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Formation of 1*H*-Phenalene ($C_{13}H_{10}$) in the Taurus Molecular Cloud via Methylidyne Addition-Cyclization-Aromatization (MACA)

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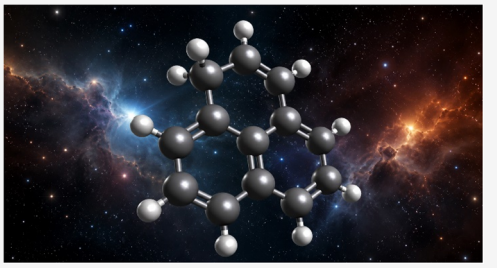
ABSTRACT: The formation of 1*H*-phenalene ($C_{13}H_{10}$) in cold molecular clouds, such as the Taurus Molecular Cloud-1 (TMC-1), presents a significant challenge to traditional astrochemical models, which predominantly suggest high-temperature pathways for polycyclic aromatic hydrocarbon (PAH) formation. In this study, we explore computationally the Methylidyne Addition-Cyclization-Aromatization (MACA) mechanism as a viable, barrierless pathway for phenalene synthesis under low-temperature conditions. Through electronic structure calculations and Rice−Ramsperger−Kassel−Marcus (RRKM) statistical methods, we demonstrate that the reaction of 1-vinylnaphthalene ($C_{10}H_7C_2H_3$) with the methylidyne radical (CH) leads to the formation of 1H-phenalene via a bimolecular reaction, a process that is exoergic and without entrance barrier. The MACA mechanism facilitates the growth of the aromatic carbon backbone via a [5 + 1] ring annulation, providing a new insight into PAH formation in cold molecular clouds. Notably, the MACA mechanism has previously been shown to form indene (C_9H_8), which was detected in TMC-1 as well, via a [4 + 1] annulation, demonstrating its potential to produce a variety of complex PAHs by addition of a five- and six-membered ring to a benzene moiety via [4 + 1] and [5 + 1] annulation, respectively. This work highlights the importance of barrierless, exoergic reactions involving MACA in the synthesis of complex aromatic molecules in space, expanding our physicochemical understanding of carbon-rich chemistry in cold molecular clouds.



1. INTRODUCTION

In recent years, radio astronomical surveys of cold molecular clouds such as of the Taurus Molecular Cloud-1 have revealed an unexpectedly rich inventory of polycyclic aromatic hydrocarbons (PAHs)[1−5]—molecules composed of two or more fused benzene rings—along with their cyano-substituted counterparts (Figure 1).[6−12] Guided by molecular beam experiments[13−27] and chemically accurate astrochemical modeling,[23,28−30] these astronomical observations advanced our fundamental understanding of how carbon-rich chemistry unfolds in deep space. The Hydrogen Abstraction−Vinylacetylene Addition (HAVA)[15] and Methylidyne Addition-Cyclization-Aromatization (MACA)[26] mechanisms have revealed that aromatic molecules, traditionally thought to be formed solely in high temperature circumstellar environments such as of dying Asymptotic Giant Branch (AGB) carbon stars and planetary nebulae as their descendants,[31−33] can also be synthesized in low temperature (∼10 K), low density (∼10^4 cm^{-3}) molecular clouds via barrierless and exoergic bimolecular reactions.[34−36] These barrierless pathways effectively expand the aromatic carbon backbone of an aryl radical through reaction with vinylacetylene (C_4H_4) by one benzene ring at a time (HAVA) or convert a vinyl functional group connected to a six-membered benzene ring via reaction with a methylidyne radical (CH) to an indenyl moiety (MACA) (Figure 2).

