

Identification of the Elusive Methyl-Loss Channel in the Crossed Molecular Beam Study of Gas-Phase Reaction of Dicarbon Molecules (C_2 ; $X^1\Sigma_g^+/a^3\Pi_u$) with 2-Methyl-1,3-butadiene (C_5H_8 ; X^1A')

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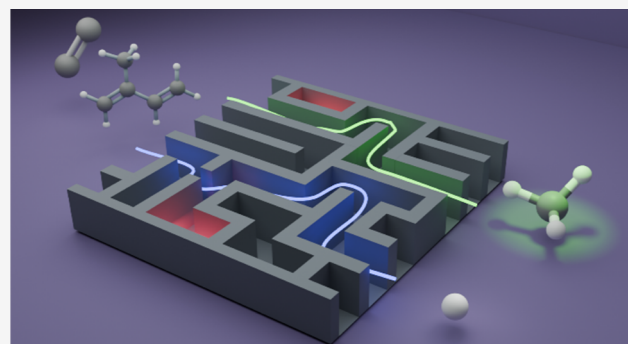
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ABSTRACT: The crossed molecular beam technique was utilized to explore the reaction of dicarbon C_2 ($X^1\Sigma_g^+/a^3\Pi_u$) with 2-methyl-1,3-butadiene (isoprene, $CH_2C(CH_3)CHCH_2$; X^1A') at a collision energy of 28 ± 1 kJ mol⁻¹ using a supersonic dicarbon beam generated via photolysis (248 nm) of helium-seeded tetrachloroethylene (C_2Cl_4). Experimental data combined with previous *ab initio* calculations provide evidence of the detection of the hitherto elusive methyl elimination channels leading to acyclic resonantly stabilized hexatetraenyl radicals: 1,2,4,5-hexatetraen-3-yl ($CH_2CC^{\bullet}CHCCH_2$) and/or 1,3,4,5-hexatetraen-3-yl ($CH_2CHC^{\bullet}CCCH_2$). These pathways are exclusive to the singlet potential energy surface, with the reaction initiated by the barrierless addition of a dicarbon to one of the carbon–carbon double bonds in the diene. In combustion systems, both hexatetraenyl radicals can isomerize to the phenyl radical (C_6H_5) through a hydrogen atom-assisted isomerization—the crucial reaction intermediate and molecular mass growth species step toward the formation of polycyclic aromatic hydrocarbons and soot.



1. INTRODUCTION

Bare carbon molecules from dicarbon (C_2) and tricarbon (C_3) to fullerenes provide fascinating examples of unusual molecular structures and chemical bonding.^{1–3} Dicarbon and tricarbon were initially detected in comets^{4–7} and continue to be the subject of extensive research in the fields of astrochemistry,⁸ combustion,^{9,10} chemical vapor deposition (CVD),¹¹ and fundamental organic chemistry. A comprehensive understanding of the chemistry of carbon-only molecules is crucial for elucidating a wide array of carbon-rich systems in the interstellar medium, as well as for gaining insights into the principles of chemical bonding and reactivity.^{12–14}

In combustion flames, cold molecular clouds, carbon-rich stars, and CVD processes, small carbon molecules like dicarbon represent key structural building blocks and molecular mass growth species toward larger carbon clusters, polycyclic aromatic hydrocarbons (PAHs), fullerenes, and soot.^{15–18} Extensive experimental and theoretical studies of dicarbon ($X^1\Sigma_g^+/a^3\Pi_u$)^{14,19–28} with unsaturated hydrocarbons revealed that these processes form resonantly stabilized free radicals (RSFR)¹³—neutral, electron-deficient chemical species stabilized by the delocalization of the unpaired electron over the carbon chain using empty p-orbitals of sp and sp² carbon atoms (Scheme 1). These RSFRs are vital drivers for

the formation and growth of PAHs and carbonaceous nanoparticles in combustion and the interstellar medium (ISM). Considering the delocalization of the unpaired electron, RSFRs are more stable than nonresonance stabilized radicals and often exhibit an entrance barrier in the reactions with closed-shell molecules; this feature allows RSFRs to accumulate in hydrocarbon-rich reaction systems. These high concentrations and the relatively fast rates for RSFR self-reactions such as propargyl ($C_3H_3^{\bullet}$) plus propargyl ($C_3H_3^{\bullet}$)²⁹ or hydrogen-assisted isomerization of the acyclic RSFRs to aromatic structures make them an indispensable part of molecular mass growth processes in hydrocarbon-rich environments.

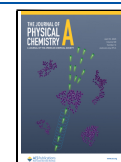
One of the most remarkable aspects of dicarbon chemistry, which enables reactions to occur even in energy-deficient environments, is the lack of an entrance barrier in the reaction with unsaturated hydrocarbons. Reactions of dicarbon with

