Directed Gas-Phase Synthesis of Triafulvene under Single-Collision Conditions

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Abstract: The triafulvene molecule (c-C₃H₄)—the simplest representative of the fulvene family—has been synthesized for the first time in the gas phase through the reaction of the methylidyne radical (CH) with methylenecyclopropene (C₃H₃CH) and allene (H₂CCCH₂) under single-collision conditions. The experimental and computational data suggest triafulvene is formed by the barrierless cycloaddition of the methylidyne radical to the π-electron density of either C₃H₄ isomer followed by unimolecular decomposition through elimination of atomic hydrogen from the CH₂ or CH₃ groups of the reactants. The dipole moment of triafulvene of 1.90 D suggests that this molecule could represent a critical tracer of microwavactive allene in cold molecular clouds, thus defining constraints on the largely elusive hydrocarbon chemistry in low-temperature interstellar environments, such as that of the Taurus Molecular Cloud 1 (TMC-1).

Introduction
Since the pioneering discovery of pentafulvenes more than 100 years ago by Thiele,[1] the fulvenes triafulvene (1), pentafulvene (2), heptafulvene (3), and nonafulvene (4); Scheme 1) have fascinated the physical organic, theoretical, and organometallic chemistry communities from the fundamental viewpoints of electronic structure[3] and chemical bonding[4] as prototypes of a class of exotic hydrocarbons formally obtained by cross-conjugating one ring and a methylidene moiety through an exocyclic carbon–carbon double bond. The resulting molecules are planar with C₂ᵥ point groups and ¹A₁ electronic ground states in the case of 1–3, whereas nonafulvene (4) adopts a twisted geometry (C₂v) with a ¹A₁ electronic ground state owing to inefficient conjugation of the exocyclic carbon–carbon double bond with the nine-membered ring.[5,6] The unique reactivity associated with the cross-conjugated π-electronic structure has led to the broad use of fulvenes in the synthesis of natural products, such as loganin and sarracenin,[7,8] and in transition-metal complexes, such as [(η⁵-C₅Me₅)Ti(η⁵-C₅H₅ = C(pC₃H₅)₂)₂]₄(η⁵-η¹-η¹-η¹-N₄).[9,10] Fulvenes also serve as fundamental molecular building blocks in fluorescent aromatic hydrocarbons, including 9-(cyclononatrienyldiene)fluorene,[11] 9-(methylidenecyclopropabenzenediyne)fluorene, and 9-(methylidenecyclopropabenzenediyne)benzocycloheptatriene.[12]

Triafulvene (1, c-C₃H₄, methylenecyclopropene)—a thermodynamically less stable (99 kJ mol⁻¹)[13] isomer of vinylacetylene (5, HCCCCH₂) and butatriene (6, H₂CCCH₂; Scheme 2)—has received particular attention as it resembles the prototype of the fulvene family, defining the simplest cross-conjugated hydrocarbon carrying a methylidene functional group in conjugation with a single carbon–carbon double bond within the cycloalkene. Although triafulvenes equipped with bulky phenyl substituents, such as 2,3-diphenyl-4,4-dicyanotriafulvene (C₈H₈N₂), are stable monomers at room temperature,[14] triafulvene (1), first synthesized by dehalogenation of 2-bromomethylenecyclopropane, was found to polymerize at temperatures above 80 K.[15,16] In
a later study on triafulvene (1) synthesis, its head-to-tail \( \text{C}_8 \text{H}_8 \) dimer \( 1 \) was successfully isolated at temperatures above 198 K,[17] and its formation was attributed to the strong dipole moment (1.90 D) associated with the dipolar resonance structure of triafulvene (1, Scheme 3).[18] Despite evidence for the formation of triafulvene (1) as a reactive intermediate, as determined by ultraviolet (UV; 193/248 nm) irradiation of butatriene (6) in 10 K argon matrices,[19] the directed synthesis and isolation of triafulvene (1) in the gas phase has eluded synthetic chemists over the last decades. Considering the difficulties in preparation, short lifetimes above 80 K, and the tendency for dimerization, free triafulvenes are one of the least explored classes of organic molecules.

