**Gas Phase Formation of 1,3,5,7-Cyclooctatetraene (C8H8) through Ring Expansion via the Aromatic 1,3,5-Cyclo­octatrien-7-yl Radical (C8H9•) Transient**

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**ABSTRACT**

Gas-phase 1,3,5,7-cyclooctatetraene (C8H8) and triplet aromatic 1,3,5,7-cyclooctatetraene (C8H8) were formed for the first time through the bimolecular methylidyne radicals (CH) - 1,3,5-cycloheptatriene (C7H8) reactions under single collision conditions on the doublet surface. The reaction involves methylidyne radical addition to the olefinic π electron system of 1,3,5-cycloheptatriene followed by isomerization and ring expansion to aromatic 1,3,5-cyclo­octatrien-7-yl radical (C8H9•). The chemically activated doublet radical intermediate undergoes unimolecular decomposition to 1,3,5,7-cyclooctatetraene. Substituted 1,3,5,7-cyclooctatetraene molecules can be prepared in the gas phase with hydrogen atom(s) in the 1,3,5-cycloheptatriene reactant being replaced by organic side groups. These findings are also of potential interest to organometallic chemists by expanding the synthesis of exotic transition metal complexes incorporating substituted 1,3,5,7-cyclooctatetraene dianion (C8H82-) ligands and to untangle the unimolecular decomposition of chemically activated and substituted 1,3,5-cyclo­octatrien-7-yl radical eventually gaining a fundamental insight of their bonding chemistry, electronic structures, and stabilities.

**1. INTRODUCTION**

     Ever since the preparation of 1,3,5,7-cyclooctatetraene (COT, C8H8) from the alkaloid pseudo­pelletierine by Willstätter et al.[1](#_ENREF_1) and through the high-pressure tetramerization of acetylene (C2H2) in the presence of nickelcyanide by Reppe at al.,[2](#_ENREF_2) the COT molecule has received substantial interest from the preparative organometallic,[3](#_ENREF_3),[4](#_ENREF_4) computational,[5](#_ENREF_5),[6](#_ENREF_6) and physical organic chemistry communities[7](#_ENREF_7),[8](#_ENREF_8) from comprehensive insights of chemical bonding[9](#_ENREF_9) and electronic structure.[10](#_ENREF_10) Low-temperature 1H-NMR studies[11](#_ENREF_11),[12](#_ENREF_12) and X-ray diffraction data[13](#_ENREF_13),[14](#_ENREF_14) revealed that COT adopts a D2d symmetric tub conformation with two distinct carbon-carbon single (147 pm) and double (134 pm) bond distances.[15](#_ENREF_15) These findings indicate that COT can be classified as a non-aromatic [8]annulene, i.e. a conjugated monocyclic hydrocarbon (CnHn with n being even) with alterna­ting carbon – carbon single and double bonds. Singlet COT under­goes ring-inversion via a D4h symmetric, planar transition state rather than via a D8h symmetric transition state due to Jahn-Teller distortion.[7](#_ENREF_7),[8](#_ENREF_8) This strongly contrasts the electronic structure of the 10π Hückel aromatic, D8h symmetric 1,3,5,7-cyclooctatetraene dianion (C8H82-), a prevalent ligand in actinide sandwich coordination com­plexes such as thorocene (Th(C8H8)2) and uranocene (U(C8H8)2) as potential contenders for single molecular magnets[16](#_ENREF_16),[17](#_ENREF_17) and nanowires.[18](#_ENREF_18),[19](#_ENREF_19)

形状, 多边形

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**Scheme 1**. Four non-equivalent resonance structures (**R1**-**R4**) along with the corresponding population (A) and the natural bond orbital (NBO) – computed bond orders (Wiberg bond indices) of 1,3,5-cyclooctatrien-7-yl (C8H9•, **i5**).

