Theoretical study of the reaction mechanism of ethynyl radical with benzene and related reactions on the C_8H_7 potential energy surface

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ABSTRACT

Ab initio G3(MP2,CC)//B3LYP/6-311G** calculations have been performed to investigate the $C_2H + C_6H_6$ and $C_4H_3 + C_4H_4$ reactions on the C_8H_7 potential energy surface. The results demonstrate that C_2H reacts with benzene without a barrier and then the $C_6H_6(C_2H)$ adduct produced loses atomic hydrogen to form phenylacetylene with overall reaction exothermicity of 28.4 kcal/mol. The reaction can be a major source of phenylacetylene under low-temperature conditions of Titan's atmosphere. The reactions of vinylacetylene and butatriene with i-C_4H_3, producing phenylacetylene, pentalene, or benzocyclobutene, are predicted to be unlikely at low temperatures because of significant barriers but may be important in combustion flames.

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1. Introduction

The ethynyl radical (C_2H) is an important ingredient of the hydrocarbon-rich atmosphere of the Saturnian moon Titan, which is produced mainly by the photolysis of acetylene (C_2H_2) [1–4]. Although Titan's atmosphere mostly consists of molecular nitrogen and methane, it also contains multi-colored, aerosol-particle based haze layers featuring rather complex organic molecules. Unsaturated hydrocarbons, such as acetylene, ethylene, diacetylene, and benzene, occurring in the atmosphere in trace amounts of only a few parts per billion [5], are nevertheless significant, as they are considered as the key intermediates to form the haze layers [6]. Complex organic molecules can eventually grow from smaller hydrocarbons via a series of chemical reactions, however, for such reactions to be viable at low-temperature conditions of Titan's atmosphere, they should occur without distinct activation barriers. The reactions of ground state ethynyl radicals, C_2H ($X^2\Sigma^+$), with unsaturated hydrocarbons are known to be fast even at extremely low temperatures and therefore may be of great importance for the synthesis of complex hydrocarbon molecules in Titan's atmosphere [7]. For instance, ethynyl is likely to be involved in the formation of the polyynes $CH_3(CC)_n$–H, H–$(C≡C)_n$–H, and H–$(C≡C)_n$ via such reactions as $C_2H + H(C≡C)_nH → H(C≡C)_{n+1}H + H$ and $C_2H + CH_3(C≡C)_nH → CH_3(C≡C)_{n+1}H + H$, which are believed to play a role in the complexation of the organic haze layers [8–10] and are included in photochemical models of Titan [11–14] and extensively studied experimentally during the last decades [15,16].

The existence of benzene on Titan has now been firmly established [17–20]. The reaction of C_6H_6 with ethynyl radical may proceed by the similar C_2H-for-H exchange mechanism and lead to the formation of phenylacetylene, C_8H_6, and thus serve as the initial step for the growth of more complex aromatic molecules, including polycyclic aromatic hydrocarbons (PAH). The viability of this reaction at low temperatures has been recently confirmed by the laboratory measurements by Goulay and Leone [21], who measured the $C_2H + C_6H_6$ rate constants at 105, 165, and 298 K to be in the range of 3.0–4.0 × 10^{-10} cm^3 molecule^{-1} s^{-1} (i.e., close to the collision kinetics limit) and to exhibit a slight negative temperature dependence. The kinetics studies however did not allow establishing the reaction products. The products can be identified in future by crossed molecular beam experiments but accurate theoretical calculations of the potential energy surface (PES) for the $C_2H + C_6H_6$ reaction should be also informative. Woon [22] reported B3LYP/6-31 + G** calculations of a region of the C_8H_7 PES most relevant to this reaction and concluded phenylacetylene to be the dominant product via the C_2H addition/H elimination channel, whereas the H abstraction pathway producing $C_6H_5 + C_2H_2$ was found to be non-competitive. Woon also computed temperature dependent rate constants for the barrierless C_2H addition to benzene and found a reasonably close agreement of the calculated values with the experimental data by Goulay and Leone [21]. Earlier [23], another facet of the C_8H_7 surface was carefully characterized by high-level ab initio/RRKM and master equations calculations in relation to the reaction of phenyl radical with acetylene, $C_6H_5 + C_2H_2 → C_8H_7 → C_6H_5C_2H + H$, also producing phenylacetylene, which was also confirmed by recent crossed molecular beam experiments [24]. Meanwhile, a radical with the stoichiometric formula C_8H_7 may have a large number of different isomers and its PES may be