Herein, we offer an exceptional glance into the fundamentally elusive chemistry of the cyclic triafulvene (1) molecule and account for its gas-phase synthesis under single-collision conditions through bimolecular reactions of the methylidyne radical \(( \text{CH}, X^\text{III})\) with methylecetlylene \((\text{CH}_3\text{CCCH}, X^\text{A_1})\) and allene \((\text{H}_2\text{CCCH}_2, X^\text{A_1})\) by utilizing the crossed molecular beams approach. Exploration at the molecular level affords fundamental perception into the underlying reaction mechanisms leading to the synthesis of highly reactive molecules, such as fulvenes. The reactions are conducted in the gas phase under single-collision conditions so that the primary reaction products fly apart undisturbed and hence do not undergo successive reactions, such as hydrogen-atom-assisted isomerization. Since dimerization of triafulvene (1) is precluded as well, crossed molecular beam experiments enable the versatile and clean gas-phase synthesis of the simplest fulvene. This system is also appealing from the physical organic chemistry viewpoint, since triafulvene (1) represents a benchmark, thus enabling the elucidation of the chemical reactivity, bond-breaking processes, and the formation of cross-conjugated cyclic molecules from acyclic precursors as an outcome of a single collision, which is not possible by traditional synthetic chemistry routes. This approach therefore provides a novel path to gain access to a hitherto rather obscure class of strained hydrocarbon molecules: substituted triafulvenes.

**Results**

**Laboratory Frame**

The reactive scattering signal of reactions of the methylidyne radical \(( \text{CH}, X^\text{III})\) with allene \((\text{H}_2\text{CCCH}_2, X^\text{A_1})\) and methylecetlylene \((\text{CH}_3\text{CCCH}, X^\text{A_1})\) was observed at mass-to-charge ratios \((m/z)\) from 48 to 52. For each system, these time-of-flight (TOF) spectra are superimposable after scaling and hence derive from a single reaction channel, namely, \( \text{CH} \) (13 amu) + \( \text{C}_8 \text{H}_8 \) (40 amu) \( \rightarrow \) \( \text{C}_9 \text{H}_9 \) (52 amu) + \( \text{H} \) (1 amu), whereby \( m/z \) 52 corresponds to the singly ionized atomic-hydrogen-loss reaction product \((\text{C}_9 \text{H}_8^+)\), with ion counts at \( m/z \) 51–48 arising from dissociative electron impact ionization of neutral \( \text{C}_8 \text{H}_8 \) products. The data therefore suggest that the \( \text{C}_9 \text{H}_9 \) isomers are formed through a methidyldene versus atomic-hydrogen exchange pathway in the reaction of the methidyldene radical with the \( \text{C}_9 \text{H}_9 \) isomers allene and methylecetlylene. Under our experimental conditions, the signal-to-noise ratio for the fragment ion at \( m/z \) 51 (\( \text{C}_9 \text{H}_8^+ \)) was better than that observed for the parent ion (\( \text{C}_9 \text{H}_9^+ \); \( m/z \) 52) for both systems studied (see Figure S1 in the Supporting Information); therefore, TOF spectra and the full laboratory angular distributions were extracted at \( m/z \) 51 (see Figures S2 and S3). The resulting laboratory angular distributions display maxima near the CM angles of \((52.4 \pm 0.4)^\circ\), about which both distributions are nearly symmetrical and span at least \( 40^\circ \) in the laboratory frame (Figure 1). The symmetry suggests that the reaction proceeds through indirect scattering dynamics involving at least one \( \text{C}_9 \text{H}_9 \) reaction intermediate that ultimately undergoes unimolecular decomposition by emitting atomic hydrogen. Notably, the laboratory data for the methidyldene reaction with allene and methylecetlyene depict nearly identical TOF spectra and laboratory angular distributions, which may indicate that similar features on the \( \text{C}_9 \text{H}_9 \) potential-energy surface (PES), such as decomposing intermediates, ultimately govern the reaction dynamics. The signal at \( m/z \) 51 could not be fit with molecular-hydrogen loss (2 amu) leading to a heavy \( \text{C}_9 \text{H}_9 \) counter fragment (51 amu). These fits would result in TOF spectra that are too fast and laboratory angular distributions that are too broad.

