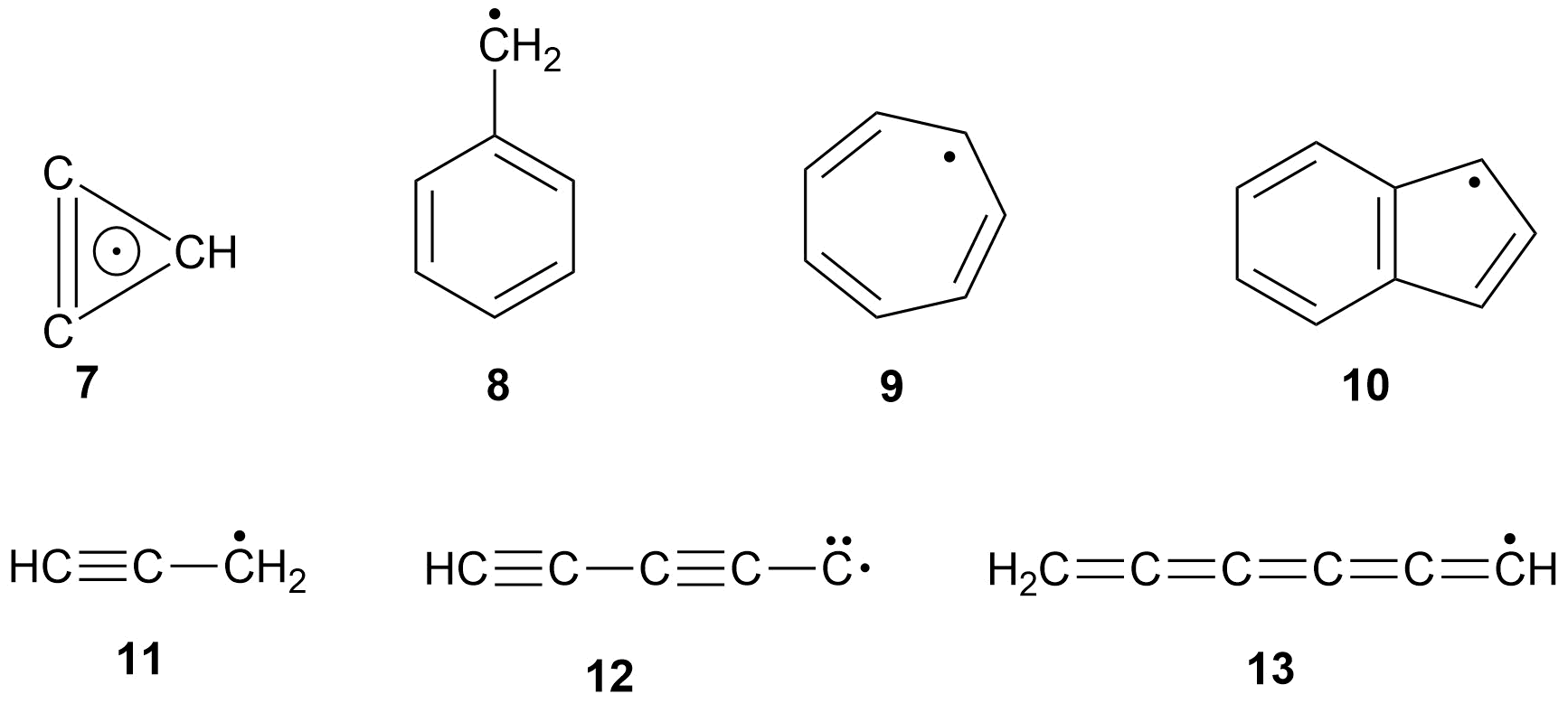


**KEYWORDS** reaction mechanisms • fulvenallenyl • fulvenallene • Resonantly stabilized free radicals • astrochemistry

Despite over a century of intensive exploration in organic chemistry, the fulvenallenyl radical (C7H5) was only proposed in 20091 and experimentally detected in laboratory in 2011 by using threshold photoionization mass spectrometry.2,3 The C7H5 family encompasses a diverse array of cyclic (***1***, ***2***, ***4***), bicyclic (***3***), and acyclic (***5****,* ***6***) radicals comprising five, six, and seven-membered rings, with the fulvenallenyl radical (***1***) holding the global minima on the potential energy surface (Scheme 1).4 This exceptional stability arises from significant resonance stabilization, attributed to its propargyl- and cyclopentadienyl-like structures (Scheme 1). These hydrogen-deficient resonantly stabilized free radicals (RSFRs) are key intermediates for molecular mass growth processes in oxygen-deficient environments such as combustion flames,5–10 extraterrestrial environments like carbon-rich circumstellar envelopes of, e.g., IRC+10216,11–18 and chemical vapor deposition process (CVD).19 Here, their unique stability and chemistry drive the molecular mass growth to polycyclic aromatic hydrocarbons (PAHs) and eventually carbonaceous nanoparticles (soot, interstellar and circumstellar dust) or fullerenes (C60, C70). The belated identification and growing significance of the fulvenallenyl chemistry1,4,20–22 highlights that RSFRs continue to expose unexpected surprises that reshape our understanding of complex chemical systems that drive the molecular evolution of carbon in our Galaxy.