relevant to various chemical reactions important not only in Titan's atmospheric chemistry but also in combustion of hydrocarbon fuels. For instance, the reaction of the C_4H_3 radical with C_4H_4 accesses the C_8H_7 surface and was suggested as a possible pathway leading to aromatic species bypassing benzene [25,26]. The goal of the present study is first to re-examine Woon's density functional results concerning the $C_2H + C_6H_6$ reaction [22] at the higher G3-type level of theory providing accuracy of 1–2 kcal/mol for relative energies of various species, and second to consider, within the same level of accuracy, the $C_4H_3 + C_4H_4$ reaction.

2. Computational methods

Geometries of all intermediates and transition states on the C_8H_7 PES as well as bimolecular fragments of this radical were optimized using the hybrid density functional B3LYP [27,28] method with the 6-311G** basis set. The same method was used to obtain vibrational frequencies, molecular structural parameters, zero-point energy (ZPE) corrections, and to characterize the stationary points as minima or first-order saddle points. To obtain more accurate energies, we applied the G3(MP2,CC)//B3LYP modification [29,30] of the original GAUSSIAN 3 (G3) scheme [31] for high-level single-point energy calculations. The final energies at 0 K were obtained using the B3LYP optimized geometries and ZPE corrections according to the following formula

$$E_0[G3(MP2, CC)] = E[CCSD(T)/6 - 311G(d, p)] + \Delta E_{MP2} + E(ZPE)$$

where, $\Delta E_{MP2} = E[MP2/G3large] - E[MP2/6-311G(d,p)]$ is the basis set correction and $E(ZPE)$ is the zero-point energy. $\Delta E(SO)$, a spin-orbit correction, and $\Delta E(HLC)$, a higher level correction, from the original G3 scheme were not included in our calculations, as they are not expected to make significant contributions into relative energies. Here and below we denote this G3-type approach used in our computations as G3 for brevity. We applied the GAUSSIAN 98 [32] program package to carry out B3LYP and MP2 calculations, and the MOLPRO 2002 [33] program package to perform calculations of spin-restricted coupled cluster RCCSD(T) energies.

3. Results and discussion

3.1. $C_2H + C_6H_6$

The potential energy map for pathways related to the reaction of ethynyl radical with benzene calculated at the G3 level is illustrated in Fig. 1, along with optimized geometries of various intermediates and transition states. One can see that C_2H addition to the benzene ring occurs without a barrier to form intermediates **1** (where C_2H adds to a ring C atom) or **2** (addition to a C–C bond) with exothermicity of 42.2 and 14.2 kcal/mol, respectively. B3LYP/6-31 + G** calculations by Woon [22] gave similar values for the addition reaction energies, 42.6 and 15.9 kcal/mol, respectively. The entrance channel leading to **1** is clearly preferable thermodynamically, however, descending trajectories also exist leading from the reactants directly to the bicyclic isomer **2**. The latter is not very stable kinetically, as it readily isomerizes to **1** overcoming a barrier of 3.1 kcal/mol at TS1-2. H atom elimination from the $C(C_2H)(H)$ group in **1** produces phenylacetylene (PA) via TS1-H. The C–H bond being broken in this process is very weak, 13.8 kcal/mol, and the PA + H products reside 28.4 kcal/mol below the $C_2H + C_6H_6$ reactants (compare with 26.2 kcal/mol at the B3LYP/6-31 + G** level [22]). The calculated exit barrier at TS1-H is 10.6 kcal/mol, somewhat higher than 7.3 kcal/mol obtained by Woon. Interestingly, the energetics of the C_2H reaction with benzene, $C_2H + C_6H_6 \rightarrow C_6H_5CCH + H$, is rather similar to those with acetylene and diacetylene, $C_2H + C_2H_2 \rightarrow C_4H_2 + H$ and $C_2H + C_4H_2 \rightarrow C_6H_2 + H$, which were

