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Gas-Phase Formation of Fulvenallene (C_7H_6) via the Jahn–Teller Distorted Tropyl (C_7H_7) Radical Intermediate under Single-Collision Conditions

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remarkable (polycyclic) reaction intermediates, which cannot be studied via classical organic, synthetic methods, thus opening up a versatile path to access this previously largely obscure class of fulvenallenes.

1. INTRODUCTION

Since the pioneering discovery more than 80 years ago by Hermann Arthur Jahn and Edward Teller, the Jahn-Teller (JT) effect has been instrumental to the fundamental understanding of the electronic structure, chemical bonding, and spectroscopy of (in)organic molecules holding a degenerate electronic ground state.¹ Initially encountered in octahedral transition metal complexes such as of the d⁹ ion copper(II), the Jahn-Teller theorem states that any nonlinear molecule with a degenerate electronic ground state undergoes a geometrical distortion along nontotally symmetric vibrational modes from its highest symmetry that eliminates that degeneracy since this distortion lowers the overall energy of the molecule.²⁻⁴ The homologous series of the cyclic C_3H_3 (1), C_5H_5 (2), and C_7H_7 (3) radicals (Scheme 1) has attracted particular interest from the physical organic, theoretical chemistry, and material science communities in exploiting the Jahn-Teller theorem to unravel the exotic electronic structure and chemical bonding of prototypes of JT distorted Hückel-aromatic transient radicals⁵⁻⁷ along with implications to high-temperature superconductivity,⁸ magnetoresistance,⁹ and conical intersections.^{10,11} The D_{3h} symmetric cyclopropenyl radical C_3H_3 (1; X^2E'') distorts through vibronic coupling involving the e'' (1030 cm⁻¹), and a_2'' (778 cm⁻¹) normal modes resulting in two nearly isoenergetic species holding C_s point groups (4, 5).¹² The deformation of the

sheds light on the unusual reaction dynamics of Hückel aromatic systems and

cyclopentadienyl C_5H_5 (**2**; X^2E_1'') and cycloheptatrienyl C_7H_7 (**3**; X^2E_2'') radicals^{13–16} from their D_{5h} and D_{7h} symmetries result in C_{2v} distortions and 2B_1 diene/triene (**6**, **8**) and 2A_2 allyl-type (**7**, **9**) geometries;⁴ in both systems, the diene and allyl distortions are nearly isoenergetic and lower the energy of the degenerate system by 8 to 15 kJ mol^{-1,13–16}

Besides the viewpoint of molecular structure and chemical bonding, the cycloheptatrienyl system C_7H_7 (3, 8, 9)—also known as the tropyl radical—may undergo isomerization and unimolecular decomposition via atomic hydrogen elimination to fulvenallene (11)—a benchmark of a 6π nonbenzenoid aromatic hydrocarbon (Scheme 2);¹⁷ this is best understood in terms of its resonance structure carrying a delocalized negative charge at the five-membered ring and a localized positive charge at the central, allenic carbon atom (Scheme 3). The homologues series of nonbenzenoid aromatics comprises 3ethenylidenecyclopropene C_5H_4 (10), 5-ethenylidene-1,3cyclopentadiene/fulvenallene C_7H_6 (11), and 7-ethenylidene-

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Scheme 1. Molecular Structures, Electronic Wave Functions, and Point Groups of Cyclopropenyl (1), Cyclopentadienyl (2), and Cycloheptatrienyl (Tropyl, 3) Radicals along with Effects of Distinct Jahn-Teller Distortions (4-9)



Scheme 2. Molecular Structures, Electronic Wave Functions, and Point Groups of 3-Ethenylidenecyclopropene (10), 5-Ethenylidene-1,3cyclopentadiene (Fulvenallene, 11), and 7-Ethenylidene-1,3,5-cycloheptatriene (12)



1,3,5-cycloheptatriene C_9H_8 (12). These species are linked to (1), (2), and (3) by expanding the carbon backbone by an exocyclic vinylidene moiety (CCH₂) resulting in planar, C_{2v} symmetric closed shell aromatic systems (10, 11, 12) (Scheme 2).¹⁷ Although fulvenallenes carrying bulky substituents on the cyclopentadienyl ring such as bis(1,3-di-*tert*-butylcyclopentadienylidene)-methane $(C_{27}H_{40})^{18}$ are stable at room temperature and also in transition metal complexes like metallafulvenallenes, which are comprised of a metalla-cyclopentadiene species connected via an η^1 -vinylidene ligand,¹⁹ the parent compound fulvenallene (11)—first synthesized by