**Scheme 1.** Different C7H5 isomers with the enthalpy of formation relative to the most stable isomer **1**. Relative energies (kJ mol–1) for **2 – 4** were taken from4 and for **5 – 6** from current work.



**Scheme 2.** Resonantly stabilized free radicals synthesized in bimolecular reactions of bare carbon clusters with unsaturated hydrocarbons.

RSFRs – hydrogen-deficient carbon-bearing radicals stabilized by electron delocalization over multiple carbon atoms – are prepared through two main types of chemical processes. The first involves breaking a simple bond in closed-shell molecules via carbon–hydrogen (C–H) bond dissociation, hydrogen abstraction, carbon–carbon (C–C) β-scission, either thermally or photolytically. The second involves forming at least one new bond during the reaction pathway leading to RSFR generation via bimolecular gas-phase reactions. The most illustrative reactions in this class are those involving bare carbon clusters like atomic carbon (C), dicarbon (C2), and tricarbon (C3) with unsaturated hydrocarbons (Scheme 2).12,15,23–25 These carbon clusters were also revealed as key structural building blocks for the molecular mass growth mechanisms in carbon-rich environments – including combustion flames, cold molecular clouds, carbon-rich stars, and CVD processes – to larger, often hydrogen-deficient carbon clusters, polycyclic aromatic hydrocarbons (PAHs), 25–29 and fullerene. It is important that while atomic carbon C(3P)12,13,23,30–33 and dicarbon C2(X1/a3Πu)24,34–44 reactions usually form RSFRs via barrierless and overall exoergic pathways, thus operating even in energy-deficient environments like cold molecular clouds a 10 K, reactions of ground state tricarbon C3(X1)25,45–47 with unsaturated hydrocarbons demonstrate the opposite feature and the presence of an energy threshold of 30 – 50 kJ mol–1, which effectively shut the door to the role to the hydrocarbon chemistry of tricarbon molecules in cold astrochemical environments, while still being feasible in high-temperature environments.

Considering the preparation of C7H5 radicals, dominating attention has been directed toward the unimolecular processes of the first type via C–H bond cleavage in fulvenallene (C7H6) at high temperatures48 or *via* photolysis at 193 and 248 nm.49,50 In contrast, bimolecular reaction pathways have remained unexplored. Only reaction (1)51–54 was studied theoretically and experimentally. This reaction was found to yield 2,6-cycloheptadien-4-yn-1-yl (***4***; Scheme 1) with no accessible pathway to fulvenallenyl. Alternative radical reactions (2)–(4)4,55 access C7H5 radicals only via three-body collision conditions as the radicals emerge from initial adducts and their isomerization processes and hence are irrelevant to the chemistry of cold molecular clouds like Taurus molecular cloud (TMC-1) where bimolecular reactions operate. The radical–radical reaction (5) should also be mentioned; although the low concentrations of radicals relative to closed-shell species pose a limitation, this pathway is expected to produce fulvenallenyl with nearly 100% yield.

C(3Pj) + C6H6 (X1A1g) → C7H5 + H (1)

C3H3 + C4H2 + M → C7H5 + M\* (2)

C2H2 + *i*-C5H3 + M → C7H5 + M\* (3)

C2H2 + *n*-C5H3 + M → C7H5 + M\* (4)

*i*-C3H3 + *i*-C4H3 → C7H5 + H (5)

Here, we report the very first route leading to the formation of C7H5 isomers - among them the resonantly stabilized fulvenallenyl radical - shedding light on their origin in chemical systems via bimolecular reactions with astrophysically abundant, acyclic reactants by combining crossed molecular beam experiments with *ab initio* and statistical calculations of the reaction of ground state tricarbon (C3, X1) with 1,3-butadiene (C4H6; X1Ag).