     Nevertheless, despite the very first synthesis of COT more than a century ago, the 1,3,5-cyclo­octatrien-7-yl radical (C8H9•), which can be formed from COT by adding an atomic hydrogen to one of the four carbon-carbon double bonds, has not been inferred in any gas phase experi­men­ts to date. Lin et al.[20](#_ENREF_20) advocated that this radical may signify a hitherto overlooked transient hydrocarbon in combustion processes accessed through the phenyl radical (C6H5) - ethylene (C2H4) reaction possibly via the phenyl radical addition to ethylene followed by isomerization to a bicyclic complex and ring opening to the 1,3,5-cyclo­octatrien-7-yl radical. Heat of formation at 0 K of 325 kJ mol-1 suggested by electronic structure calculations reveals that the 1,3,5-cyclo­octatrien-7-yl radical is thermodynamically less stable than the o-, m-, and p-xylyl (CH3C6H4CH2•) structural isomers by 144−158 kJmol-1.[21-23](#_ENREF_21) Characteristically, 1,3,5-cyclo­octatrien-7-yl represents a resonantly stabilized free radical (RSFR), which can be visualized through four non-equivalent resonance structures (Scheme 1), in which the spin den­sity of the radical center transfers through the ring from C2 (**R1**) via C4 (**R2**) and C6 (**R3**) to C8 (**R4**). The radical center location directs the chemistry of molecular mass growth processes through radical – radical reactions or degradation via recombination with molecular oxygen followed by oxidation; hence, bimolecular gas phase reac­tions of C8H9• may tetrafurcate through distinct barrierless addition intermediates represented through the radical centers in **R1** to **R4**.

     Herein, an exceptional glimpse is afforded into the previously overlooked chemistry of the 1,3,5-cyclo­octatrien-7-yl (C8H9•) transient accessed in a bimolecular methylidyne radical (CH) - 1,3,5-cycloheptatriene (C7H8) reaction under single collision conditions via ring expansion (reaction [1]) (Experimental Section). Under single-collision conditions, 1,3,5-cyclo­octatrien-7-yl undergoes predominantly unimolecular decomposition to 1,3,5,7-cyclooctatetraene (C8H8, COT) plus atomic hydrogen thus providing an unconventional, previously elusive route to COT via a resonantly stabilized, chemically activated and partially aromatic 1,3,5-cyclo­octatrien-7-yl radical intermediate in combustion systems. This reaction is also stimulating from the view­point of physical-organic chemistry community acting as a prototype in the elucidation of the chemical reactivity, isomerization pathways, bond rupture processes, and the preparation of resonantly stabilized free radical (RSFR) intermediates along with a highly unsaturated, cyclic molecule (COT), which cannot be explored by traditional synthetic routes.

[1] CH (13 amu) + C7H8 (92 amu) → C8H9• → C8H8 (104 amu) + H (1 amu)

**2. RESULTS**

**2.1 LABORATORY FRAME**

     In the methylidyne radical (CH, X2Π; 13 amu) - 1,3,5-cycloheptatriene (C7H8, X1A'; 92 amu) reaction, scattering signal could be detected at mass-to-charge (m/z) ratios of 104 (C8H8+/13CC7H7+) and 103 (C8H7+/13CC7H6+).

图表, 折线图

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**Figure 1**. Laboratory angular distribution (LAD) (a) and selected TOF spectra (b) recorded at m/z of 103 (C8H7+). The open and the solid circles define the experimental data, and the solid red lines indicate the best fits. Carbon and hydrogen atoms are color coded in gray and white, respectively.

After scaling, the time-of-flight (TOF) spectra at 104 and 103 were found to be superimposable suggesting that signal at m/z 103 originates from dissociative ionization of the parent at m/z = 104. Figure 1 displays representative TOF spectra collected at different angles at 103. The corresponding LAD is extracted by integrating the TOF spectra. This distribution reveals a maximum around 59.5 ± 0.3o (center-of-mass (CM) angle) and is spread over 25o within the scattering plane (Table S1), which indicate indirect scattering dynamics[24](#_ENREF_24) and the existence of chemically activated C8H9 complexes decomposing through atomic hydrogen loss to C8H8 isomer(s).[25](#_ENREF_25),[26](#_ENREF_26) Therefore, our raw data alone reveal the methylidyne versus hydrogen atom exchange pathway to C8H8 isomer(s) (reaction [1]). Recall that the QMS is operated in the TOF mode, recording the flight time from the interaction region to the detector of a selected, well-defined m/z (Figure 1); this instrument does not collect a traditional mass spectrum of an organic compound as available from, e.g. the NIST database.[27](#_ENREF_27)