As the hydrogen atom can be ejected from the methidyldene and/or from the \( \text{C}_9 \text{H}_9 \) reactant, we conducted crossed beam experiments of methidyldene \(( \text{CH})\) with \([\text{D}_2]\)methylecetlylene \((\text{CD}_3\text{CCCD})\) and \([\text{D}_2]\)allene \((\text{D}_2\text{CCCD})\) to extract the position(s) of the atomic-hydrogen and deuterium losses. In the \( \text{CH}/\text{D}_2\text{CCCD}_2 \) and \( \text{CH}/\text{CD}_2\text{CCCD}_2 \) systems, the hydrogen- \((\text{CD}_3)\) and deuterium-loss \((\text{CD}_4)\) products are expected to depict ion counts of the parent molecule at \( m/z \) 56 and 55, respectively. The product at \( m/z \) 56 cannot fragment to \( m/z \) 55, but only to \( m/z \) 54. Therefore, the identification of signals at \( m/z \) 56 and 55 would represent explicit evidence of the formation of the hydrogen- \((\text{CD}_3)\) and deuterium-loss product \((\text{CD}_4)\), respectively. In both systems, reactive scattering signals were observed at \( m/z \) 55 and 54, but not at \( m/z \) 56. These findings alone suggest the existence of the atomic-deuterium-loss channel, with deuterium ejected from the \( \text{C}_9 \text{D}_9 \) reactants to form \( \text{C}_9 \text{HD}_9 \) products \((55 \text{ amu}; \text{see Figures S4–S7})\). Therefore, the results of the \( \text{CH}/\text{D}_2\text{CCCD}_2 \) system reveal unambiguously the formation of \( \text{C}_9 \text{HD}_9 \) isomers with deuterium emitted from one of the four chemically equivalent deuterium atoms of the \([\text{D}_2]\)allene reactant; the methidyldene moiety stays intact. However, methylecetlylene has two sets of chemically distinct hydrogen atoms at the methyl (\( \text{CH}_3 \)) and ethynyl (CCH) moieties. To elucidate the position(s) from which the hydrogen atom is (or
hydrogen atoms are) emitted, we carried out crossed beam experiments of [D$_1$]methylidyne (CD) with partially deuterated [D$_3$]methylacetylene (CD$_3$CCH) and [D$_1$]methylacetylene (CH$_3$CCD). The hydrogen-atom-loss channel would result in the formation of C$_4$D$_4$ and C$_4$H$_2$D$_2$ and signals at m/z 56 and 54 (see Figure S5). The reactive scattering experiments at the center-of-mass (CM) angles revealed that the CD/CH$_3$CCD system yields a hydrogen-loss product (C$_4$H$_2$D$_2$); the ion counts at m/z 54 suggest that the atomic emission originates from the methyl (CH$_3$) group of the methylacetylene reactant.

**Center-of-Mass Frame**

While the laboratory data provide compelling evidence for the methylidyne versus atomic hydrogen exchange pathway with the hydrogen atom emitted from allene and the methyl group of methylacetylene, respectively, our goal was to elucidate the underlying reaction mechanism(s) by exposing the identity of the isomer(s) formed. A forward-convolution fitting of the laboratory data yields CM translational energy $P(E_T)$ and CM angular $T(\theta)$ flux distributions that offer a glimpse into the reaction dynamics (Figure 2). Within our error limits, the best-fit CM functions achieved using a product mass combination of C$_4$H$_5$ (52 amu) plus H (1 amu) were nearly identical for both systems. The derived $P(E_T)$ distributions reveal maximum translational energy releases $(E_{\text{max}})$ of (181 ± 12) and (178 ± 12) kJ mol$^{-1}$. Accounting for

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Figure 1. a) Time-of-flight (TOF) spectra and b) laboratory angular distribution recorded at m/z 51 (C$_3$H$_5^+$) for the reaction of the methylidyne radical with allene at a collision energy of (18.6 ± 0.3) kJ mol$^{-1}$. c) TOF spectra and d) laboratory angular distribution recorded at m/z 51 (C$_3$H$_5^+$) for the reaction of the methylidyne radical with methylacetylene at a collision energy of (18.7 ± 0.2) kJ mol$^{-1}$. The circles represent the experimental data and the solid lines the best fits.