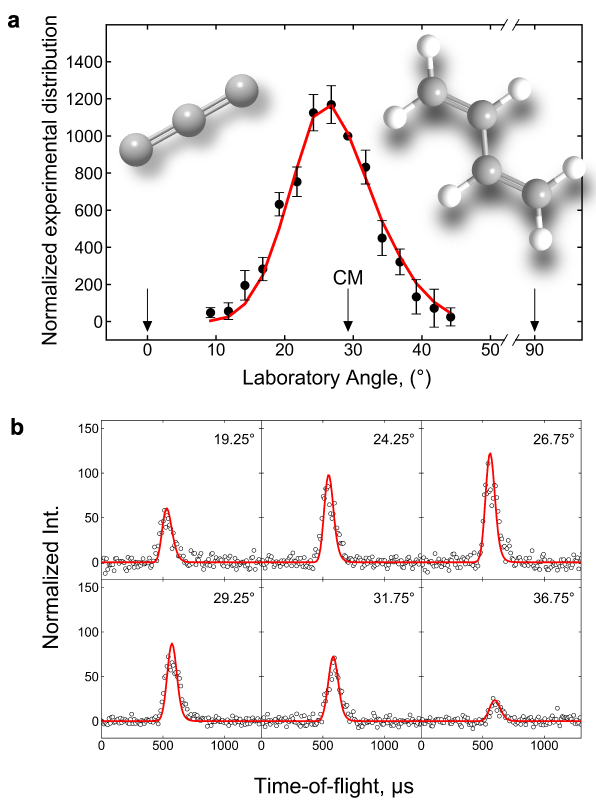
Reactive scattering signal for the reaction of tricarbon (C3; 36 amu) with the 1,3-butadiene (C4H6; 54 amu) was monitored at the mass-to-charge (*m/z*) ratios of *m/z* = 89 (C7H5+) and *m/z* = 88 (C7H4+) for the atomic hydrogen (reaction (6)) and/or molecular hydrogen loss pathways (reaction (7)). No signal was detected at *m/z* = 88, indicating the presence of only an atomic hydrogen loss channel (reaction 6), leading to the formation of exclusively the C7H5 product (Figure S1). Hence, the corresponding TOF spectra of the reaction of tricarbon with 1,3-butadiene were collected at *m/z* = 89 and were then normalized to the signal at the CM angle to obtain the laboratory angular distribution (LAD) (Figure 1a) with a width of at least 30° and asymmetry around the CM angle at 30 ± 2°. These findings propose that the C7H5 products were formed via indirect scattering dynamics through complex formation involving one or more C7H6 intermediates.12,18,56

C3 (36 amu) + CH2CHCHCH2 (54 amu) → C7H5 (89 amu) + H (1 amu) (6)

C3 (36 amu) + CH2CHCHCH2 (54 amu) → C7H4 (88 amu) + H2 (2 amu) (7)

C3 (36 amu) + CD2CHCHCD2 (58 amu)→ C7HD4 (93 amu) + H (1 amu) (8)

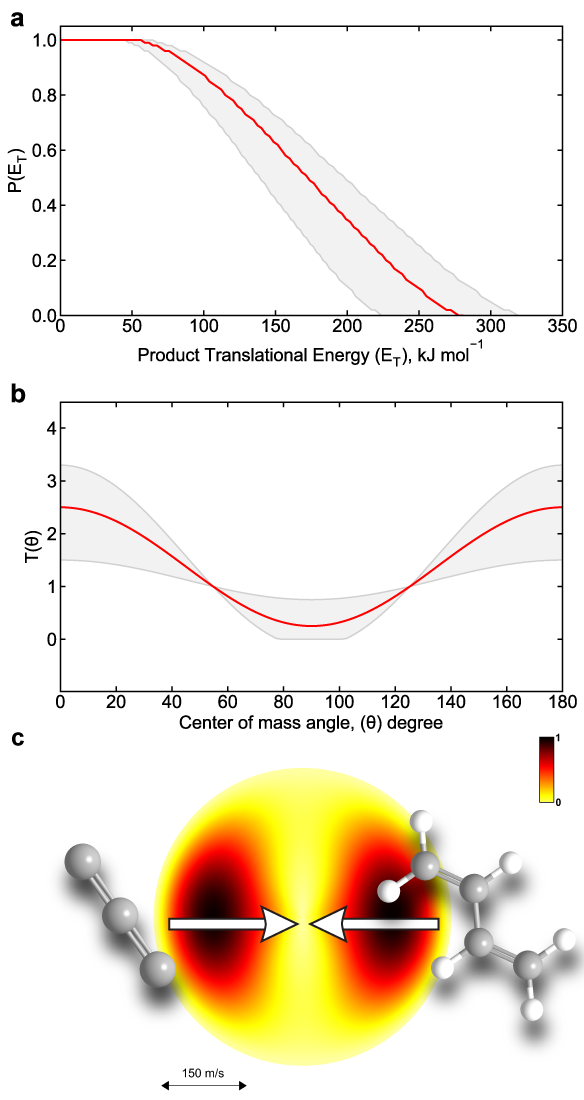
C3 (36 amu) + CD2CHCHCD2 (58 amu) → C7H2D3 (92 amu) + D (2 amu) (9)



**Figure 1**. (a) Laboratory angular distribution and (b) time-of-flight (TOF) spectra recorded at m/z = 62 for the reaction of the tricarbon (C3; X1) with the 1,3-butadiene (C4H6, X1Ag) at a collision energy of 48 ± 2 kJ mol–1. The circles represent the experimental data and the solid lines are the best fits.