Hedaya et al. via flash vacuum pyrolysis of benzyl fluoride^{20,21}—readily polymerizes to form the 5,5'-(buta-1,3-diene-2,3-diyl)dicyclopenta-1,3-diene $(13)^{22}$ possibly due to the involvement of its dipolar resonance structure attributed to its dipole moment of 0.69 D (Scheme 3).²³ Therefore, despite compelling evidence of the formation of fulvenallene (11) as a short-lived reactive intermediate in combustion flames of, e.g., *n*-propylbenzene, ethylbenzene, styrene, toluene, cyclopentene and acetylene^{24–29} leading to the formation of polycyclic aromatic hydrocarbons (PAHs) and eventually to carbonaceous nanoparticles,^{30,31} the directed synthesis and isolation of fulvenallene (11) in the gas phase has eluded synthetic chemists over the past decades. This classifies free fulvenallenes as one of the least explored classes of organic molecules.

Herein, we provide a rare glimpse into the obscure chemistry of the cyclic fulvenallene (11) molecule by unraveling its gasphase synthesis under single-collision conditions through bimolecular reactions of the methylidyne radical (CH, $X^2\Pi$) with the aromatic benzene molecule (C_6H_6 , X^1A_{1g}) via Jahn– Teller distorted tropyl C_7H_7 (3) reactive intermediates utilizing the crossed molecular beams method. The examination of bimolecular reactions at the most fundamental, microscopic level delivers unique insights into the reaction mechanisms through which highly reactive intermediates and closed shell molecules such as fulvenallene (11) are formed without successive reactions in the gas-phase. This system is also attractive from the physical organic chemistry viewpoint, since fulvenallene (11) represents a benchmark of nonbenzenoid aromatic molecules thus elucidating the chemical

Scheme 3. Dipolar Resonance Structure of Fulvenallene (11) Leading to the Head-to-Tail Dimer 13



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Figure 1. (a) Laboratory angular distribution, (b) time-of-flight (TOF) spectra recorded at a mass-to-charge (m/z) of 90, (c) best-fit translational energy $(P(E_T))$, and (d) center-of-mass angular $(T(\theta))$ flux distributions for the reaction of the methylidyne radical (CH; C_{ov} ; X² Π) with benzene $(C_6H_6; D_{6h}; X^1A_{1g})$. The directions of the methylidyne radical and benzene beams are defined as 0° and 90°, respectively. The black circles represent the experimental data. The red lines delineate the best fits; shaded areas delimit the acceptable upper and lower error limits. E_{max} defines the maximum translational energy.

reactivity, bond-breaking processes, and the formation of exocyclic vinylidene-substituted aromatic molecules as an outcome of a single collision, which is not feasible by traditional synthetic chemistry routes. Therefore, our approach represents an original route to access a rather elusive class of aromatic hydrocarbon molecules: fulvenallene (11).

2. RESULTS

2.1. Laboratory Frame. Reactive scattering signal for the reaction of the methylidyne radical (CH, $X^2\Pi$) with benzene (C_6H_6, X^1A_{1g}) was detected at mass-to-charge ratios (m/z) of 91 $({}^{13}\text{CC}_6\text{H}_6^{+})$, 90 $(\text{C}_7\text{H}_6^{+})$, and 89 $(\text{C}_7\text{H}_5^{+})$ with signal at m/z = 89 and 91 collected at a level of $80 \pm 4\%$ and $8 \pm 2\%$ with respect to m/z = 90. These time-of-flight (TOF) spectra are superimposable after scaling suggesting a single reaction channel namely the reaction of the methylidyne radical (CH, 13 amu) with benzene (C_6H_{64} 78 amu) leading to C_7H_6 (90 amu) along with atomic hydrogen (H; 1 amu) with ion counts at m/z = 90 linked to singly ionized C₇H₆. Ions at m/z = 89can be associated with dissociative electron impact ionization of the neutral C_7H_6 product, whereas m/z = 91 represents the ¹³C-substituted product ¹³CC₆H₆⁺ based on the natural distribution of carbon atom isotopes. These findings reveal that the C_7H_6 isomer(s) are formed via the methylidyne versus atomic hydrogen replacement channel upon reaction with benzene (reaction 1). The time-of-flight (TOF) spectra and the full laboratory angular distributions were extracted at the