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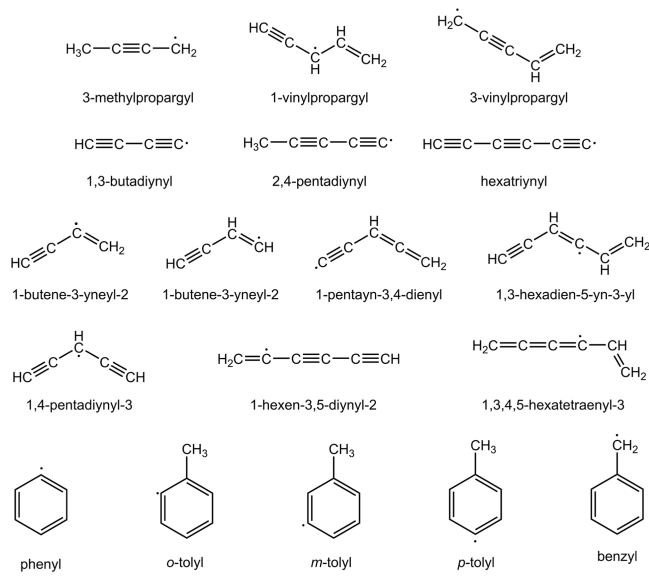
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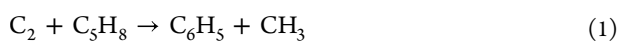
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Scheme 1. Selected Radicals Synthesized via Bimolecular Reactions of Dicarbon With Unsaturated Hydrocarbons



conjugated dienes have even shown the ability to synthesize aromatic structures such as phenyl ($C_6H_5^\bullet$), benzyl ($C_6H_5CH_2^\bullet$), and tolyl ($^\bullet C_6H_4CH_3$) radicals^{24,26,27} via a single collision (Scheme 1). The initially formed closed-shell collisional complexes decompose into two radicals via competing pathways involving C–C or C–H bond scission. Probing the C–C scission channels in crossed molecular beam experiments can represent a challenging task considering the larger recoil circles of the reaction products.^{20,30–33} Traditionally, for crossed molecular beam reactive scattering studies, a dicarbon beam has been generated via ablation of a carbon rod by the focused fourth harmonic of an Nd:YAG laser (266 nm); this also produces atomic carbon (C) within the supersonic beam.^{12,34} The dissociative ionization of products from the reaction of carbon can hinder the detection of, e.g., the methyl (CH_3)-loss channel in the studies of methyl-substituted homologues of the unsaturated hydrocarbons in experiments with electron impact ionization detection.²⁰ In the reactions of dicarbon ($X^1\Sigma_g^+/a^3\Pi_u$) with 1,3-dienes from 1,3-butadiene ($CH_2CHCHCH_2$)²⁴ to 2-methyl-1,3-butadiene (isoprene; $CH_2C(CH_3)CHCH_2$)²⁶ and 1-methyl-1,3-butadiene (1,3-pentadiene; $CH_2CHCHCHCH_3$),²⁷ according to *ab initio* and statistical calculations, the CH_3 elimination pathways are predicted to have significant branching ratios. However, in experimental studies conducted for these systems under single-collision conditions,^{26,27} the methyl elimination channels (1) were obscured by the atomic carbon reaction (2) due to the fragmentation of, e.g., C_6H_7 products in the electron impact ionizer; hence, potential methyl-loss channels have remained elusive. A recently developed photodissociation source of dicarbon from tetrachloroethylene (C_2Cl_4) does not have the abovementioned problem of atomic carbon generation and opened up the detection of the methyl elimination channel in the reaction with 1-butyne (C_2H_5CCH ; X^1A').²⁰



In this article, we present an experimental investigation of the reaction of dicarbon (C_2 ; $X^1\Sigma_g^+/a^3\Pi_u$) with 2-methyl-1,3-

butadiene (isoprene, $CH_2C(CH_3)CHCH_2$; X^1A') under single-collision conditions exploiting crossed molecular beams. Utilizing the photolysis source for dicarbon, we were able to detect the hitherto elusive methyl-loss pathways that led to two distinct resonantly stabilized hexatetraenyl radicals: 1,2,4,5-hexatetraen-3-yl ($CH_2CC^\bullet CHCCH_2$) and 1,3,4,5-hexatetraen-3-yl ($CH_2CHC^\bullet CCCH_2$). In combustion systems, both acyclic C_6H_5 radicals can undergo hydrogen-assisted isomerization leading to the formation of the phenyl radical ($C_6H_5^\bullet$)—a crucial reactant in the formation of PAHs in competing mechanisms such as Phenyl Addition Dehydro Cyclization (PAC),^{35,36} Hydrogen Abstraction— C_2H_2 (acetylene) Addition (HACA),^{37–40} and Hydrogen Abstraction Vinylacetylene Addition (HAVA).^{35,41–44}

2. EXPERIMENTAL SECTION

The reaction of dicarbon C_2 ($X^1\Sigma_g^+/a^3\Pi_u$) with 2-methyl-1,3-butadiene (isoprene, $CH_2C(CH_3)CHCH_2$; X^1A') was conducted under single-collision conditions, exploiting a crossed molecular beam machine. The experimental apparatus, data acquisition scheme, and data analysis have been previously detailed;^{12,44–47} here, we will only provide a concise summary. The crossed beam machine comprises a vacuum chamber (10^{-8} Torr) which encloses two source chambers at a crossing angle of 90° and an ultra-high-vacuum (10^{-12} Torr), rotatable, differentially pumped quadrupole mass spectrometry (QMS) detector. A pulsed (60 Hz) supersonic beam of dicarbon was prepared by photodissociation of tetrachloroethylene (C_2Cl_4 ; Sigma-Aldrich, $\geq 99\%$), purified by multiple freeze–pump–thaw cycles, seeded in helium (He, 99.9999%, Matheson) at 2.2 atm in a room-temperature (300 K) stainless steel bubbler using the output of a KrF excimer laser (248 nm; Coherent, CompEx110; 180 mJ pulse^{−1}; 30 Hz) focused (2×6 mm²) at the exit of the primary pulsed valve 2 mm downstream the exit of the Proch-Trickl pulsed valve.⁴⁸ The supersonic beam containing dicarbon was then collimated by a 1 mm diameter skimmer before entering the reaction chamber. A four-slot chopper wheel positioned between the skimmer and the cold shield selected a segment of the dicarbon beam with a well-defined peak velocity (v_p) and speed ratio (S). On-axis ($\theta = 0^\circ$) characterization of dicarbon at 34 eV electron energy reveals a high-intensity beam with a peak velocity $v_p = 1618 \pm 32$ m s^{−1} and speed ratio $S = 10.3 \pm 1.3$. The secondary molecular beam (60 Hz, $v_p = 724 \pm 17$ m s^{−1}, $S = 8.3 \pm 0.3$) of neat 2-methyl-1,3-butadiene (450 Torr, $CH_2C(CH_3)CHCH_2$; Sigma-Aldrich, 99%) was pulsed 57 μ s prior to the primary beam. The two molecular beams intersected at a 90° angle within the scattering chamber, resulting in a mean collision energy of $E_C = 28 \pm 1$ kJ mol^{−1}.