The recent identification of the polycyclic aromatic hydrocarbon 1*H*-phenalene ($C_{13}H_{10}$)−hereafter phenalene—in TMC-1 within the QUIJOTE project[2] with column densities of $(2.8 \pm 1.6) \times 10^{13}$ cm^{-2}, comparable to indene (C_9H_8; 1.6×10^{13} cm^{-2}), challenges conventional astrochemical models since the canonical high-temperature formation pathways to phenalene via, e.g., the bimolecular gas-phase reactions of the 1-naphthyl radical ($C_{10}H_7$)[30] with methylacetylene (CH_3CCH) and allene (H_2CCCH_2)[37] probed in a chemical microreactor have entrance barriers of 7−14 kJmol^{-1} and, hence, are inefficient at the cold temperatures characterizing dark clouds. Recall that in cold molecular clouds, only exoergic and barrierless reactions operate.[34] Likewise, computational investigations of the naphthalene ($C_{10}H_8$)−propargyl (C_3H_3), indene (C_9H_8)−1-buten-3-ynyl (n-C_4H_3), and acenaphthylene ($C_{12}H_8$)−methyl (CH_3) systems revealed prohibitive entrance barriers,[2,38,39] overall suggesting that barrierless and exoergic, bimolecular reaction pathway(s) to phenalene are still unexplored. Thus, the discovery of phenalene in TMC-1 not only adds a new PAH to the growing census of cold-cloud chemistry, but also highlights a fundamental gap in our understanding of

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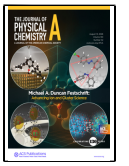

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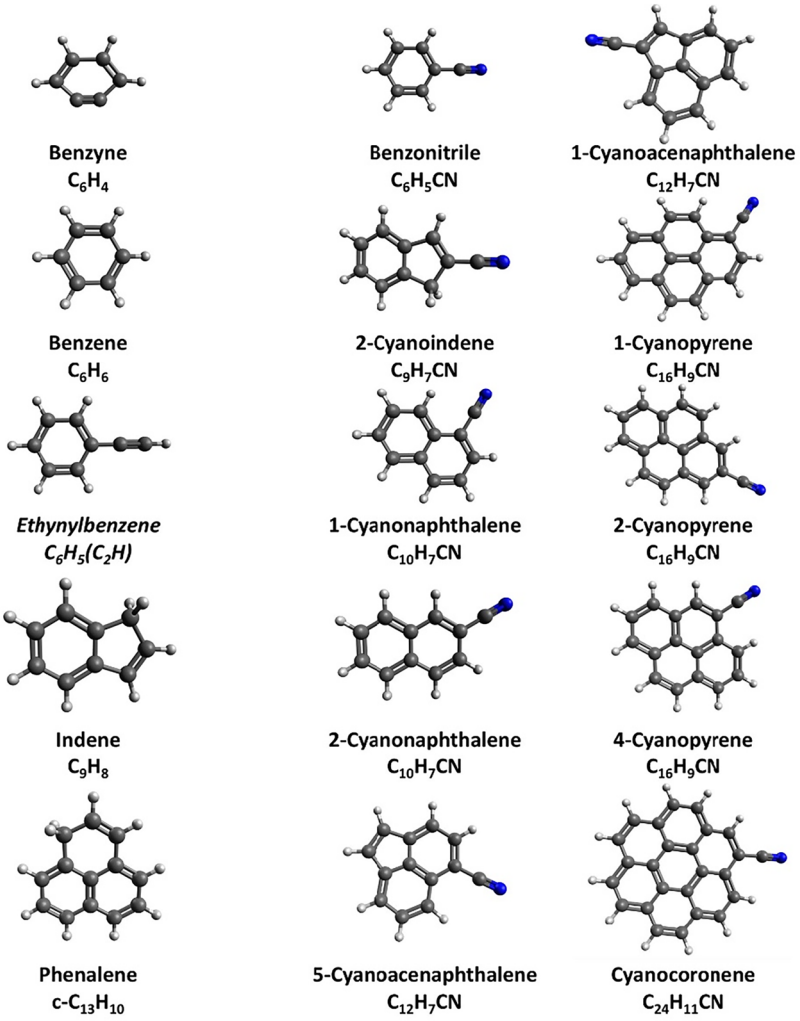

Figure 1. Aromatic molecules detected in the interstellar medium. Note that benzene was identified infrared spectroscopically.

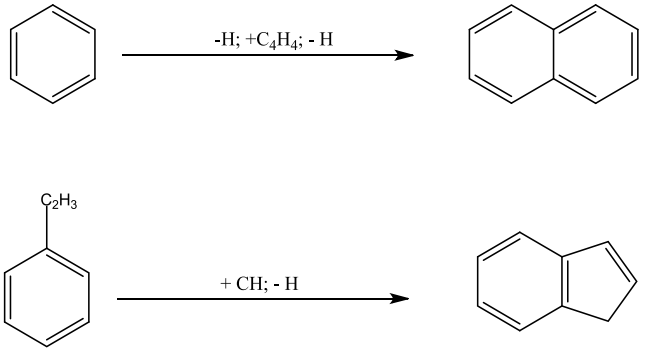

Figure 2. Barrierless Hydrogen Abstraction−Vinylacetylene Addition (HAVA) (top) and Methylidyne Addition-Cyclization-Aromatization (MACA) mechanism (bottom) via ring annulation leading to benzene and cyclopentadiene moieties, respectively.