computed to be exothermic by 28.3 and 29.7 kcal/mol, respectively, at similar theoretical levels [34]. The exit barriers for H elimination in those reactions are lower, 5–7 kcal/mol, which may be related to the fact that the decomposing C_4H_3 and C_6H_3 intermediates reside in deeper potential wells than the C_8H_7 isomer **1**.

Other reaction channels starting from **1** or **2** are not expected to be competitive. For instance, **1** can undergo 1,2-H shift in the ring to form intermediate **3** with a ring CH_2 group. Although **3** is 8.3 kcal/mol more stable than **1**, the barrier for the H migration at TS1-3 is 38.6 kcal/mol, 14.2 kcal/mol higher than that for H elimination leading to PA, thus making the formation of **3** rather unlikely. H loss from the CH_2 group in **3** also gives PA via a barrier of 28.1 kcal/mol at TS3-H, with the reverse barrier for H addition being 6.0 kcal/mol. Woon [22] found a pathway leading from **1** to a significantly more stable isomer **4**, $C_6H_5C_2H_2$, 63.4 and 59.9 kcal/mol below the reactants at the B3LYP/6-31 + G** and G3 levels, respectively. Although we were able to reproduce the corresponding TS1-4 using B3LYP with the 6-31 + G** basis set, this transition state does not survive basis set expansion. The TS search starting from the B3LYP/6-31 + G** optimized geometry, which was carried out with the 6-311G** or 6-311 + G** basis sets, led to TS1-H for H elimination from **1** rather than to TS1-4 for the H shift. Single-point G3 calculations of TS1-4 with the B3LYP/6-31 + G** optimized structure give the relative energy of −7.9 kcal/mol, about 10 kcal/mol higher than that of TS1-H. We can unambiguously conclude here that the direct H loss from **1** should be the dominant process and the H migrations are not probable. Ring opening in **1** producing a chain intermediate **5** is hindered by a high barrier of 51.0 kcal/mol with the corresponding TS1-5 lying 8.8 kcal/mol higher in energy the initial reactants. We will see in the subsequent section that **5** may play a role in the $C_4H_3 + C_4H_4$ reaction. The bicyclic intermediate **2** undergoes ring expansion to form a seven-member ring structure **6** rather easily, via a ~4 kcal/mol barrier. However, **6** represents a dead end on the reaction pathway, as both H elimination and migration in this structure exhibit prohibitively high barriers.