The products resulting from reactive scattering underwent ionization by electron ionization at 80 eV (2 mA) at the entrance of the rotatable detector, separated according to mass-to-charge ratios (m/z) by the QMS instrument (Extrel, QC 150; 2.1 MHz), and detected with a Daly-type particle ion counter.⁴⁹ The detector can be rotated within the scattering plane defined by the primary and secondary beams. Angularly resolved time-of-flight (TOF) spectra were recorded at discrete laboratory angles between 22.25° and 64.25° . By operating the laser at 30 Hz and the pulsed valves at 60 Hz, instant background subtraction (“laser-on” minus “laser-off”) was possible during the TOF recording.

To obtain insights on the reaction dynamics, TOF spectra and the laboratory angular distribution (LAD) were fitted with

the forward-convolution technique.^{50,51} In this approach, the trial user-defined angular flux $T(\theta)$ and translational energy $P(E_T)$ distributions in the center-of-mass (CM) frame are used to simulate the laboratory data (TOFs and LAD). The CM functions were iteratively adjusted until the TOF spectra and LAD showed the best fit. Together, the CM functions represent the reactive differential cross section $I(\theta, u)$, where θ and u are the CM angle and velocity, respectively, $I(u, \theta) \sim P(u) \times T(\theta)$, which is represented as a flux contour map, thus depicting an overall image of the reaction outcome.

3. RESULTS AND DISCUSSION

3.1. Laboratory Frame. Taking into account previously studied systems where dicarbon was generated via photodissociation of tetrachloroethylene²⁰ to untangle the experimental results, it was necessary to check reactive scattering not only at the center-of-mass (CM) angle of the reaction of dicarbon (C_2 ; 24 amu) with 2-methyl-1,3-butadiene (C_5H_8 , 68 amu) but also for the potential reaction of chloroethynyl ($C_2^{35}Cl$, 59 amu) with 2-methyl-1,3-butadiene at its CM angle (Figure 1). Initially, potential reaction products were

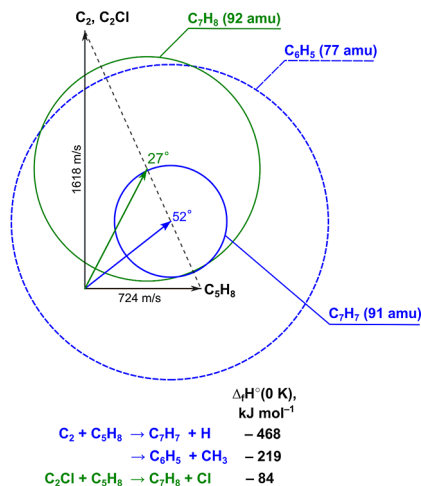


Figure 1. Newton diagram for the atomic hydrogen (solid blue) and methyl-loss (dashed blue) channels in the reaction of dicarbon (C_2) with 2-methyl-1,3-butadiene (isoprene, C_5H_8) (blue circles); the atomic chlorine-loss channel for the C_2Cl —2-methyl-1,3-butadiene reaction is also shown (solid green).

monitored at mass-to-charge ratios (m/z) 89 ($C_7H_5^+$), 90 ($C_7H_6^+$), 91 ($C_7H_7^+$), 92 ($C_7H_8^+$), and 77 ($C_6H_5^+$) at the CM for the reaction of dicarbon with 2-methyl-1,3-butadiene at 52° . We were able to collect TOFs for each mass except for $m/z = 92$, with the best signal-to-noise ratio for $m/z = 89$. The TOFs at $m/z = 89$ –91 are superimposable after scaling, but the signal at $m/z = 77$ appears to be wider (Figure 2) and 1 order of magnitude weaker. These findings suggest two distinct channels: an atomic hydrogen-loss channel (reaction 3) and a methyl-loss channel (reaction 4), with signals at $m/z = 90$ and 89 originating from the fragmentation of $C_7H_7^+$ in the detector. Note that the previous study in crossed molecular beams of dicarbon with 2-methyl-1,3-butadiene²⁶ was able to observe reactive scattering signal only for the hydrogen-loss channels, considering the aforementioned experimental complications.