PAH formation and evolution under cold molecular cloud conditions.

Understanding the formation of phenalene ($C_{13}H_{10}$) therefore demands an investigation into low temperature reaction mechanisms involving entrance-barrierless and exoergic bimolecular reactions. A retrosynthetic strategy commencing with naphthalene moieties provides various options involving C10−C3, C11−C2, and C12−C1 routes with C11 and C12 molecular building blocks carrying the naphthalene backbone. The aforementioned discussion already excluded C10−C3 systems naphthalene ($C_{10}H_8$)−propargyl (C_3H_3) and 1-naphthyl radical ($C_{10}H_7$)[30] - methylacetylene (CH_3CCH)/allene (H_2CCCH_2), as contributors to phenalene formation. However, recent crossed molecular beam experiments of the 1-propynyl radical ($CCCH_3$)−an isomer of propargyl (C_3H_3)−with unsaturated[40−46] and aromatic[47] hydrocarbons revealed barrierless and exoergic molecular mass growth processes. Hence, the naphthalene ($C_{10}H_8$)−1-propynyl ($CCCH_3$) system represents a plausible candidate to phenalene formation to be explored. The C11−C2 route covers the reactions of 1-methylnaphthalene ($C_{10}H_7CH_3$) plus ethynyl (C_2H) and 1-naphthylmethyl ($C_{10}H_7CH_2$) plus acetylene (C_2H_2). Similar to the resonantly stabilized benzyl radical ($C_6H_5CH_2$), the 1-naphthylmethyl ($C_{10}H_7CH_2$) radical has an entrance barrier of at least 50 kJmol^{-1} upon reaction with acetylene.[48] Further, ethynyl adds to the naphthalene moiety, but no ring closure with the sp^3 hybridized carbon atom of the methyl group can succeed. Hence, phenalene is inaccessible via the C11−C2 route. However, the C12−C1 route carries a fascinating possibility and could involve the formation of phenalene ($C_{13}H_{10}$) via the bimolecular reaction of 1-vinylnaphthalene ($C_{10}H_7C_2H_3$) with methylidyne (CH) via the Methylidyne Addition-Cyclization-Aromatization (MACA) pathway. Nevertheless, as the naph-

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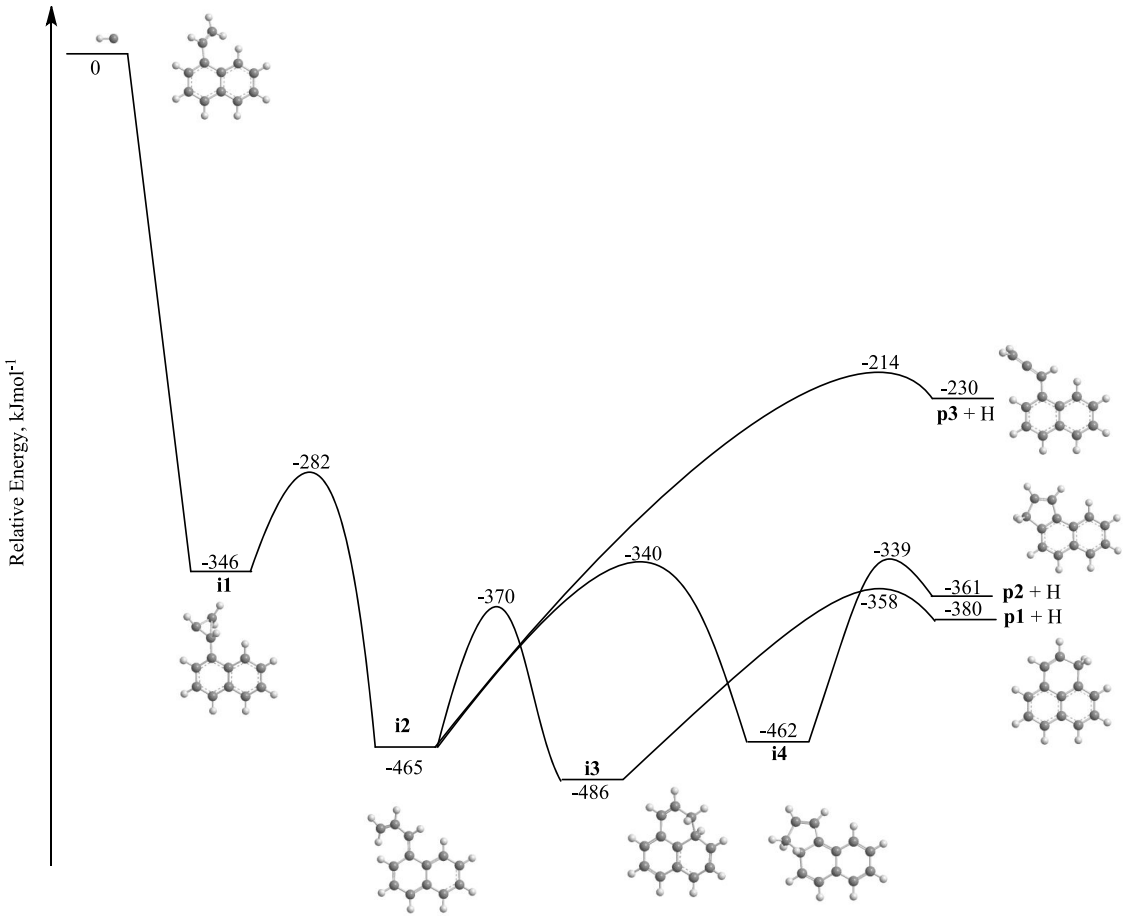