best signal-to-noise ratio of m/z = 90. The consequential laboratory angular distribution displays a maximum at the center-of-mass (CM) angle of $58.6^{\circ} \pm 0.3^{\circ}$ spanning at least 25° in the laboratory frame (Figure 1 and Table S1). The forward-backward symmetry with respect to the center-ofmass angle suggests that the reaction proceeds through indirect scattering dynamics involving at least one C_7H_7 reaction intermediate that ultimately undergoes unimolecular decomposition by emitting atomic hydrogen to the neutral C_7H_6 product.

Since atomic hydrogen can be emitted from the methylidyne and/or from the benzene reactant, the reaction of methylidyne (CH) with benzene- d_6 (C₆D₆) was carried out as well. For the CH/C_6D_6 system, the hydrogen- (C_7D_6) and deuterium-loss (C_7HD_5) products are expected to depict ion counts of the parent molecule at m/z = 96 and 95, respectively (reactions 2) and 3). It is critical to highlight that the product at m/z = 96cannot fragment to m/z = 95. Therefore, the identification of signal at m/z = 96 and/or 95 would represent explicit evidence on the existence of the hydrogen- (C_7D_6) and deuterium-loss (C7HD5) products, respectively. In our experiment, signal at m/z = 96 and 95 are both observed (Figure S1). Accounting for the ¹³C isotopic contributions totaling to 7.7% for seven carbon atoms and integrating the ion counts, the branching ratio of the hydrogen atom loss (reaction 2) versus deuterium loss (reaction 3) is determined to be 5.8 ± 0.8 :1. In brief, the isotope experiments reveal that for the methylidyne radical



Figure 2. Schematic representation of the potential energy surface of the reaction of the methylidyne radical with benzene. Energies calculated at the CCSD(T)-F12/cc-pVTZ-f12//B3LYP/6-311G(d,p) + ZPE(B3LYP/6-311G(d,p) level are shown in kJ mol⁻¹ and are relative to the energy of the separated reactants.

(2)

(CH) with benzene (C_6H_6) system, the hydrogen loss originates from both reactants favoring the emission from the benzene reactant. Accounting for the number of hydrogen atoms, statistically, a ratio of 6:1 for emission from benzene to methylidyne is expected (Figure S2).

 $CH (13 amu) + C_6 D_6 (84 amu)$

$$\rightarrow C_7 HD_5 (95 \text{ amu}) + D (2 \text{ amu})$$
(3)

2.2. Center-of-Mass Frame. The laboratory data deliver explicit evidence of hydrogen emission from the methylidyne *and* from the benzene reactants. Our central goal is to elucidate the nature of the C₇H₆ isomers formed and to unravel the underlying reaction mechanism(s) on the pertinent C₇H₇ potential energy surface (PES) accessed via the bimolecular reaction of the methylidyne radical (CH, X²Π) with benzene (C₆H₆, X¹A_{1g}). To accomplish these objectives, a forward-convolution fitting of the laboratory data results in a CM translational energy $P(E_T)$ and CM angular $T(\theta)$ flux distribution (Figure 1). Within our error limits, the best-fit CM functions were obtained using a single channel fit with the product mass combination of C₇H₆ (90 amu) plus H (1 amu). The maximum translational energy releases (E_{max}) was derived

from the $P(E_{\rm T})$ as 123 ± 19 kJ mol⁻¹. Considering energy conservation, the maximum translational energy (E_{max}) , collision energy $(E_{\rm C})$, and the reaction energy $(\Delta_{\rm r}G)$ for products without internal excitation are connected via $E_{\text{max}} =$ $E_{\rm C} - \Delta_{\rm r} G$; therefore, the reaction energy computes to be -104 \pm 19 kJ mol⁻¹. Further, the $P(E_{\rm T})$ distributions reveals a maximum slightly away from zero translational energy located at only 10 ± 2 kJ mol⁻¹. The average translational energy of the products was derived to be 35 ± 6 kJ mol⁻¹ suggesting that only $28 \pm 4\%$ of the maximum energy is released into the translational degrees of freedom of the products. These findings propose indirect scattering dynamics involving C₇H₇ intermediate(s) undergoing unimolecular decomposition through loose exit transition state(s) via a simple bond rupture process.³² Finally, the $T(\theta)$ distributions show a pronounced forward-backward symmetry with a maximum at 90° (sideways scattering) and provide additional information on the scattering dynamics. The symmetry of the $T(\theta)$ distributions suggests a decomposing C7H7 intermediate holding a lifetime longer than its rotational period(s). The sideways scattering highlights strong geometrical constraints on the decomposing intermediate revealing that the hydrogen atom is eliminated perpendicular to the rotational plane of the decomposing complex and hence almost parallel to the total angular momentum vector.^{33,34}