Now we are focusing our attention now on the position of the atomic hydrogen loss. Note that the chemical structure of 1,3-butadiene (CH2CHCHCH2) reactant contains two chemically distinct sets of hydrogen atoms: four methylene hydrogens (CH2) positioned at two terminal carbon atoms (C1 and C4) and two methylidyne hydrogens (CH) located at the central carbon atoms (C2 and C3), while tricarbon does not possess any hydrogen atoms. This makes it sufficient to use only one partially deuterated 1,3-butadiene isotopologue – 1,3-butadiene-1,1,4,4-d4 (CD2CHCHCD2) – to study the position of the atomic hydrogen loss in the reaction. The tricarbon plus 1,3-butadiene-1,1,4,4-d4 reaction can form C7HD4 (93 amu) plus H (1 amu) and/or C7H2D3 (92 amu) plus D (2 amu). We monitored for singly ionized reaction products at *m/z* = 93 (C7HD4+) and *m/z* = 92 (C7H2D3+) and detected a reactive scattering signal at each mass-to-charge ratio. No signal was detected for the *m/z* = 88 in the reaction of the tricarbon with the 1,3-butadiene fragmentation, and the molecular hydrogen loss channel does not contribute to a signal at *m/z* = 92 in the reaction with partially deuterated 1,3-butadiene; therefore, both the atomic hydrogen and atomic deuterium pathways are present. After integration and taking into account the dependence of the signal from the center-of-mass velocity of the scattering product, it was found that C7HD4 (*m/z* = 93) and C7H2D3 (*m/z* = 92) are formed at fractions of 34±1% and 66±1%, respectively. Notably, the sum of the signals at *m/z* = 93 and 92 reproduces the signal at *m/z* = 89 in the reaction with 1,3-butadiene (Figure S1). The probed C3/CD2CHCHCD2 system (reactions (8) and (9) explicitly shows that 66 ± 1% of the reaction products were formed by ejection of a deuterium atom from the terminal C1 position (CD2) and 34±1% by ejection of a hydrogen atom is from the C2 position in the diene. Therefore, the laboratory data alone expose that tricarbon (C3) reacts with 1,3-butadiene (C4H6) involving at least two channels. With the aid of isotopic labelling, atomic hydrogen emission was found to originate with the twice higher probability from the 1,3-butadiene C1 than from the C2 position.

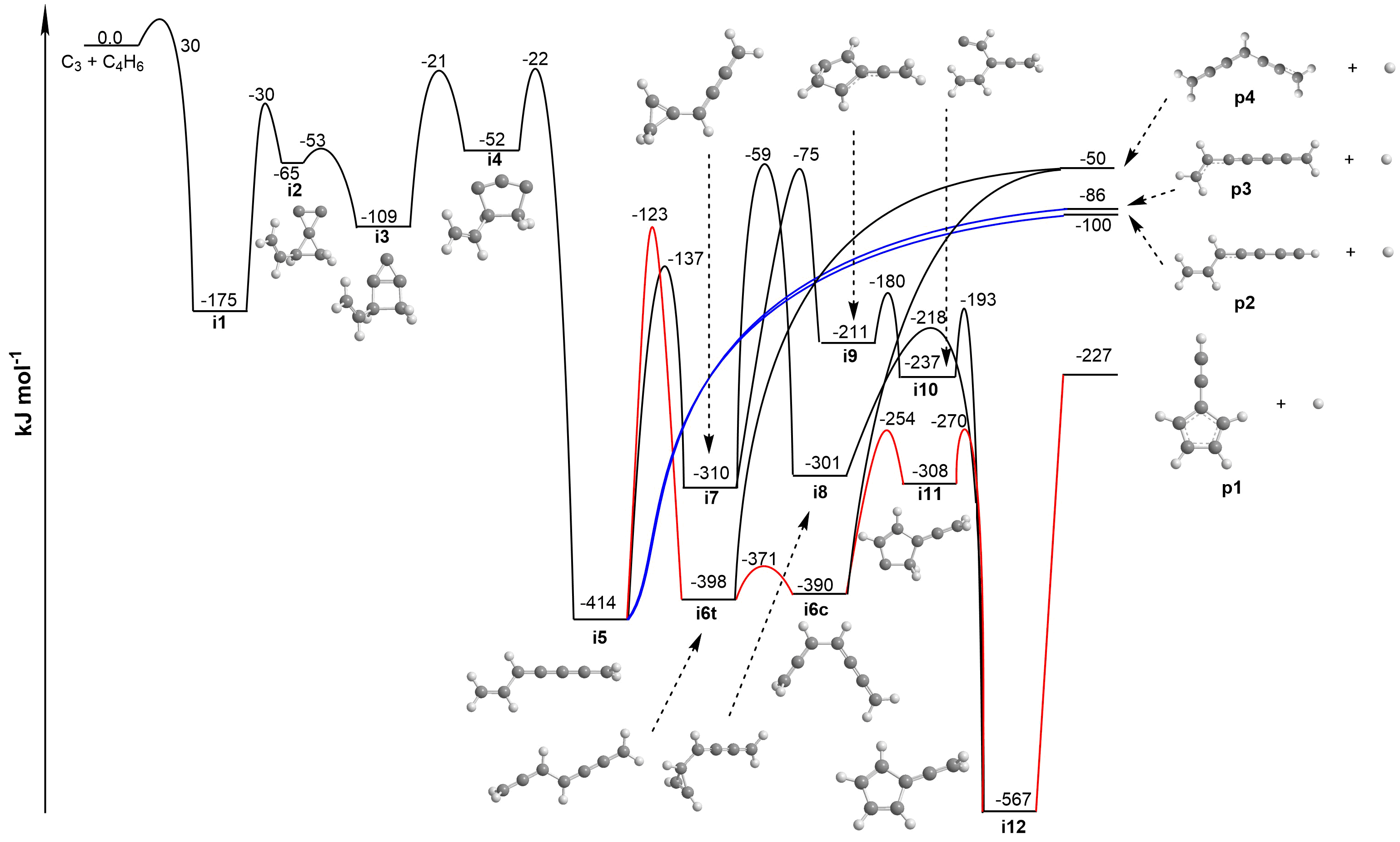
In case of complex, polyatomic systems, it is of advantage to combine our experimental results with electronic structure and statistical calculations to reveal the underlying reaction mechanism and nature of the isomer(s) formed. Exploiting a forward-convolution routine,57–59 the laboratory data (TOFs, LADs) for the tricarbon–1,3–butadiene system were converted into the center-of-mass reference frame via a single channel fit (reaction 6) with a threshold energy to reaction of 40 kJ mol–1. The best-fit CM functions are depicted in Figure 2. The error ranges of the translational energy (P(ET)) and angular flux (T(θ)) functions are determined within the 1σ limits of the corresponding laboratory angular distribution and beam parameters (beam spreads, beam velocities) while maintaining a good fit of the laboratory TOF spectra and LAD. The translational energy flux distribution P(ET) (Figure 1a) offers critical insights into reaction dynamics and thermodynamics. The derived P(ET) distribution exhibits a maximum translational energy release (Emax) of 271±47 kJ mol–1. Energy conservation dictates that for those molecules born without internal excitation, Emax is the sum of the collision energy (EC) and the reaction exothermicity. Taking into account the collision energy of 48±2 kJ mol–1, the reaction energy was determined to be exoergic by 223±49 kJ mol–1. The P(ET) reveals a plateau starting at zero translational energy and going up to 57±10 kJ mol–1, suggesting that the C7H6 complex dissociates to C7H5 plus H without an exit barrier.60 The average translational energy of the products was derived to be 93±16 kJ mol–1, suggesting that 34±12% of the total available energy is channeled into the translational degrees of freedom of the products; this implies that the reaction mechanism proceeds through the formation of a covalently bound C7H6 intermediate.18,12,56