Besides PA + H, the other possible exothermic reaction products are phenyl radical and acetylene, 19.3 kcal/mol below $C_2H + C_6H_6$. They may be formed either by direct hydrogen abstraction or C_2H_2 elimination from intermediate **4**, which however is not accessible by the $C_2H + C_6H_6$ reaction. At the B3LYP/6-31 + G** level, Woon [22] could not locate an H abstraction transition state, but based on a limited search using single-point ROMP2/6-31 + G** calculations he concluded that the barrier height is about 2 kcal/mol. We searched for the hydrogen abstraction transition state at the B3LYP/6-311G** level and located a saddle-point structure denoted as TS1-C_2H_2 in Fig. 1. The structure looks like an early TS for the direct H abstraction and has relative energy of 1.8 kcal/mol with respect to the reactants at the G3 level. However, at B3LYP/6-311G** the relative energy of this TS is 1.8 kcal/mol lower than that of $C_2H + C_6H_6$ indicating that it cannot directly connect these reactants with the $C_2H_2 + C_6H_5$ products. To clarify the nature of TS1-C_2H_2 we ran intrinsic reaction coordinate (IRC) [35] calculations, which converged to $C_2H_2 + C_6H_5$ in the forward direction. In the reverse direction, no van der Waals complex was found lying below the TS, but instead the minimal energy path reached the intermediate **1**. Thus, alternatively to intermolecular H abstraction, we observe here intramolecular hydrogen abstraction via the roaming mechanism; starting from **1**, the C_2H fragment leaves the molecule, but before it is completely eliminated, it picks up a hydrogen atom from benzene to eventually form $C_2H_2 + C_6H_5$. Therefore, these products cannot be formed directly from the reactants, but only via the C_8H_7 intermediate **1**. Since the barrier at TS1-C_2H_2 is about 20 kcal/mol higher than that for the H loss from **1** at TS1-H, the $C_2H_2 + C_6H_5$ products are not expected to compete with PA + H even at higher temperatures. Apparently,
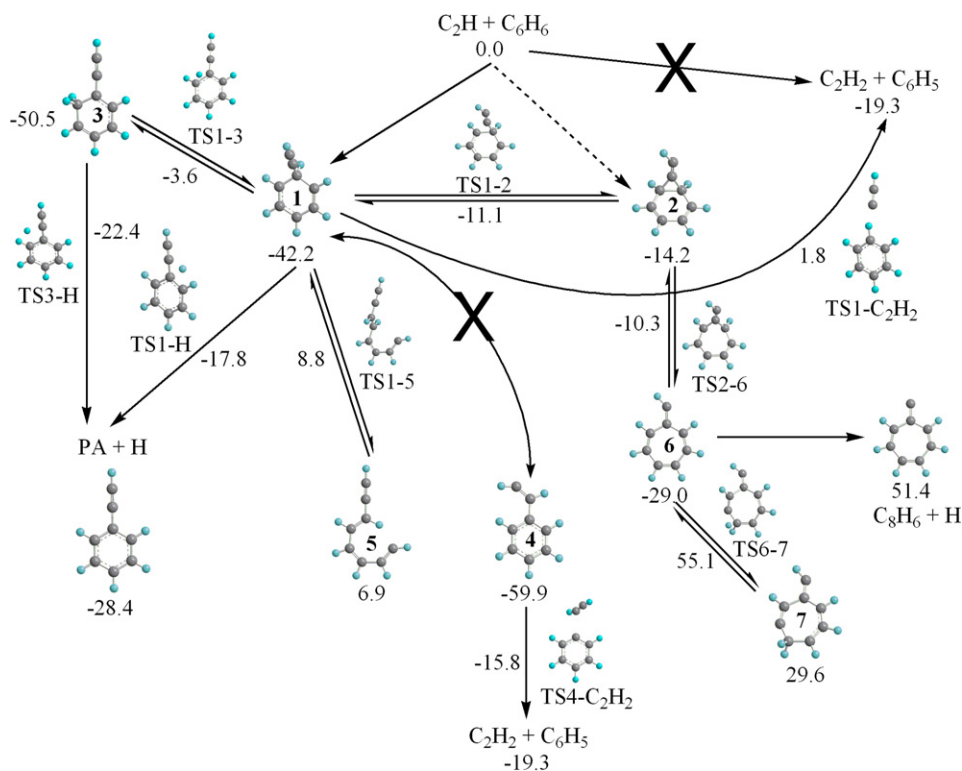
Fig. 1. Potential energy diagram for the $C_2H + C_6H_6$ reaction calculated at the G3(MP2,CC)//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory. All energies are given in kcal/mol.

the direct H abstraction is not feasible because of the attractive nature of PES as C_2H approaches benzene and forms new C–C bonds in **1** or **2**.