Figure 2. a) Center-of-mass translational energy $P(E_T)$ and b) angular $T(\theta)$ flux distributions for the reaction of the methylidyne radical with allene (blue) and methylacetylene (red) forming C$_4$H$_5$ isomer(s) by atomic-hydrogen emission. Solid lines represent the best fit, while shaded areas indicate the experimental error limits.
the energy conservation, the high-energy cutoff of the \( \text{C}_2\text{H}_4 \) products formed without internal excitation is best understood with the maximum energy \( E_{\text{max}} \) related to the collision energy \( (E_c) \) plus the reaction energy \( (\Delta G) \) available for product translational degrees of freedom by \( E_{\text{max}} = E_c - \Delta G \). The reaction energies calculated for the CH/ allene and CH/ methylacetylene systems were \((-162 \pm 12)\) and \((-159 \pm 12)\) kJ mol\(^{-1}\), respectively. Furthermore, the \( P(E_c) \) distributions peaked at 36 and 33 kJ mol\(^{-1}\). This off-zero peaking suggests that the hydrogen atom is lost through a repulsive energy release involving a tight exit transition state. This process can be best understood in terms of the reverse reaction of a hydrogen atom reacting with a closed-shell \( \text{C}_2\text{H}_4 \) isomer to form a \( \text{C}_2\text{H}_6 \) intermediate, which involves an entrance barrier. Also, the average translational energies of the products were calculated to be \((53 \pm 4)\) and \((51 \pm 4)\) kJ mol\(^{-1}\), that is, fractions of \((29 \pm 3)\%\) of the maximum energy release to form \( \text{C}_2\text{H}_6 \). These findings suggest indirect scattering dynamics involving \( \text{C}_2\text{H}_4 \) intermediates(s) that undergo unimolecular decomposition through tight exit transition state(s) as characterized by a repulsive energy release and significant electron rearrangement to form the final \( \text{C}_2\text{H}_6 \) products\(^{[20]}\).

Finally, the \( T(\theta) \) distributions contain additional information on the scattering dynamics in revealing product flux over the entire angular range; furthermore, these distributions show a pronounced forward–backward symmetry with a maximum at \(90^\circ\) (sideways scattered). The symmetry of the \( T(\theta) \) distributions suggests a decomposing \( \text{C}_2\text{H}_4 \) intermediate with a lifetime comparable to or exceeding its rotational period. In a sense the reaction intermediate “lost” its memory of how the reactants approached initially, and the intermediate thus loses a hydrogen atom in all directions. The sideways scattering in particular indicates strong geometrical constraints on the decomposing intermediate with a preference for atomic-hydrogen loss perpendicular to the rotational plane of the decomposing intermediate and hence nearly parallel to the total angular momentum vector\(^{[20,21]}\). Thus, for the reverse reaction, the hydrogen atom adds perpendicularly to the \( \text{C}_2\text{H}_6 \) product to allow maximum overlap of the 1s orbital of the hydrogen atom with the \( \pi \)-electron density of the \( \text{C}_2\text{H}_4 \) molecule.

Discussion

We now combine the aforementioned experimental findings with available data from electronic structure calculations in an attempt to elucidate the underlying reaction dynamics and the nature of the structural isomer(s) produced. Ribeiro and Mebel explored the \( \text{C}_2\text{H}_4 \) PES and revealed the formation of three distinct \( \text{C}_2\text{H}_4 \) isomers through the reactions of methyldiene with allene and methylenecyclopropane\(^{[22]}\). These three isomers are vinylacetylene (\( \text{HCCCCCH} \); \( \text{p}_1 \); \( \Delta G = (-269 \pm 5) \) kJ mol\(^{-1}\)), 1,2,3-butatriene (\( \text{HCCCCCH} \); \( \text{p}_2 \); \( \Delta G = (-239 \pm 5) \) kJ mol\(^{-1}\)), and triafulvene (\( \text{c-C}_2\text{H}_2 \); \( \text{p}_3 \); \( \Delta G = (-171 \pm 5) \) kJ mol\(^{-1}\)), with overall reaction energies given for the methyldiene/methylenecyclopropane system. The crossed molecular beams approach has the unique advantage of extracting the nature of the isomer(s) formed by comparing the experimentally determined reaction energies \((-162 \pm 12)\) kJ mol\(^{-1}\); \((-159 \pm 12)\) kJ mol\(^{-1}\) with the computed reaction energies for distinct \( \text{C}_2\text{H}_4 \) isomers \( \text{p}_1 \sim \text{p}_3 \) (Figure 3)\(^{[23]}\).