3. DISCUSSION

In case of polyatomic systems, it is always beneficial to combine the experimental data with electronic structure calculations to untangle the underlying reaction mechanism(s)

Figure 3. Computed geometries of the exit transition states leading to fulvenallene (p1) and 1-ethynylcyclopenta-1,3-diene (p2). Angles of the departing hydrogen atoms are given in degrees with respect to the rotation plane of the decomposing complex.

(Figure 2; Table S4). Our electronic structure calculations identified the existence of seven atomic hydrogen loss products (p1-p5, p7, p8) along with one acetylene loss channel (p6). These are fulvenallene (p1; $\Delta_r G = -104 \pm 4 \text{ kJ mol}^{-1}$), 1ethynylcyclopenta-1,3-diene (**p2**; $\Delta_r G = -95 \pm 4 \text{ kJ mol}^{-1}$), cyclohepta-1,2,4,6-tetraene (p3; $\Delta_r G = -55 \pm 4 \text{ kJ mol}^{-1}$), phenylcarbene (**p4**; $\Delta_r G = 14 \pm 4 \text{ kJ mol}^{-1}$), norcaradienyllidene (**p5**; $\Delta_r G = 276 \pm 4 \text{ kJ mol}^{-1}$), cyclopentadienyl (C₅H₅) plus acetylene (C₂H₂) (**p6**; $\Delta_r G = -182 \pm 4 \text{ kJ mol}^{-1}$), benzocyclopropene (p7; $\Delta_r G = -76 \pm 4 \text{ kJ mol}^{-1}$), and bicyclo[3.2.0]hepta-1,3,6-triene (p8; $\Delta_r G = -20 \pm 4 \text{ kJ}$ mol^{-1}), with the overall reaction energies provided in parentheses. It should be noted that p6 cannot be observed in the present experiment because of the unconquerable background counts of C₅H₅⁺ and C₂H₂⁺ fragments originating from dissociative electron impact ionization of the benzene reactant. A comparison of the experimentally derived reaction energy of -104 ± 19 kJ mol⁻¹ with the aforementioned energetics suggests that fulvenallene (p1) and/or 1-ethynylcyclopenta-1,3-diene (p2) are likely reaction products. The higher energy isomers p3, p4, p7, and p8 might be masked in the low energy section of the CM translational energy distribution $P(E_{\rm T})$. For example, if **p3** or **p4** is solely formed, the resulting translational energy distributions would terminate close to 74 kJ mol⁻¹ or 5 kJ mol⁻¹. This is clearly not observed experimentally. Finally, the synthesis of p5 with a computed reaction energy of 276 \pm 4 kJ mol⁻¹ is highly endoergic and hence not feasible under our experimental conditions considering a collision energy of only 18.7 ± 0.4 kJ mol⁻¹. Therefore, we can conclude that our experiments lead to the formation of at least fulvenallene (p1) and/or 1-ethynylcyclopenta-1,3-diene (p2) under single collision conditions in the gas phase.

With the identification of fulvenallene (p1) and/or 1ethynylcyclopenta-1,3-diene (p2), we would like to reveal the underlying reaction mechanism(s) to their formation and to quantify their contributions to the reactive scattering signal. The methylidyne radical (CH) was found to add to the delocalized π -electron system of the benzene molecule without entrance barrier (Figure 2). Formally, addition to a carboncarbon double bond leads to a bicyclic C7H7 intermediate il that is bound by 216 kJ mol⁻¹ with respect to the separated reactants. This intermediate undergoes facile ring opening via a barrier of only 2 kJ mol⁻¹ to the Jahn-Teller distorted, tropyl radical (i2). Competing pathways of i1 leading to p5 plus atomic hydrogen and isomerization to i6 are energetically unfavorable. The cyclic tropyl radical (i2) represents the central transient species connecting eventually to p1 and p2. According to our calculations, i2 is C_{2v} cycloheptatrienyl structure with the ²B₁ electronic term, which corresponds to structure 8. The allylic structure 9 $({}^{2}A_{2})$ and D_{7h} -symmetric 3 $({}^{2}E_{2}")$ reside 1 and 19 kJ mol⁻¹ above 8, respectively.