Figure 3. Potential energy surface of the reaction of 1-vinylnaphthalene with the methylidyne radical calculated at the G3(MP2,CC)//B3LYP/6−311G(d,p) level of theory.

thalene ($C_{10}H_8$)−1-propynyl ($CCCH_3$) system, this reaction has neither been explored experimentally in molecular beams nor computationally. Here we reveal via modern electronic structure and statistical Rice−Ramsperger−Kassel−Marcus (RRKM) calculations that the bimolecular reaction of 1-vinylnaphthalene ($C_{10}H_7C_2H_3$) with methylidyne (CH) is barrierless, exoergic, and may efficiently synthesize phenalene ($C_{13}H_{10}$) in the gas phase. The elementary reaction of naphthalene ($C_{10}H_8$) with the 1-propynyl radical ($CCCH_3$), however, only yields 1—propynyl-1-naphthalene ($C_{10}H_9CCCH_3$), but no phenalene. These considerations highlight the versatility of elementary reactions to PAH formation[13,14] allowing us to predict and verify pathways to aromatic molecules (to be) newly observed in deep space.

2. COMPUTATIONAL METHODS

Since multiple reactions on the $C_{13}H_{11}$ potential energy surfaces, including 1-/2-naphthyl plus methylacetylene/allene (C_3H_4),[37,49] 1-/2-methylnaphthyl plus acetylene (C_2H_2), and unimolecular isomerization and decomposition of the *ortho*-methylbiphenylyl radical,[50] have been previously studied by our group, here we employ the same theoretical approach to incorporate new reaction channels into the earlier explored PES and kinetic scheme. In particular, geometries of the reactants, products, intermediates, and transition states participating in the methylidyne plus 1-vinylnaphthalene and 1-propynyl (H_3CCC) plus naphthalene reactions were optimized at the hybrid density functional B3LYP/6−311G(d,p) level of theory[51,52] with vibrational frequencies computed using the same method. Then, energies of all optimized structures were rectified by single-point calculations using the composite G3(MP2,CC) model chemistry scheme,[53−55] which normally provides accuracy of 5−10 kJ mol^{-1} or better for relative energies. The T1 diagnostics were checked in CCSD(T) calculations to confirm that the wave functions do not exhibit a significant multireference character. The Gaussian 16[56] and MOLPRO 2021[57] program packages were used for the electronic structure calculations. The Rice-Ramsperger-Kassel-Marcus (RRKM) theoretical approach was employed to compute temperature-dependent rate constants and product branching ratios at the limit of zero pressure by solving the one-dimensional master equation using the MESS program package.[58,59] Densities of states for local minima and numbers of states for transition states and partition functions were assessed within the Rigid-Rotor, Harmonic-Oscillator (RRHO) approximation. Asymmetric Eckart potentials were used to compute tunneling corrections for the rate constants. For the barrierless entrance channels, such as those for the methylidyne plus 1-vinylnaphthalene and 1-propynyl (H_3CCC) plus naphthalene reactions, the phase space theory was employed.[60] It should be noted that product branching ratios at the zero-pressure limit are independent of these entrance-channel rate constants. The MESS input files are based on those published in our previous works on the 1- and 2-naphthyl methylacetylene/allene (C_3H_4) and 1-/2-methylnaphthyl acetylene (C_2H_2) reactions with inclusion of additional structures accessed via CH addition to the double bond in the