     Since the atomic hydrogen can be eliminated from the methylidyne and/or the 1,3,5-cyclo­heptatriene reactant(s), we also conducted a crossed beam experiment of D1-methylidyne (CD, X2Π; 14 amu) with 1,3,5-cycloheptatriene and collected signal at 105 and 104; note that for this system, signal at 104 can also from the C8H7D parent via dissociative electron impact ionization. Our experiments revealed signal at 105 *and* 104 at a ratio of (0.46 ± 0.03) : 1 (Figure S1). However, since the branching ratio of the ion counts for ionization of the C8H8 product (m/z = 104) versus the ion counts from dissociative ionization (m/z = 103) was determined to be (0.44 ± 0.03) :1 for reaction [1], the contributions of dissociative electron impact ionization from C8H7D (reaction ([2b]) and reactive scattering signal forming C8H8 (reaction [2a]) can be untangled. Within the error limits, the bran­ching ratios for the CH/C7H8 and CD/C7H8 systems are identical revealing that the atomic hydrogen is ejected from the 1,3,5-cycloheptatriene reactant.

[2a] CD (14 amu) + C7H8 (92 amu) → C8H8 (104 amu) + D (2 amu)

[2b] CD (14 amu) + C7H8 (92 amu) → C8H7D (105 amu) + H (1 amu)

**2.2 CENTER-OF-MASS FRAME**

     With the identification of the C8H8 product prepared via the H loss pathway, we are moving on to the nature of the C8H8 isomer(s) and the underlying formation mechanisms.[28](#_ENREF_28) This is accomplished by converting the laboratory data (TOF, LAD) into the CM reference frame. This procedure effectively yields (*P(E*T*)*) and (*T(θ)*) distributions as shown in Figure 2.

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**Figure 2**. CM translational energy (a), angular flux distributions (b) and the flux contour map (c). The solid red lines and shaded areas define the best fit and the error limits, respectively.

Best fits could be accomplished by reproducing the laboratory data with a single reaction channel (product masses: 104 amu (C8H8) plus 1 amu (H)). The *P(E*T*)* prolongs to a maximum (Emax) release of 278 ± 19 kJmol-1, which can be utilized to compute the reaction energy of the reaction [1] and to identify the product(s) formed in the bimolecular reaction. Considering energy conservation and the lack of excitation in the reaction, Emax resembles the collision energy (20.8 kJmol-1) plus the reaction exoergicity. Consequently, this relationship leads to a reaction exoergicity of 257 ± 19 kJmol-1. In addition, a distribution maximum of close to 30 kJmol-1 of the *P(E*T*)* is depicted, suggesting a tight exit transition state associated with an extensive reorganization of the electron density upon unimolecular decomposition of the C8H9 complex(es) to the C8H8 (104 amu) plus H (1 amu) products. Furthermore, the forward-backward symmetric *T(θ)* indicates that the reaction proceed through indirect scattering dynamics via the involvement of C8H9 complex(es) with lifetime(s)longer than the rotational period.[24](#_ENREF_24) The distribution maximum at 90o strongly infers geometrical constraints upon decomposition of the C8H9 intermediate with an emission of the atomic hydrogen nearly perpendicularly to the plane spanned through the rotation of the molecule.[29](#_ENREF_29) This finding is also supported by the flux contour map, which shows an overall image of the reaction and the scattering process.