Considering the barriers of isomerization, the tropyl radical (i2) either undergoes an out-of-plane [1,4] hydrogen migration or cyclization forming intermediates i3 and i4, respectively. Here, the $i2 \rightarrow i4$ isomerization can be rationalized as pseudorotation i2 $(8) \rightarrow 9$ via 3 followed by an electrocyclic ring closure. Six consecutive isomerization steps from i3 involving [4,2] hydrogen shift (i5), cyclization (i6), ring opening forming an exocyclic CH₂ moiety (i8), cyclization (i11), ring opening leading to a five-membered ring intermediate (i12), hydrogen shift (i13), and atomic hydrogen elimination accompanied by aromatization lead to p1. Considering intermediate i4, the latter may ring open (i7), undergo two consecutive hydrogen migrations (i9, i10), and then emit atomic hydrogen forming **p1**. Note that **p1** may also be formed via fragmentation of i12 without passing through intermediate i13. Alternatively, i9 undergoes unimolecular decomposition to p2 plus atomic hydrogen. Therefore, we identified three possible pathways to **p1** and one reaction route to p2 with all reaction sequences commencing with the tropyl radical (i2).

How can we narrow down the aforementioned pathways to p1 and/or p2 even further? First, a close inspection of the center-of-mass angular distribution revealed a maximum at 90° (sideways scattering) suggesting that the dominating decomposition pathway of the C₇H₇ intermediate involves a hydrogen atom which is ejected perpendicularly to the rotational plane of the decomposing complex. The computed geometries of the exit transition states leading to p1 and p2 reveal that all transition stated connecting the intermediates to p1 can account for the sideways scattering with hydrogen emitted at angles of 88.04° , 87.33° , and 76.91° with respect to the rotating plane of the decomposing complex (Figure 3). However, i9—the only intermediate connecting to p2—loses a hydrogen atom within the plane of the decomposing complex. Therefore, i9 can be excluded as a decomposing complex, since the sideways geometry cannot be replicated, and p2 can be eliminated as a predominant product. Second, the distribution maximum of the center-of-mass translational energy distribution of 10 ± 2 kJ mol⁻¹ predicts a loose exit transition state. The aforementioned exclusion of p2 suggests that this exit transition state must connect C_7H_7 intermediate(s) to p1. Fulvenallene (p1) can be formed via unimolecular decomposition of intermediates i10, i12, and i13 via an exit transition state located 11, 24, and 6 kJ mol⁻¹ above the energy of the separated products. Therefore, intermediates i10 and/or i13 represent the most likely decomposing complexes. Finally, we exploited Rice-Ramsperger-Kassel-Marcus (RRKM) theory to calculate the branching ratios of the observable C₇H₆ isomers and predicted within a limit of complete energy randomization the dominant hydrogen atom loss pathway(s) from the C_7H_7 intermediate(s) (Table S2). These studies reveal that fulvenallene (p1), 1-ethynylcyclopenta-1,3-diene

(**p2**), and cyclohepta-1,2,4,6-tetraene (**p3**) contribute 92.56%, 7.37% and 0.07% of the total yield of all isomers at a collision energy of 18.6 kJ mol⁻¹, respectively. Further, for the dominating product fulvenallene (**p1**), dissociation from intermediate **i10**, **i12**, and **i13** supplies 55.26%, 0.92%, and 43.82% of all molecules, respectively. Therefore, RRKM calculations and experiments correlate nicely revealing a dominant formation of fulvenallene (**p1**) via loose exit transition states involving intermediates **i10** and **i13** through indirect scattering dynamics.