These data are in strong agreement with the formation of triafulvene in both systems; the formation of the vinylacetylene (\( \text{p}_1 \)) or 1,2,3-butatriene (\( \text{p}_2 \)) isomers would increase the experimental reaction exoergicity by 98 or 65 kJ mol\(^{-1}\), which is clearly outside the error limits of the experiments. By examining the PES, we can gain insight into the reaction dynamics leading to the formation of triafulvene (\( \text{p}_3 \)). The electronic structure of the methyldiene radical in its \( ^2\Pi \) electronic ground state opens the possibility for two types of barrierless entrance channels through addition to the \( \pi \)-electron density at carbon–carbon double or triple bonds or insertion into C–H or C–C bonds. Key reaction pathways leading to triafulvene (\( \text{p}_3 \)) are highlighted in Figure 4. In the CH/CH, \( \text{C}_2\text{H}_4 \) system, barrierless cycloaddition of the methyldiene radical to the acetylene moiety forms cyclic collision complexes \( \text{i}_1 \) and \( \text{i}_2 \), whose molecular geometries are distinguished by the location of the unpaired electron.

Intermediate \( \text{i}_1 \) possesses a planar carbon skeleton but only \( \text{C}_1 \) symmetry due to the nonsymmetric positioning of the hydrogen atoms in the CH group. The radical is essentially delocalized on the two sp\(^2\)-hybridized carbon atoms in the three-membered ring carrying the C–H groups and linked by an ordinary C–C bond. Notably, the rotation of the methyl group is nearly free, and hence a \( \text{C}_1 \) symmetric structure with the plane of symmetry containing all four carbon atoms is almost degenerate with the \( \text{C}_1 \) local minimum \( \text{i}_1 \). In \( \text{i}_2 \) the radical center resides on the carbon atom carrying the methyl group, and the C–H groups in the ring are linked by a double C=C bond, thus resulting in a \( \text{C}_1 \) symmetric structure with the mirror plane perpendicular to the three-membered ring. Both intermediates can interconvert readily with a barrier of only \(20\) kJ mol\(^{-1}\). Alternatively, intermediate \( \text{i}_1 \) can undergo a simultaneous hydrogen migration–ring opening to yield intermediate \( \text{i}_8 \), which in turn isomerizes through hydrogen migration–ring closure to \( \text{i}_9 \). The unimolecular decomposition of both \( \text{i}_2 \) and \( \text{i}_9 \) releases a hydrogen atom, thereby establishing the cross-conjugated \( \pi \)-system in the heavy coproduct: triafulvene (\( \text{p}_3 \)). In the CH/\( \text{H}_2\text{CCCH} \) system, the methyldiene radical can add to the carbon–carbon double bond to yield the collision complex \( \text{i}_9 \).

The theoretically predicted geometries of the exit transition states involved in the \( \text{i}_2 \rightarrow \text{p}_3 + \text{H} \) and \( \text{i}_9 \rightarrow \text{p}_3 + \text{H} \) pathways depict the hydrogen atom departing at angles of 8.9 and 30\(^\circ\), respectively, with respect to the total angular momentum vector. These geometries are consistent with the best-fit \( T(\theta) \) distributions, whose shapes are suggestive of a sideways-scattered reaction product, whereby the \( \text{C}_2\text{H}_4 \) flux in the methylenecyclopropane and allene reaction is highest at \(90^\circ\), with 62 and 75\%, respectively, of the maximum product flux appearing near the poles (0\(^\circ\) and 180\(^\circ\)). Importantly, the \( T(\theta) \) for the CH/\( \text{H}_2\text{CCCH} \) reaction is isotropic within the error limits of the experimental data and may account for the relatively wide-angled departure of the hydrogen atom for the \( \text{i}_9 \rightarrow \text{p}_3 + \text{H} \) pathway.
Most importantly, our experiments exploiting (partially) deuterated reactants support the aforementioned findings. First, the experiments along with the extracted reaction mechanisms reveal that the hydrogen atom is emitted from the methyl group (CH/CH₃CCH) and from the CH₂ moiety (CH₂/CCCH₂). In the case of the CD/CH₃CCH system, this process is rationalized by the addition of the [D₁]methylidyne radical to the carbon–carbon double bond of allene to yield intermediate i₉, which ejects atomic hydrogen to give [D₁]triafulvene (D₁-p₃; Figure 5). For CD/CH₃CCH, the initial addition of [D₁]methylidyne forms i₁₀/i₂; the latter can eject atomic hydrogen to give [D₂]triafulvene (D₂-p₃). In principle, i₂ could isomerize to i₈, which may rearrange to i₂ and emit atomic deuterium to give [D₃]triafulvene (D₃-p₃; C₄H₂D; 53 amu; Figure 5). However, the absence of atomic-hydrogen-loss signals from methylidyne (CH) or the acetylenic end of CH₃CCH, as determined from the CH/CD,CCH and CD/CD,CCH reactions (see Figure S5), suggests that intermediate i₈ does not play a significant role in the reaction dynamics of the methylidyne–methylacetylene system and that
the mechanism involves the unimolecular decomposition of $d_{12}$.