**3. DISCUSSION**

     The nature of the C8H8 isomer is now identified through a comparison of the experi-mentally derived exoergicity of 257 ± 19 kJmol-1 with those reaction energies extracted from calculations. The geometries of C8H8 isomers together with C8H9 intermediates were explored through electronic structure calculations at an accuracy of ±8 kJmol-1; statistical calculations exploiting RRKM theory were also conducted (Figure 3, Figure S3 and Table S2-3).[30](#_ENREF_30),[31](#_ENREF_31) This study revealed the existence of multiple exit channels forming ten distinct C8H8 isomers (**p1**-**p10**) with overall reaction exoergicities between 68 and 410 kJ mol-1. These ten isomers can be arranged in four groups with i) one eight membered ring (**p1, p6**), ii) a fused six and four membered ring (**p2, p5, p7, p8, p9**), iii) two fused five-membered rings (**p3, p4**), and iv) a six-membered ring connected to a vinyl group (**p10**). Recall that the results from the CD/C7H8 system revealed an exclusive hydrogen loss from the closed shell hydrocarbon reactant, but no atomic deuterium elimination from the D1-methylidyne radical. This finding can be applied to eliminate **p2**, **p5, p7** and **p10** as possible products. Here, the channels to these products would involve hydrogen *and* deuterium losses (Figure S4); since deuterium elimination has not been observed experimentally, these products can be discounted. With the elimination of **p2**, **p5, p7** and **p10**, we are comparing now the experimental reaction exoergicity of 257 ± 19 kJmol-1 with com­puted reaction ener­gies of the remaining product isomers (Figure 3). An analysis of the experimental reac­tion energy and the computed energetics suggest that 1,3,5,7-cyclooctatetraene (**p1**, C8H8, COT) matches the experimental (-257 ± 19 kJmol-1) with the computed (-260 ± 8 kJmol-1) well. A detail inspection of the PES reveals that unimolecular decomposition of chemically activated **i5** can lead to1,3,5,7-cyclooctatetraene (**p1**) through atomic hydrogen loss involving a tight exit transition state located 19 kJmol-1 above the

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**Figure 4.** Computed geometries of the exit transition states leading to **p1** and **p8**.

separate reactants. The geometries of the exit transition state forming **p1** reveal that the atomic hydrogen is emitted nearly perpendicular (61.7o; Figure 4) to the plane of the rotating complex, agreeing with the sideways scattering fitting of the *T(θ)* distributions. Overall, the bimolecular reaction is initiated through barrierless addition of methylidyne to one of the carbon-carbon double bonds forming bicyclic reaction intermediates **i1**, **i2**, and/or **i3,** which eventually isomerize to **i5** via opening of the annulated three-membered ring moiety to the eight-membered ring structure.

      The electronic structure and chemical bonding of **i5** are peculiar. The natural bond orbital population analysis (NBO) reveals that bond delocalization in **i5** is described through four resonance structures contributing about 30 % (**R1, R2**) and 20 % (**R3, R4**) (Scheme 1). This intermediate is non-planar but possesses Cs symmetry along with the X2A' ground electronic state. A C2v stationary point (**TS**), in which all eight carbon atoms are in one plane, is 36 kJmol-1 higher in energy than **i5** and represents an inversion transition state; no local minimum exists with seven CH moieties in the same plane and the remaining CH2 group out of plane. This inversion barrier is much lower than that in the cyclooctatrienyl cation (C8H9+), i.e. 93 kJ mol-1.[29](#_ENREF_29) The lower isomerization barrier would essentially result in a floppy intermediate **i5**, in which all carbon atoms are in one plane hence resulting in a hydrogen atom elimination nearly perpendicular to the rotating plane of the decomposing intermediate.

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**Figure 3.** Potential energy surface (PES) for the reaction of the methylidyne with 1,3,5-cycloheptatriene (3a) and reaction pathways start with **i10** leading to **p9** and **p10** (3b).



**Figure 5.** Molecular orbitals of1,3,5-cyclo­octatrien-7-yl radical (C8H9•) **i5.**

Note that an assignment of the C2v symmetric transition state as homoaromatic within a Hückel-like model is not feasible. Homoaromatic molecules are classified as organic compounds that show aromatic character even though the molecular conjugation is interrupted by a CH2 moiety. The C2v structure of the cyclooctatrienyl cation (C8H9+) was assigned as 8π antiaromatic considering that the CH2 bridge provides 2 pseudo π electrons into the π system, whereas the C2v structure of the cyclooctatrienyl anion (C8H9-) is 10π aromatic.[32](#_ENREF_32) However, in the C8H9 radical **i5**, we have 9 π electrons, which is an intermediate case (Figure 5). Likewise, the non-planar structure of the cyclooctatrienyl cation (C8H9+) can be assigned as 8π Möbius aromatic.[33](#_ENREF_33) However, this term is not appropriate for the C8H9 radical **i5**, since formally there are 9π electrons in the radical. Nevertheless, ring delocalization in **i5** is clearly present as it is evidenced by the NBO-computed bond orders (Wiberg bond indices), which show some π-character for all C-C bonds, even for the CH-CH2-CH moiety and non-zero values even across the ring (Scheme 1, Figure 3). Also, the molecular orbital picture (Figure 5) shows that the three highest doubly occupied molecular orbitals (HOMO, HOMO-1, and HOMO-2) exhibit a clear π-bonding character typical for an aromatic ring system and with participation of the CH2 group in HOMO and HOMO-2, whereas HOMO-3 represents an ensemble of σ bonds. Alternatively, the singly occupied and lowest unoccupied molecular orbitals (SOMO and LUMO) display a typical π\*-antibonding character.