4. CONCLUSIONS

In conclusion, our study revealed the first directed gas phase synthesis of the aromatic fulvenallene (p1) molecule formed via the bimolecular reaction of the methylidyne radial (CH) with benzene (C_6H_6) under single-collision conditions. Fulvenallene was generated through a barrier-less cycloaddition of the methylidyne radical to the π -electron density of benzene resulting in a rovibrationally excited, Jahn-Teller distorted tropyl radical intermediate (C_7H_7) followed by isomerization of the initial collision complex via hydrogen shifts along with ring opening and ring closure processes with two decomposing intermediates-vinylcyclopentadienyl and α -(cyclopenta-1,3-dien-1-yl)vinyl—emitting atomic hydrogen though loose exit transition states. This reaction accesses the hitherto poorly studied potential energy surface (PES; C₇H₇) together with exotic (bicyclic) reaction intermediates such as resonantly stabilized free radicals (RSFRs) vinylcyclopentadienyl and α -(cyclopenta-1,3-dien-1-yl)vinyl, which are difficult to "make" via traditional organic synthetic approaches. Scrambling of the hydrogen and deuterium atoms in the fragmenting complex of the benzene- d_6 and methylene system is complete ultimately yielding a branching ratio of the deuterium versus hydrogen loss of 5.8 \pm 0.8:1, which agrees within the error limits with the deuterium to hydrogen ratio in the decomposing C₇D₆H complexes of 6:1. This scrambling occurs in the tropyl radical intermediate i2-a pivotal structure for all decomposition pathways. i2 undergoes pseudorotation via the D_{7h} -symmetric structure residing only 12–19 kJ mol⁻¹ above the C_{2v} local minimum^{15,16} making all H (D) atoms equivalent and thus erasing the "memory" of their origin either from the methylidyne (CH) or benzene- d_6 (C₆D₆) reactants.

Beyond the fundamental chemical dynamics considerations, the reaction mechanisms uncovered in this study are exceptionally relevant to the combustion and astrochemical regimes.^{35–42} In combustion systems, the C_7H_7 surface is of critical relevance for multiple important reactions besides the CH-C₆H₆ system such as cyclopentadienyl-acetylene, fulvenallene-atomic hydrogen, and unimolecular decomposition of benzyl, tropyl, and vinylcyclopentadienyl radicals⁵³ with high level temperature- and pressure-dependent rate constants and product branching ratios provided in the Supporting Information (Figure S3-S12 and Table S3). In deep space, both the methylidyne radical and benzene have been detected. Methylidyne is ubiquitous in cold molecular clouds such as the Taurus Molecular Cloud (TMC-1) and Orion Molecular Cloud (OMC-1) holding temperatures as low as 10 K;^{43,44} benzene has been detected toward the proto-planetary nebula CRL 618.⁴⁰ Benzene—the simplest neutral 6π -Hückel aromatic system-represents the key molecular building block of polycyclic aromatic hydrocarbons (PAHs)^{45,46} with spectroscopic signature inferred in the ultraviolet (200-400 nm) and the infrared $(3-20 \ \mu m)$ regions via the

predominantly enigmatic diffuse interstellar bands (DIBs) and unidentified infrared (UIRs) bands.⁴⁵ Since methylidyne radicals react without barrier with benzene leading essentially to *ring contraction* and the formation of an exocyclic allenic moiety (=CCCH₂), even in molecular clouds, PAHs and their derivatives are expected to react with methylidyne radicals leading to the effective formation of fulvenallene-substituted PAHs (Scheme 4). In combustion systems, fulvenallene^{24–29}





and its key decomposition product—the resonance-stabilized fulvenallenyl^{47–49} radical—are contemplated as long-lived reaction intermediates playing a fundamental role in molecular mass growth processes leading eventually to soot particles.^{47,50–52} Here, the reactions of fulvenallene and acetylene might produce indene;⁵³ the self-recombination of two fulvenallenyl radicals might lead even to phenanthrenes,⁵⁰ thus highlighting the critical need of fundamental reaction dynamics studies relevant to the formation of aromatic systems and their exotic precursors such as fulvenallene (**p1**) in combustion systems and in the interstellar medium.