**Figure 2.** (a) Center-of-mass translational energy (P(ET)), (b) angular distributions (T(θ)), and (c) corresponding flux contour map for the reaction of the tricarbon (C3; X1) with the 1,3-butadiene (C4H6, X1Ag). For the T(θ), the direction of the C3 beam is defined as 0° and of the C4H6 as 180°. Solid lines represent the best fit, while shaded areas indicate the error limits.

The center-of-mass angular distribution T(θ) can provide additional information about the reaction dynamics (Figure 2b). The tricarbon plus 1,3-butadiene system reveals forward-backward symmetry with respect to 90°; this finding also suggests an indirect reaction mechanism involving long-lived C7H6 intermediate(s) that have a lifetime longer than their rotational period.61 Finally, the maxima of the T(θ) at 0° and 180° (“coplanar scattering”) highlights that at least one channel with a long-lived intermediate C7H6 emits a hydrogen atom in the rotational plane of the decomposing complex.60,62 Foresaid findings are also enclosed in the flux contour map (Figure 2c), which depicts an overall image of the reaction scattering process.

Now we combine our experimental results with electronic structure and statistical calculations to unlock the underlying chemical dynamics and reaction mechanism(s) of tricarbon (C3, X1) reaction with 1,3-butadiene (C4H6, X1Ag) in the gas phase. Computations discovered 13 reaction intermediates leading to four feasible, distinct products on the potential energy surfaces (PES) (Figure 3). Results of Rice–Ramsperger–Kassel–Marcus (RRKM) calculations (Tables S1 and S2) are compiled in the Supporting Information. The computational results indicate that the reaction commences with the addition of a tricarbon molecule, specifically through its terminal carbon atom to one of the double bonds of 1,3-butadiene. This step proceeds over an entrance barrier of 30 kJ mol–1 and leads to the formation of a three-membered ring intermediate (**i1**), which is stabilized by 175 kJ mol–1 with respect to the separated reactants. Further, the C3 moiety of **i1** may insert into the C1-C2 bond in the 1,3-butadiene unit, ultimately yielding **i5** via the reaction sequence **i1→i2→i3→i4→i5**. Subsequently, intermediate **i5** undergoes hydrogen atom elimination via two distinct pathways: loss from the terminal methylene (CH2) group yields **p2** (1-heptene-4,6-diyn-3-yl), while hydrogen elimination from the methine (CH) group leads to **p3** (1,3,4,5,6-heptapentaen-3-yl).



**Figure 3.** Potential energy surface for the bimolecular reaction of the tricarbon (C3; X1) with the 1,3-butadiene (C4H6; X1Ag) leading to C7H5 isomers plus the atomic hydrogen calculated at the CCSD(T)-F12/cc-pVTZ-f12//ωB97X-D/6-311G(d,p) + ZPE(ωB97X-D/6-311G(d,p)) level of theory, with exception of structures with high T1 diagnostics, for which CASPT2(8,8)/cc-pVTZ were employed (see the COMPUTATIONAL section for more detail.