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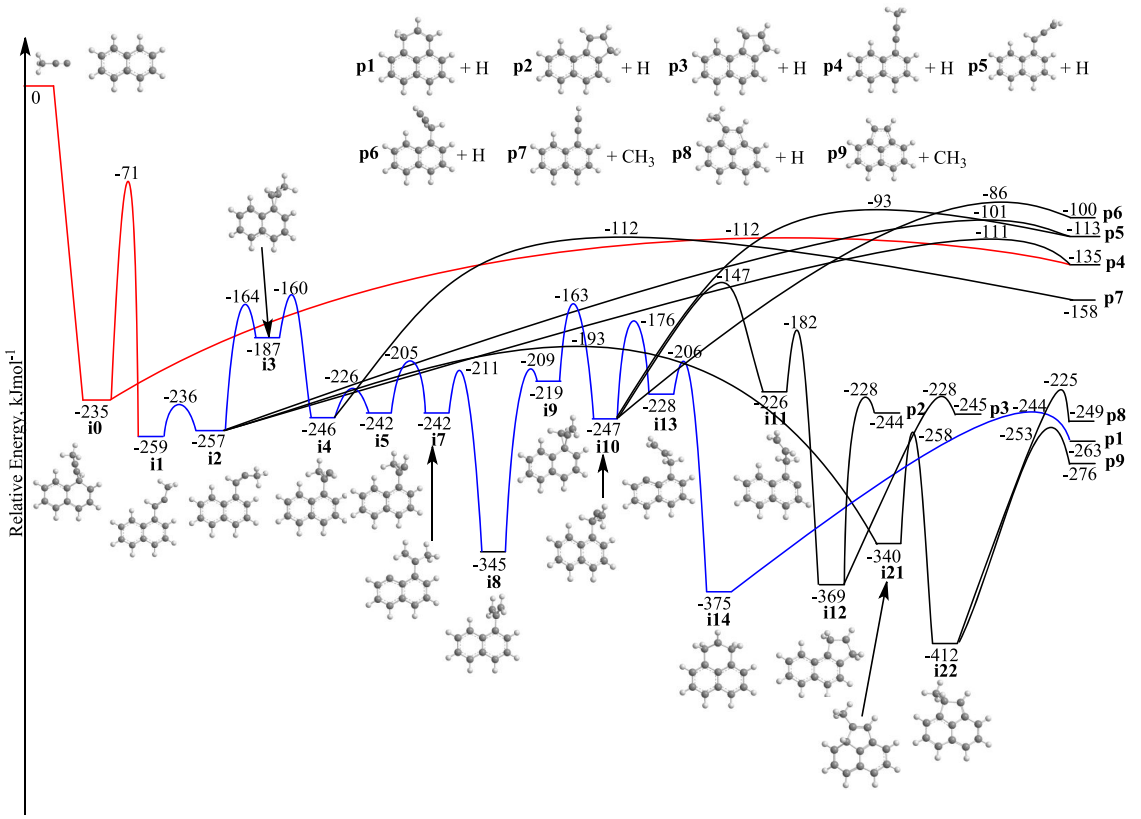

Figure 4. Potential energy surface of the reaction of naphthalene with the 1-propynyl radical calculated at the G3(MP2,CC)//B3LYP/6−311G(d,p) level of theory. The red line indicates the preferred reaction path, whereas the blue line characterizes the path to the required product.

side chain of 1-vinylnaphthalene and 1-propynyl addition to the α-C atom in naphthalene.