Previous experimental studies under “bulk” conditions essentially led to the conclusion that the reactions of methylidyne with allene and methylacetylene proceeded by an addition or insertion mechanism that ultimately yields low-lying $C_4H_4$ isomers alongside hydrogen atoms. Daugey et al. proposed that methylidyne radicals undergo fast reactions with allene and methylacetylene at rates of few $4 \times 10^8$ molecule$^{-1}$ s$^{-1}$ (77–170 K).[23] Products could not be identified. Goulay et al. probed the methylidyne reaction with allene and methylacetylene using vacuum ultraviolet (VUV) photoionization to photoionize the products. Their study sampled vinylacetylene ($p_1$), 1,2,3-butatriene ($p_2$), and triafulvene ($p_3$)/cyclobutadiene, with the latter only appearing in the methylacetylene system.[24] Although the contribution of the cyclic $C_4H_4$ isomers triafulvene and/or cyclobutadiene could not be disentangled under their experimental conditions, the recent ab initio and statistical analysis by Ribeiro and Mebel found an overall agreement with their bulk-phase (4 torr) product distribution with the conclusion that the cyclic isomer was most likely triafulvene.[22] As compared to the single-collision conditions afforded by the present crossed molecular beams study, reaction intermediates undergo a few thousand collisions with the buffer gas at relatively high pressures of 4 torr; therefore, the internal energy of any intermediates can be diverted to the buffer gas, thus providing a different outcome of the reaction owing to distinct internal energies of the reaction intermediates that ultimately influence the measured product distribution.

We also carried out energy-dependent Rice–Ramsperger–Kassel–Marcus (RRKM) calculations of product branching ratios under single-collision conditions[25,26] using the potential energy surface and molecular parameters computed by Ribeiro and Mebel (see Table S2 in the Supporting Information).[22] At the experimental collision energy of 19 kJ mol$^{-1}$, methylidyne addition to the triple bond in methylacetylene is statistically predicted to result in the production of about 67% triafulvene, 18% vinylacetylene, and 14% butatriene. Alternatively, insertion of methylidyne into a C(sp)$^3$–H bond and the single C–C bond should nearly exclusively produce vinylacetylene, whereas the insertion into the C(sp)$^3$–H bond should form nearly equal amounts of vinylacetylene and butatriene at about 47 and 53%, respectively. Since the triple-bond addition is dynamically preferred, our present experimental results for the methylidyne plus methylacetylene reaction qualitatively agree with the statistical picture showing triafulvene as the dominant reaction product. However, since the RRKM approach based on chemically accurate ab initio calculations of relative energies and molecular parameters has been shown to closely reproduce experimental product branching ratios for numerous chemical reactions when the system explored exhibits statistical behavior, the non-observation of vinylacetylene and butatriene in experiment indicates deviation from the statistical RRKM behavior. The contrast between the RRKM
and experimental results is much more dramatic for the methylidyne–allene system, for which the calculations predict that the dynamically favorable methylidyne addition to the double bond should almost solely form vinylacetylene, whereas the insertion into a C–H bond should give mostly acetylene plus vinyl radicals with vinlylcetylene as a minor product. Negligible amounts of triafulvene are statistically formed in both cases, and thus the methylidyne–allene system under single-collision conditions clearly demonstrates non-RRKM behavior of this system.