Both processes proceed through barrierless exit channels and are exoergic with associated reaction energies of –100 kJ mol–1 and –86 kJ mol–1, respectively. Alternatively, **i5** can overcome a barrier of 277 kJ mol–1 to access **i7** *via* ring closure involving C4, C3, and C2 atoms from the 1,3-butadiene moiety, coupled with a [1,2] hydrogen atom shift to the carbon atom of the tricarbon moiety. Intermediate **i7** can then undergo two competitive isomerization processes commencing with either ring expansion (**i7→i9**) or hydrogen atom migration (**i7→i8**), eventually leading to the most stable intermediate on the PES – fulvenallene (**i12**; –567 kJ mol–1) – via the **i7→i9→i10→i12** or **i7→i8→i9→i12** pathways. Finally, we consider the pathway initiated by a [1,3] hydrogen shift in intermediate **i5**, proceeding through a 306 kJ mol–1 barrier, leading to the formation of 1,2,3,5,6-heptapentaene (**i6t)**.Latter can be converted to its rotational isomer **i6c** via a barrier of 33 kJ mol−1. Both **i6t** and **i6c** have barrier-free exit channelsto the thermodynamically least stable heptapentaenyl radical: 1,2,4,5,6-heptapentaen-3-yl (**p4**; –50 kJ mol–1). Alternatively, **i6c** undergoes a five-membered ring closure to **i11,** which can access the most stable C7H6 isomer **i12** (fulvenallene; –567 kJ mol–1) via a small barrier of 44 kJ mol–1. Fulvenallene (**i12**) can finally undergo unimolecular decomposition via hydrogen atom emission from the terminal methylene group to the most thermodynamically favorable product in this reaction – fulvenallenyl radical (**p1**; –227 kJ mol–1) – also via a barrier-free exit channel. The absence of exit barriers on the investigated PES correlates well with the experimentally derived P(ET) distribution, which exhibits a maximum plateau that starts from 0 kJ mol–1.

The RRKM calculations predict that the most likely product is the acyclic resonantly stabilized C7H5 radicals **p2** (1-heptene-4,6-diyn-3-yl; –100 kJ mol–1) with an overall yield of about 80%. Alternative RSFRs **p3** (1,3,4,5,6-heptapentaen-3-yl; –86 kJ mol–1) and the most stable C7H5 isomer on the PES **p1** (fulvenallenyl; –227 kJ mol–1) form with similar sizeable fractions of up to 10% at our collision energy of 48 kJ mol–1. Finally, the heptapentaenyl radical **p4** (1,2,4,5,6-heptapentaen-3-yl; –50 kJ mol–1) is predicted not to be formed via unimolecular decomposition of **i6t** and **i6c** due to the highest reaction thresholds 385 and 375 kJ mol–1 of all exit channels. The experimentally derived reaction energy of –223±49 kJ mol–1 for the hydrogen atom loss elimination channels supports the formation of fulvenallenyl (**p1**)under our experimental conditions, while other products may be masked in the lower part of the P(ET).

Fortunately, the topological characteristics of the computed PES enable a confident narrowing of the reaction pathways to a single, predominantly favored route. Statistical calculations indicate that the two most probable products – resonantly stabilized radical **p2**– can only arise through the unimolecular decomposition of intermediate **i5**, occurring prior to any branching of the reaction pathways. Consequently, pathway (10) emerges as the inevitably dominant mechanism driving the reaction.

**i1→i2→i3→i4→i5→p2** (10)

Complementary experiments using 1,3-butadiene-1,1,4,4-d4 (CD2CHCHCD2) yielded additional evidences for dominant reaction channel. Analysis of the C3/CD2CHCHCD2 experiment (reactions (8) and (9)) revealed that 66±1% of the products resulted from deuterium atom ejection at the terminal C1 position (CD2), while 34±1% originated from hydrogen atom loss at the C2 position. Given that deuterium elimination is only feasible *via* reaction pathways leading to products **p1** and **p2** (Figure S2), this observation qualitatively supports the predominance of the **p2** formation channel in the overall reaction mechanism. The discrepancy between the experimentally determined branching ratio (66:34) and that predicted by RRKM theory (90:10) for the **p1** and **p2** channels versus **p3** could arise from differences in C–D and C–H bond dissociation energies, which can significantly influence the product distributions. Hence, additional *ab initio* and statistical calculations were conducted for the C3/CD2CHCHCD2 system (Figure S2, Table S2). Their results improve agreement (66:34 versus 84:16), i.e. about 2:1 versus 5:1. However, the channel to the **p3** (H-loss) has no distinct TS, and variational calculations are normally less accurate than those with a distinct transition state, which likely accounts for the remaining deviation.