     Aromaticity of a molecule is usually considered in terms of three criteria, structural, energetic, and magnetic.[34](#_ENREF_34) The non-planar Cs-symmetric structure of cyclooctatrienyl cation has been assigned as strongly aromatic[35](#_ENREF_35) and hence, here we assess the aromaticity of C8H9 **i5** by comparing the three criteria in the radical and the cation. Structurally, the C-C bond alteration (in Å, as optimized at the B3LYP/6-311G(d,p) level) in the radical, 1.507, 1.353, 1.433, 1.399, is similar but somewhat higher than that in the cation, 1.490, 1.377, 1.403, 1.399. The aromatic stabilization energy for **i5** computed using the isodesmic reaction [3] is 219 kJmol-1. This is close to the stabilization energy of the corresponding cyclooctatrienyl cation (C8H9+) of 230 kJmol-1 computed earlier via equation [4].[33](#_ENREF_33) Therefore, compared to the aromatic ring stabilization energy for benzene (equation [5]) of 274 kJmol-1, both the cation and **i5**have to be classified as less aromatic. Interestingly, the energetic stabilization of the cation and the C8H9 **i5** radical can be partially explained in terms of double hyperconjugation, as for antiaromatic singlet D2d-symmetric COT,[36](#_ENREF_36" \o "Wu, 2012 #1304) in addition to the π bond conjugation. Although the structures of both C8H9+ and **i5** are less puckered/twisted than that of COT, the CCCC dihedral angles for the seven C atoms in C8H9+ and **i5** taking part in C-C bonds with a delocalized π component are in the 11-32° range compared to 56° in COT. According to the NBO analysis by Schleyer and co-workers,[36](#_ENREF_36) both π bond conjugation and double hyperconjugation contribute to the enhancement of bonding at these angles. Finally, we explored magnetic properties of the radical using the nuclear independent chemical shift (NICS)[37](#_ENREF_37) scan method.[38](#_ENREF_38),[39](#_ENREF_39) It is known that the out-of-plane component of the magnetic shielding tensor, NICSZZ, displays a profound minimum at 0 Å in aromatic molecules, has a maximum in antiaromatic species, and a shallow minimum in non-aromatic compounds .[35](#_ENREF_35),[37](#_ENREF_37) As seen in Figure S7, NICSZZ of **i5** displays a deep minimum at 0 Å, with the lowest value of -16.5 ppm. The minimum is not as deep as that for the cation, -31.7 ppm, and considering all three criteria of aromaticity together, we conclude that C8H9 **i5** is aromatic, though less aromatic than the non-planar C8H9+ cyclooctatrienyl cation.

[3] C8H9 + 7CH4 + CH3 → 3C2H6 + 3C2H4 + 2C2H5

[4] C8H9+ + 7CH4 + CH3+ → 3C2H6 + 3C2H4 + 2C2H5+

[5] C6H6 + 6CH4 → 3C2H6 + 3C2H4

The identification of the 1,3,5-cyclo­octatrien-7-yl radical (C8H9•) **i5** as the decomposing intermediate along with the analysis of alternative deomposition pathways of **i5** suggest that the formation of 1,3,5,7-cyclooctatetraene (**p1**, C8H8) is preferred. Formation of the thermody-namically preferred products **p3** and **p4** require a hydrogen elimination from **i12**, which can be only accessed via isomerization through ring closure of **i5** involving a barrier of 270 kJmol-1. This pathway is clearly unfavorable compared to the **i5 → p1**+ H channel with a transition state 61 kJmol-1 below the transition state for **i5 → i12**. Analogous arguments such as the energy of the transition states compared to the **i5 → p1**+ H channel render the formation of **p2, p7**, and **p8** less likely leaving only the barrierless decomposition **i5 → p6** (triplet aromatic 1,3,5,7-cyclooc-tatetraene, a3A1g) + H slightly competitive. These conclusions are also corroborated by statistical RRKM calculations (Supporting Information; Table S2). Here, from **i5**, 1,3,5,7-cyclooctatetraene (**p1**) and triplet aromatic 1,3,5,7-cyclooctatetraene (**p6**) dominate the overall product yields with nearly 80 % with a branching ratio of **p1** to **p6** of about 4.