3. RESULTS AND DISCUSSION

3.1. 1-Vinylnaphthalene ($C_{10}H_7C_2H_3$)-Methylidyne (CH)

The electronic structure calculations predict that the reaction of 1-vinylnaphthalene ($C_{10}H_7C_2H_3$) with methylidyne (CH) can be initiated by a barrierless addition of the methylidyne radical to the vinyl moiety of 1-vinylnaphthalene forming a naphthalene-substituted cyclopropyl intermediate **i1** on the doublet surface (Figure 3). This collision complex can undergo ring opening via a barrier of only 64 kJ mol^{-1} to **i2**, which represents a naphthyl-substituted allyl radical. This entrance channel followed by ring opening proceeds analogously to the elementary reaction of methylidyne (CH) with ethylene (C_2H_4) studied in a crossed molecular beams experiment:[61] formation of a cyclopropenyl radical, stabilized by 352−360 kJ mol^{-1} followed by ring opening to the allyl radical, which is stabilized by 475 kJ mol^{-1} with respect to the separated reactants. The fate of **i2** is 3-fold. Ring closure can form a six-membered (**i3**) or five-membered ring (**i4**) via barriers of 95 and 125 kJ mol^{-1}, respectively. The preferential formation of the six-membered ring is consistent with the higher strain associated with forming the five-membered alternative. Alternatively, **i2** can undergo unimolecular decomposition to 1-naphthylallene (**p3**) in an overall exoergic reaction. Both **i3** and **i4** dissociate unimolecularly via atomic hydrogen loss to phenalene (**p1**) and −benzoindene (**p2**), respectively, with the hydrogen atom emitted from the C1 and C2 carbon atoms of the naphthalene moiety via tight exit transition states. Considering the isomerization and exit barriers to **p1** and **p2**, the formation of phenalene ($C_{13}H_{10}$) is expected to be preferred. Statistical Rice−Ramsperger−Kassel−Marcus (RRKM) support these predictions and predict branching ratio of 82% versus 18% of **p1** and **p2** at the limit of zero collision energy and zero pressure, with no significant contributions from **p3**. As the temperature is increased to 2500 K as found in circumstellar envelopes of carbon stars close to the central star, branching ratios of **p1** and **p2** decrease to some 9% versus 8%, with that of **p3** rising to 83%. It should be pointed out that the methylidyne radical can also add to the benzene moieties of the 1-vinylnaphthalene ($C_{10}H_7C_2H_3$) as shown experimentally for the methylidyne−benzene (C_6H_6)[62] and methylidyne−styrene ($C_6H_5C_2H_3$) systems.[26] These pathways are not expected to form phenalene. The rate constant for methylidyne addition to the double bond in the vinyl group is anticipated to be similar to that for the prototype CH + C_2H_4 reaction, i.e., in the range of 3−5 × 10^{-10} cm^3 molecule^{-1} s^{-1} for 23−300 K[63,64] and 2−3 × 10^{-10} cm^3 molecule^{-1} s^{-1} for 300−700 K.[65] Taking the rate constant value of this reaction measured experimentally at the lowest temperature of 23 K, 3.96 × 10^{-10} cm^3 molecule^{-1} s^{-1},[63] and using the branching ratio to form phenalene, 82%, we recommend the rate constant for methylidyne plus 1-vinylnaphthalene → phenalene + H as 3.25 × 10^{-10} cm^3 molecule^{-1} s^{-1} for model implementation under cold molecular clouds conditions. It should be noted that methylidyne can add without barrier not only to the double C═C bond in the side chain in 1-vinylnaphthalene but also to the aromatic C−C bonds in the rings, which may result in products different from phenalene. Therefore, the relative yield of the latter depends on the branching in the entrance reaction channel. In our previous work on the methylidyne plus styrene reaction, we used variable

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reaction coordinate transition state theory (VRC-TST) calculations of methylidyne addition to the aromatic ring in benzene and to the double C═C bond in ethylene to find that the rate constants for the former are by a factor of typically 1.5 higher than those for the latter in the same low-temperature range. Correcting for the number of aromatic C−C bonds in naphthalene vs benzene (11 vs 6), we can expect the entrance channel branching as 2.75:1 in favor of methylidyne addition to naphthalene rings vs that to the C═C bond in the side chain, where the ring additions may not form phenalene. While this entrance channel branching does not affect the rate constant for the phenalene formation channel, it reduces its relative yield.