At the CM of the reaction of $C_2^{35}Cl$ (59 amu) with 2-methyl-1,3-butadiene at 27° , a signal was observed at $m/z = 77$, 89, and 92. The signal at $m/z = 92$ indicates that $m/z = 92$ originates from the reaction of chloroethynyl (C_2Cl) with 2-methyl-1,3-butadiene (reaction 3). All three TOFs overlap after scaling (Figure 3), evidencing that signals at $m/z = 77$

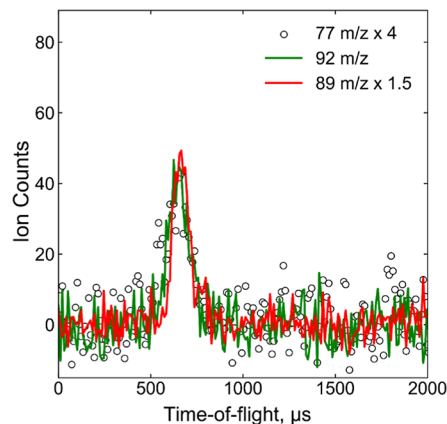


Figure 3. Time-of-flight (TOF) spectra recorded at different m/z at the center-of-mass (27°) of the reaction chloroethynyl (C_2Cl) with 2-methyl-1,3-butadiene ($CH_2C(CH_3)CHCH_2$).

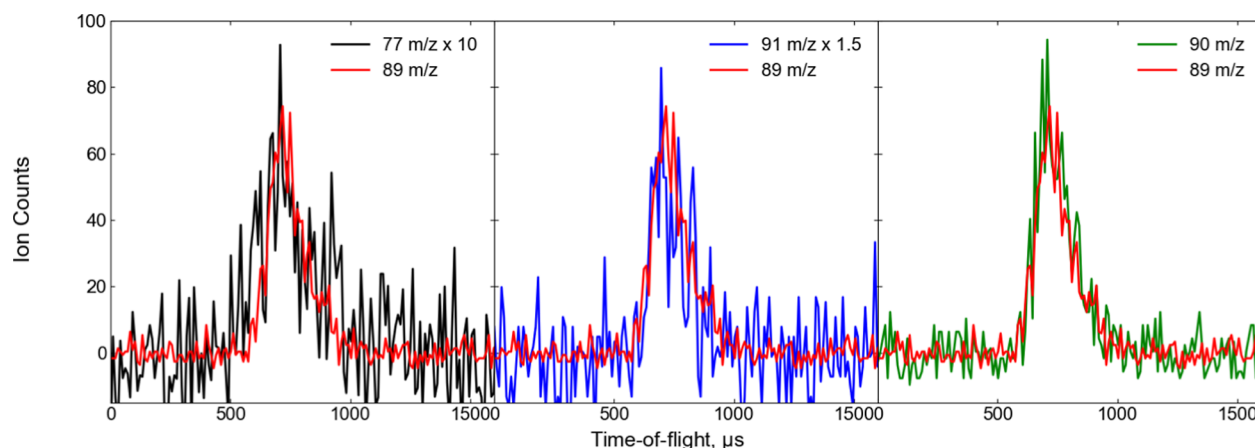
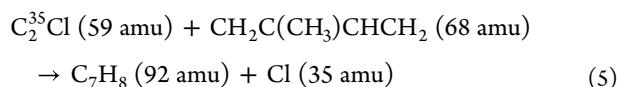
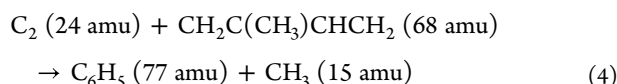
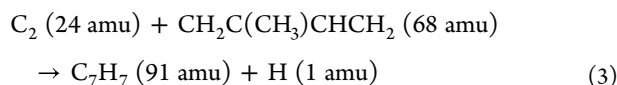


Figure 2. Time-of-flight (TOF) spectra recorded at different m/z , with the detector positioned at the center-of-mass angle (52°) of the reaction of dicarbon C_2 ($X^1\Sigma_g^+/a^3\Pi_u$) with 2-methyl-1,3-butadiene (isoprene, $CH_2C(CH_3)CHCH_2$; X^1A').

and 89 likely occur from a combination of dissociative electron impact ionization of the product detected at $m/z = 92$ and from reaction channels (3) and (4), respectively.



To unravel the signal origin in this system, the corresponding LADs were recorded for $m/z = 77$, 89, and 92 (Figure 4). While all LADs have one common feature—a

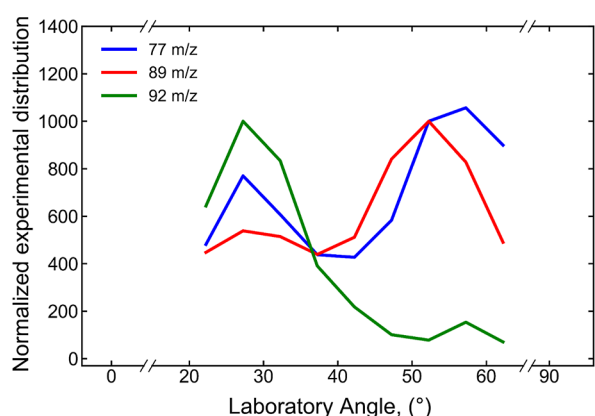


Figure 4. Comparison of the recorded LADs taken at 77 m/z (blue), 89 m/z (red), and 92 m/z (green) produced from the scattering of dicarbon (C_2) and chloroethynyl (C_2Cl) with 2-methyl-1,3-butadiene ($\text{CH}_2\text{C}(\text{CH}_3)\text{CHCH}_2$). LADs with error bars are displayed in Figures 5, 6, and 7, respectively.

symmetric peak at 27° —their behavior around 52° is different, indicating that they represent the combinations of distinguished reaction channels. The LAD for $m/z = 92$ shows almost no intensity at 52° ; the LAD at $m/z = 89$ has a symmetric peak around this angle and reflects a forward–backward symmetry, while the LAD at $m/z = 77$ depicts a higher flux in the backward hemisphere with respect to 52° . These findings support that the signal at $m/z = 92$ originates solely from atomic chlorine loss in reaction (3); however, due to the dissociative fragmentation of C_7H_8 in the ionizer, the LADs for $m/z = 89$ and 77 are composed of a combination of atomic hydrogen-loss channel (3) with reaction (5) and methyl-loss channel (4) with reaction (5), respectively.