**4. CONCLUSIONS.**

     To sum up, our combined computational and experimental study of the bimolecular gas phase reaction of the simplest organic radical - methylidyne radical (CH) – with 1,3,5-cyclo-heptatriene (C7H8) revealed a facile and barrierless gas-phase preparation of 1,3,5,7-cycloocta-tetraene (C8H8) and triplet aromatic 1,3,5,7-cyclooctatetraene (C8H8) under single collision conditions. The formation route involves addition of the methylidyne radical to the olefinic π electron system of 1,3,5-cyclo-heptatriene (C7H8) followed by isomerization of the collision complexes and ring expansion to the aromatic 1,3,5-cyclo­octatrien-7-yl radical (C8H9•) **i5**. McIntosh et al.[40](#_ENREF_40) proposed the existence of matrix isolated 1,3,5-cyclo­octatrien-7-yl upon 60Co γ irradiated 1,3,5,7-cycloocta-tetraene (C8H8) based on Electron Spin Resonance (ESR) and Intermediate Neglect of Differential Overlap (INDO) calculations. This matrix isolation study was verified by Korth et al.[41](#_ENREF_41) through an radiation induced carbon-hydrogen bond rupture from the methylene (CH2) moiety within the seven-membered ring in bicyclo[5.1.0]octa-2,5-diene followed by ring opening of the doublet radical to the 1,3,5-cyclo­octatrien-7-yl radical via a barrier of about 100 kJmol-1. The barrierless gas-phase preparation of 1,3,5,7-cyclooctatetraene (C8H8) and triplet aromatic 1,3,5,7-cyclo-octatetraene (C8H8) accesses exotic and aromatic doublet radical intermediates such as the 1,3,5-cyclo­octatrien-7-yl radical on the doublet surface, which cannot be synthesized through classical synthetic chemistry protocols. Further, substituted 1,3,5,7-cyclooctatetraene molecules can be prepared in the gas phase with hydrogen atom(s) in the 1,3,5-cycloheptatriene (C7H8) reactant being replaced by organic side groups. Therefore, prospective crossed molecular beam and theoretical studies of exotic, substituted doublet radical intermediates and singlet/triplet 1,3,5,7-cyclooctatetraene are clearly endorsed to systematically unravel the unimolecular decomposition of aromatic doublet radical intermediates to afford a comprehensive knowledge of their unimolecular decomposition dynamics along with bonding chemistry, electronic structures, and stabilities.

**5. EXPERIMENTAL AND COMPUTATIONAL**

**5.1. EXPERIMENTAL:** The gas-phase reaction of methylidyne (CH, X2Π) with 1,3,5-cycloheptatriene (C7H8, X1A') was performed in a crossed molecular beam machine.[28](#_ENREF_28),[42](#_ENREF_42) The supersonic beam of methylidyne was generated through photodissociation (COMPex 110; 248 nm; 30 Hz) of bromoform (CHBr3; Aldrich; ≥ 99 %; 283 K; helium-seeded; 2.2 atm).[43](#_ENREF_43) After the skimmer and chopper wheel, the selected CH beam was defined with a *v*p (peak velocity) of 1857 ± 19 m s-1 and a S (speed ratio) of 13.2 ± 0.6 (Table S1). Using laser-induced fluorescence, the rotational temperature of 14 ± 1 K of CH radical beam was determined .[44](#_ENREF_44),[45](#_ENREF_45) The supersonic beam of 1,3,5-cycloheptatriene (TCI) seeded in krypton (Praxair, 99.999%) was released by a second piezoelectric pulse valve (550 Torr; *v*p:445 ± 7 m s-1; S:15.0 ± 0.2). Bromoform-d was also used as a precursor yielding a D1-methylidyne beam (*v*p:1845 ± 21 m s-1, S:13.5 ± 0.8). Both primary and secondary reactants were held in a stainless-steel bubbler. The primary beam crossed the C7H8 beam perpendicularly, leading to a collision energy of 20.8 ± 0.4 kJ mol-1 and a of 59.5 ± 0.3o (Table S1). The whole detector is rotatable to collect the TOF spectra at desired angles. After electron-impact ionization,[46](#_ENREF_46) the products were monitored using a QMS (Extrel, QC 150) and a Daly type ion counter,[47](#_ENREF_47) under ultrahigh-vacuum conditions (7×10-12 Torr). A forward convolution method was employed to fit the data and the *P(E*T*)*, the *T(θ)* flux distributions and the contour flux map, *I(u, θ) ≈ P(u) × T(θ)*, with the CM velocity *u* and angle *θ* are provided. The *T*(*θ*) and *P*(*ET*) flux distributions are varied iteratively until a best fit of the laboratory TOF spectra and angular distribution is obtained.[24](#_ENREF_24)