**Conclusion**

In conclusion, our study enabled the first unambiguous identification of the triafulvene (p3; c-C4H3) isomer as a reaction product of the gas-phase reaction of methylidyne (CH) radicals with allene (H2CCCH3) and methylacetylene (CH3CCH) under single-collision conditions. Triafulvene was formed by the barrierless cycloaddition of the methylidyne radical to the π-electron density, thus resulting in vibrational-excitation C4H6 intermediates that undergo unimolecular decomposition through hydrogen-atom emission. Systematic analysis of the crossed molecular beams data combined with electronic structure calculations suggests that isomerization on the C4H6 PES proceeds most likely through an addition/elimination mechanism. Beyond fundamentally abstract considerations, the reaction mechanisms uncovered in this study are most relevant to the combustion and astrochemical regimes. With respect to the combustion scenario, the C4H6 reaction intermediates, for example, could react with acetylene (C2H2) to eventually form C4H8 isomers, such as fulvene and ultimately benzene,27,28 linking them to the sooting process via polycyclic aromatic hydrocarbons (PAHs) through mass-growth protocols, such as the hydrogen-abstraction C2H2-addition (HACA) mechanism.29,30 Triafulvene, if formed, could undergo collision-induced isomerization to the thermodynamically favored vinylacetylene (p1; HCCCCH3) — a key component for PAH formation and growth in a complex reaction scheme with applicability at the opposing extremes of hydrocarbon combustion and interstellar space,31,32 where, for example, the CH and CH3CCH molecules are known to exist in high abundance. Despite this insight, our study under single-collision conditions highlights that the reactivity of nascent triafulvene and the effects of its cross-conjugated π system on the radical-driven chemistry of high-temperature combustion systems are essentially unknown.

**Experimental Section**

The methylidyne (CH; X′TI) gas-phase reactions with methylacetylene (CH3CCH; X′;A) and allene (H2CCCH2; X′;A) along with their fully and partially deuterated isotopologues were conducted under single-collision conditions using the crossed molecular beams method.33 A pulsed supersonic beam of methylidyne radicals was produced by photodissociation of bromoform (CHBr3, Aldrich Chemistry, ≥ 99%), first cooled to 283 K then diluted in helium (99.9999%; AirGas), using the focused 248 nm output of an excimer laser (Coherent; CompEx 110) 1 mm downstream of the nozzle.34

The methylidyne radicals were velocity-selected by a chopper wheel before crossing perpendicularly with a supersonic beam of pure methylacetylene (Organic Technologies, 99% +) or allene (H2CCCH3; Organic Technologies, 99% +) with resulting collision energies of 19 kJ mol−1 (see Table S1); typical rotational temperatures of the methylidyne radical beam of (14 ± 1) K were achieved.35 Where necessary, experiments with (partially) deuterated reactants were carried out utilizing [D2]methylidyne (CD), produced analogously to the methylidyne radical by exploiting CDBr3 (Aldrich Chemistry, 99.5% +) as a precursor, [D2]methylacetylene (CD2CH); CDN Isotopes, 99% +), [D2]methylacetylene (CD2CCD; CDN Isotopes, 99% +), [D4]methylacetylene (CH3CCD; CDN Isotopes, 99% +), and [D4]allene (D4CCCD2; CDN Isotopes, 98% +) as appropriate.

The neutral reaction products were ionized by electron impact (80 eV) and then filtered according to their m/z ratio using a quadrupole mass spectrometer. The detection equipment was housed within a differentially pumped and rotatable chamber that allowed the collection of product velocity distributions by measuring angularly resolved time-of-flight (TOF) spectra in the plane of the reactant beams. The laboratory data were analyzed by a forward-convolution routine36,37 that relies on user-defined center-of-mass (CM) translational energy PE(T) and angular T(θ) flux distributions that are varied iteratively until a best fit of the experimental dataset is obtained. These functions comprise the reactive differential cross section I(θ, α), which is taken to be separable into its CM scattering angle θ and CM velocity u components, I(u, θ) = Pu(u) × T(θ). Errors of the PE(T) and T(θ) functions were 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.

**Computational Details**

We employed RRKM theory38–40 to calculate energy-dependent rate constants of all unimolecular reaction steps on the C4H6 potential energy surface (PES) accessed after the initial association of the methylidyne radical with allene and methylacetylene. The PES itself and molecular parameters of all the species (reactants, products, intermediates, and transition states) were computed earlier and reported in a previous publication.22 In this study, internal-energy-dependent rate constants were assessed within the harmonic approximation employing our in-house code,40 which automatically processes GAUSSIAN09 log files to evaluate numbers of states for transition states and densities of states for local minima using the direct count method. The calculations were carried out at the zero-pressure limit corresponding to crossed molecular beam conditions. RRKM rate constants were then used to evaluate product branching ratios by solving first-order kinetic equations within steady-state approximation.22–40 This ab initio/RRKM approach has been shown to closely reproduce experimental product branching ratios when the system exhibits statistical behavior.32,41–43

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Conflict of interest

The authors declare no conflict of interest.

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