3.2. Center-of-Mass Frame. To extract information on the reaction mechanisms, a forward convolution routine was utilized to convert the laboratory data (TOFs and LADs) for each $m/z = 77$, 89, and 92 into the center-of-mass (CM) reference frame.^{50,51}

3.2.1. Data for $m/z = 92$. First, data for $m/z = 92$ were fit with a single reaction channel (reaction 5). The best-fit LAD and TOF are depicted in Figure 5. The extracted CM functions ($T(\theta)$, $P(E_T)$; Figure S1) were then used as a second channel in the forward convolution routines for $m/z = 77$ and 89. A

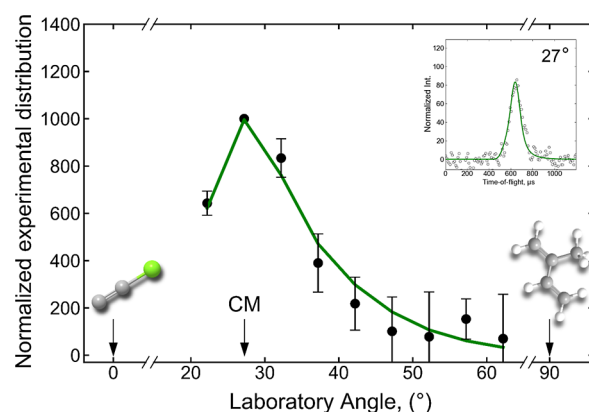


Figure 5. LAD and time-of-flight (TOF) spectra recorded at $m/z = 92$ for the reaction of the chloroethynyl radical with 2-methyl-1,3-butadiene at a collision energy of $28 \pm 1 \text{ kJ mol}^{-1}$. The circles represent the experimental data and the solid lines the best fits. The time-of-flight spectrum recorded at the center-of-mass angle of this reaction (27°) is shown as an inset (open circles—experimental data; solid line—best fit from the center-of-mass functions). The corresponding center-of-mass functions used for the simulation are presented in the Supporting Information.

detailed discussion and investigation of chloroethynyl chemistry are beyond the scope of this manuscript.

3.2.2. Data for $m/z = 89$. We were able to fit data for $m/z = 89$ (Figure 6) using a two-channel fit combining reactions (3)

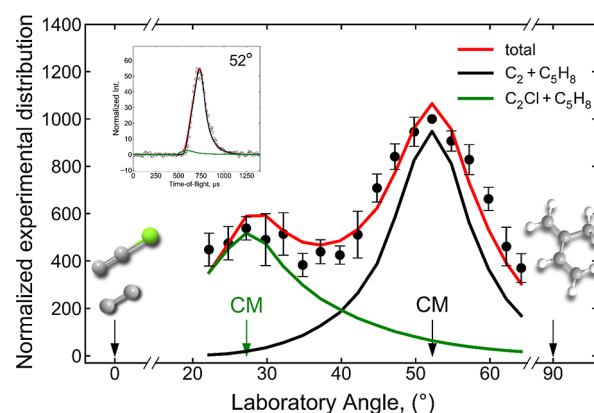


Figure 6. LAD recorded at a mass-to-charge ratio (m/z) 89 produced from the scattering of dicarbon (C_2) and chloroethynyl (C_2Cl) with 2-methyl-1,3-butadiene (C_5H_8). The time-of-flight spectrum recorded at 52° is shown as an inset (open circles—experimental data; solid line—fit from the center-of-mass functions). On both, experimental data are indicated by dots, and the two-channel simulations are represented by a red curve; contributions originating from dicarbon (C_2) and chloroethynyl (C_2Cl) channels are indicated by black and green curves, respectively. CM defines the center of mass. The corresponding center-of-mass functions used for the fit are presented in the Supporting Information.

and (5), with the relative ratios of the channels of 1:1.15, respectively. CM functions (Figure S2) for the reaction channel (1) were originally taken from work²⁶ where dicarbon was generated via an ablation source. However, due to the better signal-to-noise ratio of our data after a small tuning of original CM functions, we were able to archive a slightly better agreement of the experimentally determined reaction energy (from 474 ± 32 to $463 \pm 34 \text{ kJ mol}^{-1}$) compared to the calculated 468 kJ mol^{-1} . In summary, we were able to verify

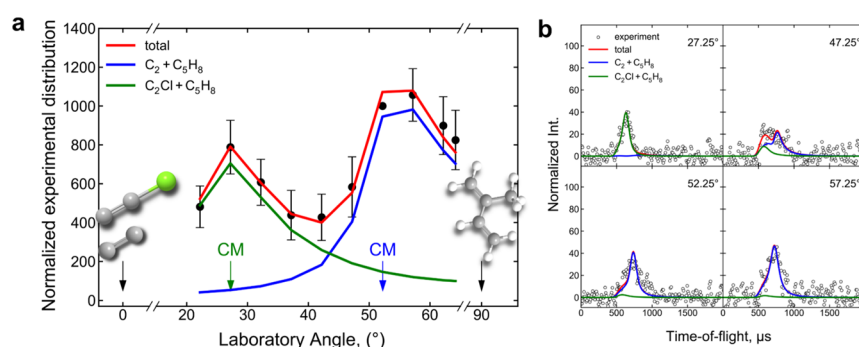


Figure 7. (a) LAD and (b) time-of-flight spectra recorded at a mass-to-charge ratio (m/z) 77 produced from the scattering of dicarbon (C_2) and chloroethynyl (C_2Cl) with 2-methyl-1,3-butadiene (C_5H_8). On both, experimental data are indicated by dots, and the two-channel simulations are represented by a red curve; contributions originating from the dicarbon (C_2) and chloroethynyl (C_2Cl) channels are indicated by blue and green curves, respectively. CM defines the center of mass.

the same reaction channel that was reported in ref 26 without any significant changes.