By integrating crossed molecular beam experiments with high-level electronic structure and RRKM calculations, we have elucidated the chemical dynamics of the gas-phase reaction between tricarbon (C3, X1Σg+) and 1,3-butadiene (C4H6, X1Ag). The reaction is initiated by terminal-carbon addition of C3 to a double bond of 1,3-butadiene, forming a three-membered ring intermediate (**i1**) stabilized by 175 kJ mol–1. Subsequent *de-facto* C3 insertion to the double bond via ring opening of **i4** leads to intermediate **i5**, whose unimolecular decomposition via barrierless hydrogen atom loss yields two acyclic heptapentaenyl radicals: **p2** (–100 kJ mol–1) with a branching ratio 83%, and **p3** (–86 kJ mol–1) contributing about 9%. The most thermodynamically favorable channel produces the fulvenallenyl radical (**p1**; –227 kJ mol–1) with yields 7%, while formation of **p4** (–50 kJ mol–1) is kinetically suppressed. It has been shown that intermediate **i5** can decompose to fulvenallenyl with a branching ratio of up to 18% at its internal energy corresponding to zero collisional energy. Although the title reaction has an entrance barrier of 30 kJ mol–1, RRKM calculations at collisional energies below this threshold are not directly relevant to the studied system. However, if alternative barrierless entrance channels to the C7H6 PES exist, such as C2(X1) plus C5H6,and lead to the formation of **i5**, then up to 18% fulvenallenyl may still be produced under low-energy conditions. The absence of exit barriers across the PES aligns with the experimentally observed P(ET) plateau near zero translational energy. The result of statistical calculation combined with the topological features of the PES identifies the channel (10) as the prevailing pathway driving product formation in this system, what was corroborated by experimental data obtained using deuterated 1,3-butadiene-1,1,4,4-d4. While the main product of this reaction is acyclic C7H5 isomer **p2**,itstill can further undergo hydrogen-assisted isomerization to reach the deepest well on the C7H5 surface – fulvenallenyl radical. The substantial energy barrier of 30 kJ mol–1 suggests that tricarbon (C3, X1Σg+) can undergo addition to 1,3-butadiene (C4H6, X1Ag), forming resonantly stabilized C7H5 radicals exclusively under high-temperature conditions. Such environments include combustion flames and astrophysical settings like the circumstellar envelope of IRC+10216 and interstellar shock regions. In contrast, these reaction pathways are inaccessible in low-temperature conditions, such as cold molecular clouds and in hydrocarbon-rich atmospheres of planets and their moons, such as Titan. Ultimately, we unveiled a previously unexplored route for the formation of C7H5 isomers, enriching our understanding of RSFR formation during both terrestrial and cosmic chemical evolution. These findings invite further exploration into the role of small carbon clusters that drive the molecular complexity of our universe – from the flicker of a flame to the death of a star.

**MATERIALS AND METHODS**

**Crossed molecular beams.** The gas-phase reaction of tricarbon (C3; X1) with the 1,3-butadiene (C4H6; X1Ag) was carried out under single-collision conditions using the crossed molecular beams machine.33,63,64 The experimental setup, data acquisition, and data processing are described elsewhere in detail.51,65–68 Briefly, a supersonic molecular beam of tricarbon was prepared *in situ* in the primary source chamber by laser ablation (3mJ, 266nm, 30 Hz; Quanta-Ray) from a rotating carbon rod. The ablated species were seeded in neat carrier gas (Helium, 99.9999%, Airgas) released by a Proch-Trickl pulsed valve operating at 60 Hz and a backing pressure of 4 atm. A four-slot chopper wheel located between the skimmer of the primary source and the cold shield allowed to select the segment of the pulsed tricarbon beam with a peak velocity of *v*­p = 1969 ± 42 m s–1 and speed ratio S = 3.4 ± 0.2. This beam intersected with a neat 1,3-butadiene (Aldrich Chemistry, ≥99%) pulsed molecular beam (vp = 760 ± 20 m s−1, S = 8.0 ± 0.5) perpendicularly in the reaction chamber with a mean collision energy of 48 ± 2 kJ mol−1. Experiments with partially deuterated reactant were performed using 1,3-butadiene-1,1,4,4-d4 (CD2CHCHCD2; Cambridge Isotopes, 98% atom D) to identify the position of the hydrogen and/or deuterium loss.

The reaction products scattered from a collisional region were monitored using a triply differentially pumped (10–12 Torr) quadrupole mass spectrometric detector (QMS; Extrel, QC 150; 1.2 MHz) operated in the time-of-flight (TOF) mode with electron ionization (80eV, 2mA).69 Only ions with selected mass-to-charge (*m/z*) pass through the quadrupole mass filter and are detected using Daly-counter. This detector can be rotated within the plane defined by the primary and the secondary reactant beams to record angular resolved TOF spectra, which were then integrated and normalized to extract the product angular distribution in the laboratory frame (LAD) – the signal intensity of an ion with a specific *m/z* versus the laboratory angle. To gain information on the reaction dynamics, TOF spectra and the laboratory angular distribution (LAD) were transformed from the laboratory to the center-of-mass (CM) frame by a forward-convolution routine.57–59 This approach uses initially a trial angular flux T(θ) and translational energy P(ET) distributions of products in the CM frame to simulate the laboratory data (TOFs and LAD). CM functions were iteratively varied until the best fit of the TOF spectra and LAD was achieved. Together, the CM functions constitute the reactive differential cross sections I(θ, u) ∼ P(u) × T(θ), where u is the CM velocity, θ is the angle in the CM system. The reactive differential cross sections can be represented as a flux contour map that depicts the probability of the products to scatter at a specific angle (θ) with the specific kinetic energy (u). Since the reactions of tricarbon molecules with unsaturated hydrocarbons have characteristic threshold energies (E0), we utilized an energy-dependent cross section (σ) from collisional energy (Ecoll), by applying the line-of-center model through Eq. (11) 60,70 in the fitting routine.