5. EXPERIMENTAL AND COMPUTATIONAL

5.1. Experimental Section. The gas phase reactions of the methylidyne (CH; $X^2\Pi$) radical with benzene (C₆H₆; X^1A_{1g}) and benzene- d_6 (C₆D₆; X¹A₁₀) were performed under single-collision conditions using a universal crossed molecular beams machine at the University of Hawaii.⁵⁴ In the primary chamber, a pulsed supersonic beam of methylidyne radicals was produced by photodissociation (COMPex 110, Coherent, Inc.; 248 nm; 30 Hz) of a gas mixture of bromoform (CHBr₃, Aldrich Chemistry, ≥99%) seeded in helium (99.9999%; AirGas) held in a stainless steel bubbler at 283 K with a stagnation pressure of 2.2 atm.⁵⁵ After flying through the skimmer, the methylidyne radicals were velocity-selected by a four-slot chopper wheel with a peak velocity v_p of 1772 ± 10 m s⁻¹ and speed ratio S of 13.0 ± 0.4 (Table S1). Rotational temperatures of the methylidyne radical beam was determined to be 14 ± 1 K exploiting laser-induced fluorescence technique.⁵⁶ In the secondary chamber, the supersonic beam of pure benzene (≥99.9%; Aldrich Chemistry), which was regulated at 550 Torr with $v_p = 471 \pm 10$ m s⁻¹ and $S = 14.0 \pm 0.3$ (Table S1), crossed perpendicularly with the methylidyne radicals in the main chamber leading to a collision energy (E_c) of 18.7 \pm 0.4 kJ mol^{-1} and a center of mass angle (Θ_{CM}) of 58.6 \pm 0.3. For the corresponding fully deuterated reactant experiment, the benzene- d_6 (>99.9%; Aldrich Chemistry) beam was characterized by $v_{\rm p} = 461 \pm$ 10 m s⁻¹ and S = 14.0 \pm 0.3 resulting in $E_{\rm C}$ = 18.9 \pm 0.4 and $\Theta_{\rm CM}$ = 60.0 ± 0.3 (Table S1).

The neutral reaction products entering the detector were ionized by electron impact (80 eV),⁵⁷ then filtered according to mass-tocharge ratio (m/z) utilizing a quadrupole mass spectrometer (QMS,

Extrel, QC 150), and eventually recorded by a Daly type ion counter.⁵⁸ The detector is housed within a differentially pumped and rotatable chamber that allows the collection of angularly resolved time-of-flight (TOF) spectra in the plane of the both reactant beams. To obtain the information on the reaction dynamics, a forwardconvolution method is used to transform the LAB data into the center of mass frame (CM),^{59,60} which represents an iterative method whereby user defined CM translational energy $P(E_{T})$ and angular $T(\theta)$ flux distributions are varied until a best fit of the laboratoryframe TOF spectra and angular distributions are achieved. These functions comprise the reactive differential cross section $I(\theta, u)$, which is taken to be separable into its CM scattering angle θ and CM velocity u components, $I(u, \theta) \sim P(u) \times T(\theta)$. The error ranges of the $P(E_{\rm T})$ and $T(\theta)$ 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.

5.2. Computational Section. Geometries of all species involved in various chemical reactions accessing the C7H7 PES including reactants, intermediates, transition states, and products were optimized at the B3LYP/6-311G(d,p) level of theory 61,62 and vibrational frequencies were computed using the same method. Single-point energies were further refined using the explicitly correlated coupled clusters CCSD(T)-F12 method^{63,64} with Dunning's correlation-consistent cc-pVTZ-f12 basis set.^{65,66} The GAUS-SIAN 0967 and MOLPRO 201066 program packages were utilized for the ab initio calculations. Rice-Ramsperger-Kassel-Marcus (RRKM) theory,⁶⁸⁻⁷⁰ was used to compute energy-dependent rate constants of all unimolecular reaction steps on the C7H7 PES following the initial association of the CH radical with benzene and to evaluate product branching ratios under single-collision conditions. Additionally, RRKM-Master Equation (ME) calculations⁷¹ were carried out to evaluate temperature- and pressure-dependent rate constants for various reactions on the C7H7 PES relevant to combustion and/or chemistry of planetary atmospheres in the temperature range from 500 to 2500 K and pressures of 30 Torr and 1, 10, and 100 atm. The MESS program package^{72,73} was used for the calculations where the rigid rotor-harmonic oscillator approximation (RRHO) was employed in the evaluation of partition function. The rate constant for the barrier-less CH + benzene addition entrance channel at the high pressure limit was computed using variable reaction coordinate-transition state theory (VRC-TST).74-Further details of the computational methods are given in Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b13269.

Computational details, optimized Cartesian coordinates and vibrational frequencies for all intermediates, transition states, reactants and products involved in the reactions of the methylidyne radical with benzene, and additional figures and tables (PDF)

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Notes

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