3.2.3. Data for $m/z = 77$. The laboratory data for $m/z = 77$ (Figure 7) could be fit with the two reaction channels (4) and (5), with the relative ratios of the channels 2:1, respectively. The resultant CM functions (Figure 8) for the reaction channel (2) hold critical insights into the chemical dynamics of the methyl-loss pathway in the reaction of dicarbon with 2-methyl-1,3-butadiene. Energy conservation dictates that the maximum (E_{max}) on the distribution of translational energy $P(E_T)$ resembles the sum of the collision energy (E_C) plus the reaction energy release ($-\Delta_r G$) for the product molecules that were formed without internal excitation. The assessed $P(E_T)$ holds an E_{max} value of $247 \pm 46 \text{ kJ mol}^{-1}$; taking into account, E_C of $28 \pm 1 \text{ kJ mol}^{-1}$, the reaction energy was determined to be $-219 \pm 47 \text{ kJ mol}^{-1}$ for CH_3 loss. The dicarbon beam holds molecules in their first electronically excited state $a^3\Pi_u$ which lies higher by 8 kJ mol^{-1} above the ground singlet state $X^1\Sigma_g^+$,⁵² which can correct the reaction energy to be $-211 \pm 47 \text{ kJ mol}^{-1}$; however, as we will show hereinafter, methyl elimination channels come solely from the singlet surface, and this correlation is unnecessary. In addition, the $P(E_T)$ reveals pronounced distribution maxima peaking close to zero of translational energy at $5 \pm 1 \text{ kJ mol}^{-1}$ indicating the simple bond rupture process that has either no or only a small exit barrier (loose exit transition state).^{53,54} The center-of-mass angular flux distribution $T(\theta)$ illustrates a pronounced backward scattering relative to the dicarbon radical beam, suggesting that at least one of the possible methyl-loss reaction channels proceeds via a direct “rebound mechanism”^{46,55,56} and/or an extremely short-lived C_7H_9 reaction intermediate that ejects the methyl radical. These findings are also supported by the flux contour map (Figure 8c), which depicts an overall image of the reaction and scattering processes.

3.3. Reaction Mechanism. For complex polyatomic systems, it is advantageous to integrate our experimental results with electronic structure and statistical calculations. This approach allowed us to elucidate the underlying reaction mechanisms and the nature of the isomer(s) formed. The detailed potential energy surface for the reaction of $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ with 2-methyl-1,3-butadiene ($CH_2C(CH_3)CHCH_2$; X^1A') together with the Rice–Ramsperger–Kassel–Marcus (RRKM) calculations is present elsewhere.²⁶ In this paper, the authors scrutinized hydrogen atom elimination channels, and here, we will only focus on methyl-loss channels. The energies for the stationary points were calculated using the CCSD(T)/

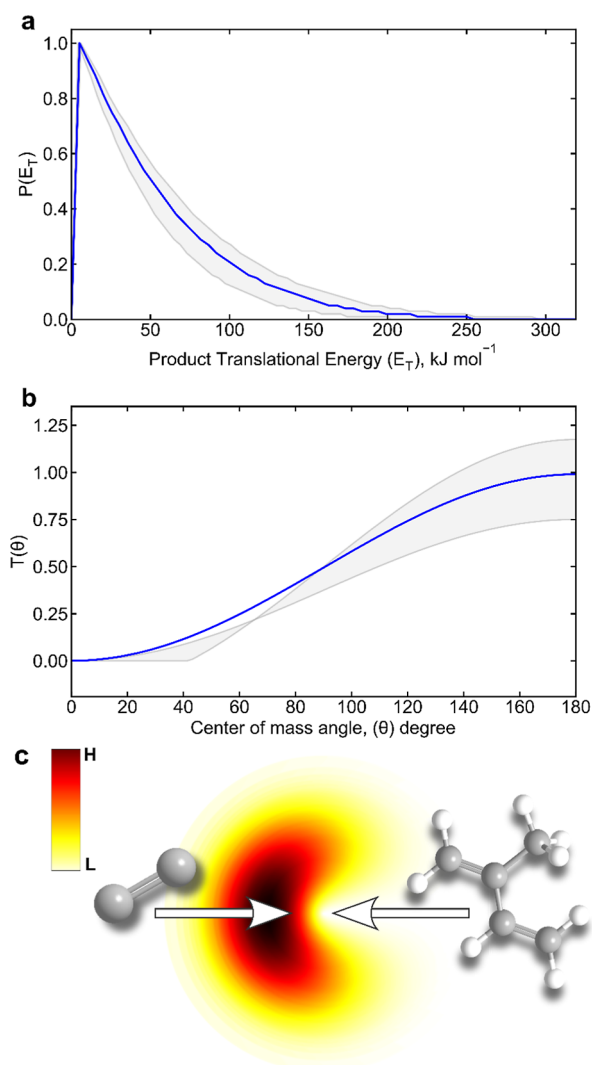


Figure 8. (a) Center-of-mass translational energy $P(E_T)$, (b) angular $T(\theta)$ flux distributions, and (c) flux contour map for the CH_3 -loss channel in the reaction of the dicarbon radical with 2-methyl-1,3-butadiene. The solid lines represent the best fit, while the shaded areas indicate the error limits. For $T(\theta)$, the direction of the dicarbon beam is defined as 0° and of the 2-methyl-1,3-butadiene as 180° .