(11)

**Computational Methods.** Geometries of various stationary structures on the C7H6 potential energy surface (PES) involved in the C3 + C4H6 reaction, such as the reactants, products, intermediates, and transition states, were optimized hybrid density functional ωB97X-D71 with the 6-311G(d,p) basis set. Since some of the structures on the PES may exhibit an open-shell singlet character, the unrestricted version of the method (UωB97X-D) was employed for all of them, with a stability check of the wavefunction carried out both in the beginning and in the end of geometry optimization. Such an approach ensured that each structure was optimized in the ground electronic state. The same UωB97X-D/6-311G(d,p) level of theory was used to calculate vibrational frequencies for each stationary species following geometry optimization. The frequencies, which differ for the C3 + CH2CHCHCH2 and C3 + CD2CHCHCD2 reactions, were utilized in the evaluation of zero-point vibrational energy corrections (ZPE) and in the calculations of rate constants taking the isotope effect into account. To obtain chemically accurate relative energies of various species on the C7H6 PES, single-point energies of all optimized structures were refined using the explicitly correlated coupled cluster CCSD(T)-F1272,73 method with Dunning’s correlation-consistent cc-pVTZ-f12 basis set.74 In general, the final CCSD(T)-F12/cc-pVTZ-f12//ωB97X-D/6-311G(d,p) + ZPE(ωB97X-D/6-311G(d,p)) relative energies are expected to be accurate within 4 kJ mol–1,75 unless the wavefunction exhibits a significant multireference character. The multireference character of the wavefunction was monitored by the T1 diagnostics in the CCSD calculations. Whenever the T1 diagnostic value exceeded the 0.02 threshold, the multireference perturbation theory CASPT2 method76,77 was employed with the active space including 8 electrons distributed on 8 orbitals and with the cc-pVTZ basis set, CASPT2(8,8)/cc-pVTZ. The final relative energy for each multireference structure was determined as its relative energy with respect to the nearest local minimum with a low T1 diagnostics computed at the CASPT2(8,8)/cc-pVTZ + ZPE level plus the relative energy of this nearest minimum with respect to the initial reactants at the CCSD(T)-F12/cc-pVTZ-f12//ωB97X-D/6-311G(d,p) + ZPE(ωB97X-D/6-311G(d,p)). The overall list of such multireference structures includes transitions states ***i3***-***i4***, ***i4***-***i5***, ***i8***-***i12***, and ***i6c***-***i11***. The GAUSSIAN 1678 and MOLPRO 202179 quantum chemistry software packages were used for the *ab initio* calculations.

The Rice−Ramsperger−Kassel−Marcus (RRKM) approach70,80,81 was used to compute energy-dependent rate constants for all unimolecular reaction steps taking place on the C7H6 PES starting from the ***i5*** intermediate where the reaction pathways begin to branch. In these calculations, the internal energy for each C7H6 intermediate was assumed to be equal to the sum of the collision and chemical activation energies, where the chemical activation energy is a negative of the relative energy of the species relative to the separated C3 + C4H6 reactants. For the barrierless H loss reaction steps, the microcanonical variational transition state theory was used.82 The rate constants calculations were performed utilizing our in-house Unimol code at the zero-pressure limit,83 to reproduce the crossed molecular beams conditions. The RRKM-computed rate constants were used to assess the product branching ratios for unimolecular decomposition of chemically activated ***i5*** within steady-state approximation.82,83

ASSOCIATED CONTENT

**Data Availability Statement**

The data that support the findings of this study are available in the article and the Supporting Information. Additional data are available from the corresponding authors upon reasonable request.

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/XXX

Signal for the isotope labeling experiment; potential energy surface for the bimolecular reaction of the tricarbon (C3; X1g+) with the 1,3-butadiene-1,1,4,4-d4 (CD2CHCHCD2; X1Ag); other possible C7H5 products not shown on the main PES; results of RRKM calculations; optimized cartesian coordinates (å) and vibrational frequencies (cm−1) for all intermediates, transition states, reactants, and products involved.

AUTHOR INFORMATION

Corresponding Authors

**Ralf I. Kaiser** − Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96888, United States; orcid.org/0000-0002-7233-7206; Email: [ralfk@hawaii.edu](mailto:ralfk@hawaii.edu)

**Alexander M. Mebel** − Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, United States; orcid.org/0000-00027233-3133; Email: [mebela@fiu.edu](mailto:mebela@fiu.edu)

Authors

**Iakov A. Medvedkov** − Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii, 96822, United States; https://orcid.org/0000-0003-0672-2090

**Zhenghai Yang** − Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States;

**Shane J. Goettl** − Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States; https://orcid.org/0000-0003-1796-5725

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

Any additional relevant notes should be placed here.

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