**5.2. COMPUTATIONAL:** Geometric structures of various species (CH and C7H8, different products, C8H9 intermediates and transition states) on the PES accessed by the reaction of methylidyne radical with 1,3,5-cycloheptatriene were optimized at the hybrid DFT B3LYP level with the 6-311G(d,p) basis set.[48](#_ENREF_48),[49](#_ENREF_49) Vibrational frequencies calculations were carried out using the same B3LYP/6-311 G(d,p) method. Single-point energies were further refined using the G3(MP2,CC)//B3LYP/6-311 G(d,p) variant of the G3 model chemistry scheme.[50-52](#_ENREF_50) The anticipated accuracy of the composite approach relative energies is typically within 5-10 kJ mol−1 or better. This estimate of accuracy is based upon average absolute deviations from experiment of calculated enthalpies of formation, ionization energies, electron and proton affinities of various molecules and radicals,[52](#_ENREF_52) as well as on the vast experience of this group in applications of the G3 model chemistry schemes to the studies of PESs and kinetics of chemical reactions involving hydrocarbons in singlet, doublet, and triplet electronic states in the last two decades. The GIAO method using B3LYP/6-311++G(d,p) for electronic structure calculations was employed to evaluate NICS values .[53](#_ENREF_53),[54](#_ENREF_54) The GAUSSIAN 09[55](#_ENREF_55) and MOLPRO 2010[56](#_ENREF_56) software packages were utilized for the ab initio calculations. For unimolecular reaction steps on the C8H9 PES, which follow initial association of CH with 1,3,5-cycloheptatriene, rate constants were assessed within the framework of Rice-Ramsperger-Kassel-Marcus (RRKM) theory.[57-59](#_ENREF_57) For the **i5** → **p6** + H decomposition channel occurring without an exit barrier, microcanonical variational RRKM theory was employed where the minimal energy path (MEP) and molecular properties of the structures along MEP were also computed at the G3(MP2,CC)//B3LYP/6-311 G(d,p) level. In the the RRKM calculations of energy-dependent rate constants, the internal energy of each species (intermediate or transition state) was assumed to be equal to a sum of the collision energy and the energy of chemical activation, which in turn equates to a negative of the relative energy of the species with regard to the CH + C7H8 reactants. The zero-pressure approach is validated by the fact that the reacting C8H9 intermediates in crossed molecular beams cannot undergo any collisional activation/deactivation. Next, first-order kinetic equations were solved in steady-state approximation[60](#_ENREF_60) using the computed RRKM rate constants and employing our won Unimol code, to obtain product branching ratios under single-collision conditions.[61](#_ENREF_61)

**SUPPORTING INFORMATION**

Experimental parameters (Table S1), statistical branching ratios at the collision energies of 0 and 20 kJ mol-1 (Table S2), optimized coordinates and calculated vibrational frequencies for stationary structures involved in the CH-C7H8 reaction (Table S3); CM TOF spectra of CH-C7H8 and CD-C7H8 reactions (Figure S1), moleculer structures of **p1** and **p6** (Figure S2), complete PES (Figure S3), the atomic hydrogen or deuterium loss channels in CD-C7H8 reaction (Figure S4), 2D and 3D structures of the products (Figure S5) and intermediates (Figure S6), and GIAO-B3LYP/6-311G++(d,p)-calculated NICS values at various positions along the z-axis (Figure S7).

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**Conflicts of Interest**

There are no conflicts to declare.

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