CBS(dt)//B3LYP/6311G** + ZPE(B3LYP/6-311G**) (plain numbers) method, and for some products, energy was refined using the CCSD(T)/CBS(dtq)//B3LYP/6-311G** +

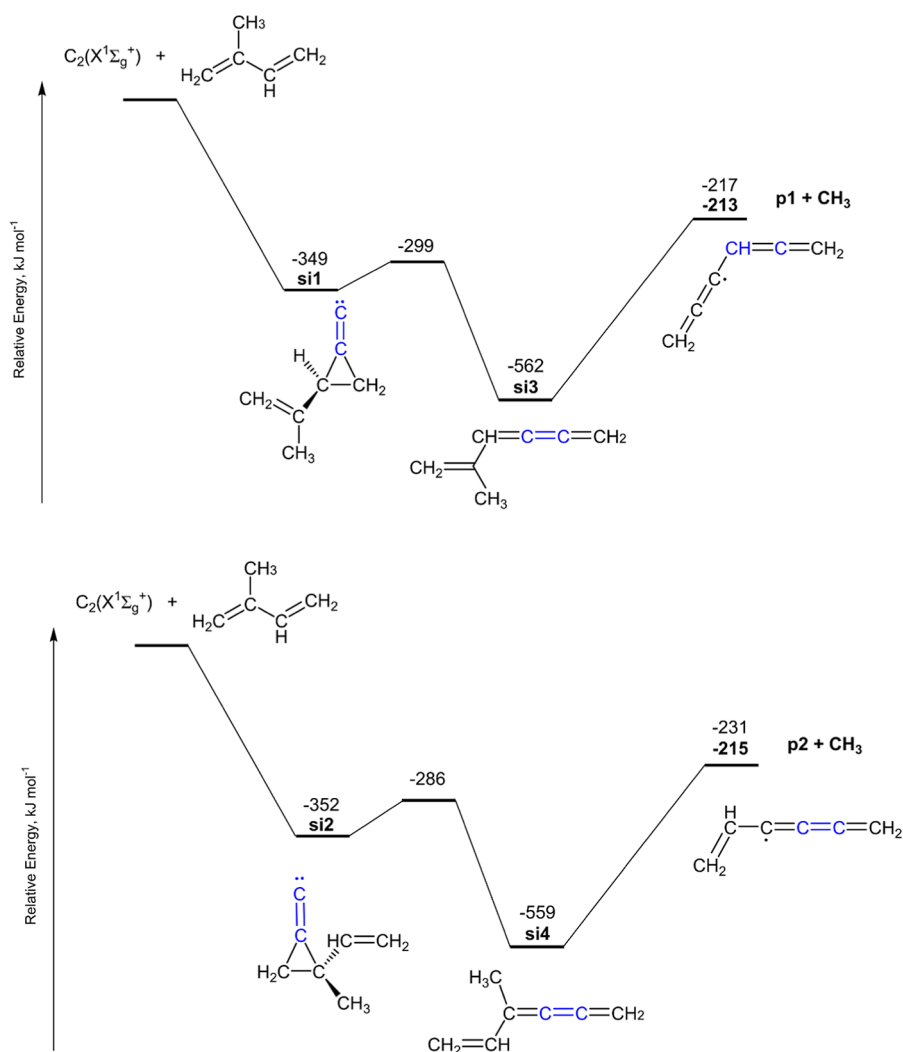


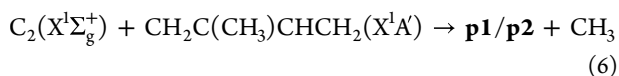
Figure 9. Reaction paths leading to the acyclic products in the dicarbon 2-methyl-1,3-butadiene reaction, based on the full potential energy surface presented in ref 26. Intermediates are labeled as **si** along with the energies relative to the separated reactants and barrier heights, where applicable, in kJ mol^{-1} , as calculated at the CCSD(T)/CBS(dt)//B3LYP/6311G** + ZPE (B3LYP/6-311G**) (plain numbers) and CCSD(T)/CBS(dtq)//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) (bold numbers) levels of theory.

ZPE(B3LYP/6-311G**) (bold numbers) level of theory (Figure 9), with the expected accuracy within ± 15 and ± 10 kJ mol^{-1} , respectively. The singlet ($X^1\Sigma_g^+$) and triplet ($a^3\Pi_u$) potential energy surfaces (PES) for the dicarbon reaction with 2-methyl-1,3-butadiene contain methyl radical-loss reaction pathways which possibly lead to a phenyl radical ($-419/-416$ kJ mol^{-1}) or two acyclic resonantly stabilized hexatetraenyl isomers **p1** (1,2,4,5-hexatetraen-3-yl, $-217/-213$ kJ mol^{-1}) and **p2** (1,3,4,5-hexatetraen-3-yl, $-231/-215$ kJ mol^{-1}). The computations predict that on the singlet and triplet surfaces, after a barrierless addition of dicarbon to the $\text{C3}=\text{C4}$ and $\text{C1}=\text{C2}$ double bonds in 2-methyl-1,3-butadiene, a phenyl radical can only be yielded via a multistep isomerization sequence involving successive hydrogen shifts.²⁶ Considering our experimental results which predict the reaction energy to be -219 ± 47 kJ mol^{-1} , we can verify the formation of only acyclic products **p1** and **p2**, but not a phenyl radical. Only the singlet surface includes two reaction channels that after dicarbon cluster insertion to the double bond lead to **p1** and **p2** (Figure 9).