3.2. Naphthalene ($C_{10}H_8$)-1-Propynyl ($CCCH_3$)

The $C_{13}H_{11}$ doublet potential energy surface (PES) has been explored previously in conjunction with molecular beams experiments for the 1-naphthyl ($C_{10}H_7$)-methylacetylene (CH_3CCH)/allene (H_2CCCH_2) systems.[37] However, the bimolecular reaction of naphthalene ($C_{10}H_8$) with 1-propynyl ($CCCH_3$) accesses an entrance channel via addition of the 1-propynyl radical to one of the chemically equivalent the C1 carbon atoms of naphthalene (Figure 4). This addition is barrierless and leads to a doublet collision complex **i0** stabilized by 235 kJ mol^{-1} with respect to the reactants. This complex can isomerize via hydrogen migration from the C1 atom of naphthalene to the C3 atom of the propynyl moiety accessing **i1** through a barrier of 164 kJ mol^{-1}. Note that **i1** represents the collision complex formed in the reaction of the 1-naphthyl radical with methylacetylene thus connecting the previously computed surfaces to the present investigation. Besides hydrogen migration, **i0** can undergo unimolecular decomposition via atomic hydrogen loss from the C1 atom of the naphthalene moiety via a barrier of only 123 kJ mol^{-1} with respect to **i0** forming 1-propynyl-1-naphthalene (**p4**). Considering the height of the barriers of 164 kJ mol^{-1} (**i0** → **i1**) versus 123 kJ mol^{-1} (**i0** → **p4** + **H**), the latter pathway is preferred. RRKM calculations predict that 1-propynyl-1-naphthalene (**p4**) plus atomic hydrogen represent practically the exclusive products. At the limit of zero temperature (zero collision energy) and zero pressure, the computed **i0** → **i1** RRKM rate constant, 3.8 × 10^2 s^{-1}, is nearly 4 orders of magnitude lower than that for **i0** → **p4** + **H**, 2.3 × 10^6 s^{-1}, and the large difference persists with collision energy.

4. CONCLUSION

The electronic structure calculations provided compelling evidence on the feasible formation of phenalene via the elementary reaction of 1-vinylnaphthalene with methylidyne under single collision conditions (3.1). This reaction is barrierless, exoergic, and follows the MACA mechanism via a [5 + 1] ring annulation. This expands the MACA framework from a [4 + 1] to a [5 + 1] effectively preparing a five- and six-membered ring, respectively. As discussed in Section 1, alternative radical − neutral reactions have prohibitive entrance barriers and can be excluded from any contributions to the formation of 1H-phenalene ($C_{13}H_{10}$). Although the 1-acenaphthyl ($C_{12}H_7$) plus methyl (CH_3) radical reaction has no entrance barrier and can access a $C_{13}H_{10}$ intermediate, methylacenaphthylene, under cold molecular cloud conditions (bimolecular reactions) the unimolecular decomposition of this $C_{13}H_{10}$ intermediate is driven by immediate atomic hydrogen loss from the methyl group to a $C_{13}H_9$ radical product, which subsequently has to overcome high barriers (∼275 kJmol^{-1}) to isomerize to the phenalenyl radical.[39]

When neutral − neutral reactions fail, the astronomical community reverts to untested ion−molecule reactions such as $C_{12}H_8 + CH_3^+ \rightarrow C_{13}H_{11}^+ + h\nu$.[2] Neutral phenalene is then proposed to be formed via dissociative recombination of internally excited $C_{13}H_{11}$ intermediates. This proposed mechanism appears to invoke a degree of structural selectivity that is difficult to reconcile with the established behavior of hydrocarbon ion−molecule systems. Such reactions frequently involve rapidly rearranging cationic intermediates and multiple energetically accessible pathways, conditions under which selective formation of a specific constitutional isomer is typically not expected. Most important, with the high energy excess typical for dissociative recombination reactions, the formation of the most thermodynamically stable tricyclic $C_{13}H_{10}$ isomer fluorene, 29 kJ mol^{-1} lower in energy than phenalene,[50] is expected. Accordingly, assignment of a distinct isomer-resolved growth pathway would require substantially stronger empirical or theoretical justification than is presently provided. Another speculated ion−molecule reaction, $C_{12}H_8$ (acenaphthylene) + $CH_3^+ \rightarrow C_{13}H_{10}$ (phenalene) + H^+ is highly endoergic, by 378 kJ mol^{-1}, based on the available thermochemical data,[66] and hence, impossible under cold molecular cloud conditions. The proposed ion−molecule formation routes therefore remain insufficiently supported.

The remaining question to be solved is the synthesis of the 1-vinylnaphthalene reactant under conditions prevailing in TMC-1. The 'shortest' route could involve the reaction of 1,3-butadiene (C_4H_6; [1]) with the vinylethynyl radical (CCC_2H_3) leading to styrene ($C_6H_5C_2H_3$, [2]) (Figure 5). This reaction has never been studied computationally or experimentally due to

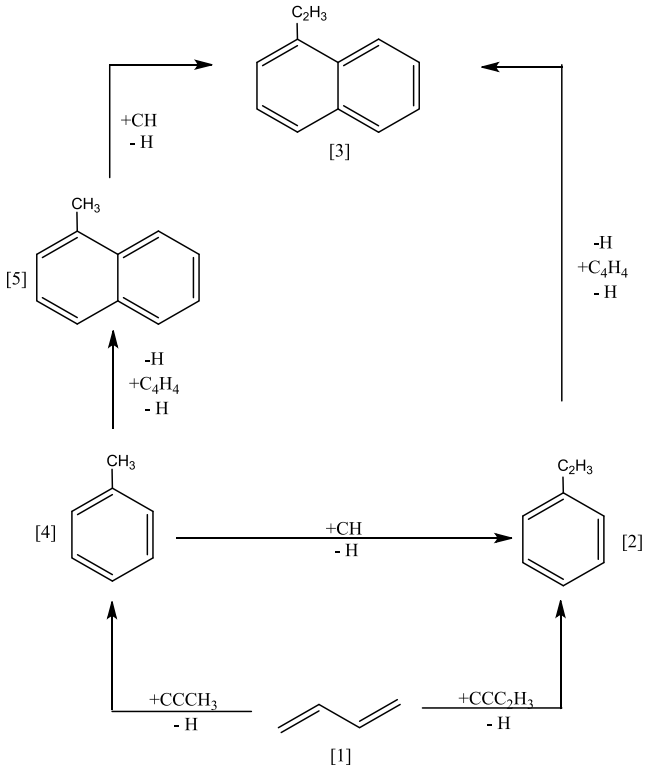

Figure 5. Schematic representation of barrierless bimolecular reactions potentially forming 1-vinylnaphthalene in TMC-1.

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the difficulties in preparing the vinylethynyl radical. However, with vinylethynyl radical classified as a substituted ethynyl radical, this reaction is expected to be barrierless. Reactions of the stem compound ethynyl (C_2H) with 1,3-butadiene[67] as well as substituted ethynyl radicals 1-propynyl ($CCCH_3$)[44] and phenylethynyl (CCC_6H_5)[68] with 1,3-butadiene synthesize benzene (C_6H_6), toluene ($C_6H_5CH_3$), and biphenyl ($C_6H_5C_6H_5$), respectively. Upon hydrogen loss from the *ortho* or *para* position by photolysis, the *o*- or *m*-tolyl radical undergoes barrierless ring annulation via HAVA forming 1-vinylnaphthalene. It should be noted that this reaction has neither been investigated computationally nor experimentally. However, both reactions of the phenyl radical (C_6H_5)[16] and of the tolyl radical ($C_6H_4CH_3$)[22,69] with vinylacetylene involving HAVA yield naphthalene ($C_{10}H_8$) and 1-/2-methylnaphthalenes ($C_{10}H_7CH_3$), respectively. Alternatively, crossed molecular beam experiments accompanied by electronic structure calculations revealed that 1,3-butadiene (C_4H_6; [1]) reacts barrierlessly with the 1-propynyl ($CCCH_3$) radical to toluene ($C_6H_5CH_3$; [4]).[44] As discussed above, the *o*- or *m*-tolyl radical generated by photolysis of toluene ring annulate upon reaction with vinylacetylene through HAVA to 1-methylnaphthalene ($C_{10}H_7CH_3$).[22,69] Upon reactions with methylidyne (CH), methyl groups can be transformed to vinyl moieties as demonstrated for the stem reaction of methylidyne with methane (CH_4).[70] Overall, both pathways involve directed, barrierless molecular mass growth processes leading ultimately to 1-vinylnaphthalene and hence to phenalene in TMC-1 (Figure 3).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.6c03215.

Cartesian coordinates and vibrational frequencies of all species (Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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