These reaction pathways start with the barrierless addition of dicarbon $\text{C}_2(X^1\Sigma_g^+)$ to either the $\text{C3}=\text{C4}$ or the $\text{C1}=\text{C2}$

carbon–carbon double bonds of diene, yielding **si1**/**si2** complexes, respectively. In both intermediates, the new tricarbon ring is formed in the plane perpendicular to the carbon chain of the 2-methyl-1,3-butadiene moiety. In the next step, these collision complexes undergo ring opening to **si3**/**si4** via a barrier of 50/46 kJ mol^{-1} , ultimately leading to defacto dicarbon insertion into the originally attacked double bond. In the last step, **si3**/**si4** forms **p1**/**p2** via the methyl-loss channel through the simple bond-rupture process. The absence of an exit barrier is also supported by experimental findings based on $P(E_T)$ analysis. For the singlet surface, RRKM calculations were not completed. However, based on the PES analysis,²⁶ it was predicted that in the case of $\text{C}_2(X^1\Sigma_g^+)$ addition to the $\text{C3}=\text{C4}$ double bond in 2-methyl-1,3-butadiene, product **p1** should hold the highest branching ratio among all channels on the PES, since energetically it is the most competitive pathway. In the case of $\text{C}_2(X^1\Sigma_g^+)$ addition to $\text{C1}=\text{C2}$, the presence of the hydrogen shift channel from **si4** to 3-methyl-1,2,4,5-hexatetraene is 36 kJ mol^{-1} lower than the energy required for methyl elimination resulting in **p2**. Taking into account the collisional energy, that all barriers in this reaction are submerged, and the expected accuracy within ± 15 kJ mol^{-1}

for the energies of the intermediates on the PES, we can conclude that **p2** can still hold a significant branching ratio on this part of the PES. In summary, we were able to experimentally observe the “state-specific” methyl elimination reaction channels (6). Based on *ab initio* and statistical calculations, the same active involvement of the methyl group was predicted for dicarbon $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ reactions with the 1-substituted diene (1,3-pentadiene),²⁷ where RRKM results estimate the branching ratios for CH_3 -loss channels to be 20–30%. However, these channels were not identified in the experiment due to interference with the products of the $C(^3P) + 1,3$ -pentadiene reaction.



4. CONCLUSIONS

The crossed molecular beam reactions of dicarbon $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ with 2-methyl-1,3-butadiene (isoprene, $CH_2C(CH_3)CHCH_2$; X^1A') were conducted at a collision energy of 28 ± 1 kJ mol^{−1} under single-collision conditions utilizing a supersonic dicarbon beam generated via the photolysis of helium-seeded tetrachloroethylene (C_2Cl_4 ; X^1A_g). The experimental data were combined with previously made *ab initio* calculations and crossed molecular beam experiment²⁶ where a dicarbon beam was generated via ablation of a carbon rod. Our data show evidence for the presence of a previously elusive methyl elimination channel leading to acyclic products. Although on full singlet and triplet PESs exist the CH_3 -loss channels that theoretically can yield phenyl radicals, the formation of aromatic structures in the methyl elimination process is not supported by our results. While hydrogen-loss pathways are active on both the triplet and singlet PESs, under our experimental conditions, the methyl elimination pathways are only active on the singlet surface. On the singlet surface, the reaction is initiated by a barrierless addition of the dicarbon reactant to the $C3=C4$ and/or $C1=C2$ carbon–carbon double bonds of 2-methyl-1,3-butadiene, ultimately leading to dicarbon insertion into one of the double bonds of the diene before forming one of the resonantly stabilized hexatetraenyl radical **p1** or **p2**, respectively. The methyl radical elimination step proceeds via a simple bond rupture. In our study, we experimentally verified that in dicarbon chemistry with the methyl 2-substituted diene, the methyl group is not merely a passive spectator but can actively participate in the reaction mechanism. Specifically, in the case of $C3=C4$ addition, methyl-loss channels can predominate over hydrogen elimination pathways in reactions with ground-state dicarbon. The previous experimental study²⁶ of the reaction of $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ with 2-methyl-1,3-butadiene (X^1A') has failed to detect methyl elimination channels. Thus, our results eloquently highlight the major advantage of the photolytic sources for generating dicarbon supersonic beams for reactive scattering studies over ablation sources: the absence of carbon atom coreactants that hinder the detection of methyl-loss channels. The studied reaction results in the formation of at least two distinct C_6H_5 RSFRs: 1,2,4,5-hexatetraen-3-yl and 1,3,4,5-hexatetraen-3-yl. In hydrocarbon-rich combustion flames, both radical isomers can undergo a hydrogen atom-assisted isomerization, yielding the thermodynamically most stable C_6H_5 isomer, the phenyl radical, a key first step on the way to PAHs and soot.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.5c00639>.

Center-of-mass translational energy $P(E_T)$ and angular $T(\theta)$ flux distributions for the atomic chlorine-loss channel in the reaction of the chloroethynyl radical (C_2Cl) with 2-methyl-1,3-butadiene (C_5H_8) and for the atomic hydrogen-loss channel in the reaction of dicarbon C_2 with 2-methyl-1,3-butadiene (C_5H_8) (PDF)

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

Notes

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