Since thermal rate constants for the $C_2H + C_6H_6$ reaction have been recently measured by Goulay and Leone [21] and computed by Woon [22], here we limit ourselves only to rough estimation of their values using long-range transition state theory developed by Georgievskii and Klippenstein [36]. In this approach, which should be most meaningful in the 10–100 K temperature range, one calculates dispersion, dipole–induced dipole, and dipole–quadrupole rate constants and the largest of them provides a reasonable first approximation to the overall rate. The data needed for these calculations, the dipole moment of C_2H, quadruple moment of benzene, and polarizabilities of C_2H and C_6H_6, were obtained at the B3LYP level with the augmented cc-pVTZ basis set, whereas ionization energies were taken from the NIST Chemistry Database [37]. The calculations show that the largest capture rate is due to dispersion. The evaluated dispersion rate constants are described by the $2.72 \times 10^{-10} T^{1/6}$ expression and range from 3.99×10^{-10} to 5.85×10^{-10} cm^3 molecule^{-1} s^{-1} for 10–100 K. Based on their measurements at 105, 165, and 298 K Goulay and Leone [21] suggested the rate expression as $3.28(\pm 1.0) \times 10^{-10} (T/298)^{-0.18(\pm 0.18)}$ cm^3 molecule^{-1} s^{-1}. Using this equation for 50 and 100 K, one obtains the rate constants of 4.52×10^{-10} and 3.99×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively. Our present long-range transition theory estimates, 5.21×10^{-10} and 5.85×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively, are in reasonable agreement with the values from the experimental rate expression, although the temperature dependence is not correctly reproduced. The values obtained by Woon using trajectory calculations are about a factor of 2 lower, 2.64×10^{-10} and 2.85×10^{-10} cm^3 molecule^{-1} s^{-1}. Apparently, a more sophisticated theoretical treatment will be required to improve the agreement between theory and experiment.

3.2. $C_4H_3 + C_4H_4$

The i-C_4H_3 radical, H_2CCCCH, is one of the major products in photodissociation of vinylacetylene, H_2CCHCCH. Based on this finding, Stearns et al. [25] suggested that the reaction of i-C_4H_3 with vinylacetylene may play a role in the formation of aromatic molecules in Titan's atmosphere following photolysis of C_4H_4. To examine this hypothesis, here we consider the region of the C_8H_7 PES relevant to the i-C_4H_3 reactions with two most stable C_4H_4 isomers, vinylacetylene and butatriene (Fig. 2). The H_2CCCCH + H_2CCHCCH reaction starts by the addition of the CH end of the radical to the acetylenic end of C_4H_4 to produce a chain intermediate **8**, H_2CCHCCHCHCCCH$_2$. This addition is computed to be 27.9 kcal/mol exothermic and to involve a significant 11.4 kcal/mol barrier at TS8-C_4H_3 (see Fig. 2). Note that a different, *trans*-conformer of **8** is formed initially but the rotation around the central single CH–CH bond is very easy. Evolution of **8** to six-member C_8H_7 precursors of PA, intermediates **1** and **4**, can occur by two different mechanisms; one involves six-member ring closure (pathway I) and second goes via eight-member ring closure followed by ring contraction (pathway II). In pathway I, **8** first undergoes a 1,3-H migration from the terminal CH$_2$ group (on the right-hand side of the molecule as shown in Fig. 2). The barrier for this process is 46.4 kcal/mol and the corresponding TS8-9 lies 18.5 kcal/mol higher in energy than the i-C_4H_3 + vinylacetylene reactants. Intermediate **9**, H_2CCHCCHCHCHCCH, is 7.7 kcal/mol more stable than **8**. The next step is 1,2-H shift from the CH group (neighboring to the terminal CH$_2$ fragment) to form H_2CCCHCHCHCHCCH, a conformer of intermediate **10**, which, after facile rotation around a CH–CH single bond, produces **10** itself. Since all rotation barriers are much lower than those for H migrations, we omit them in the present consideration. Next, intermediate **10** is subjected to another 1,2-H shift leading to the structure **5**, which we have already encountered ear-
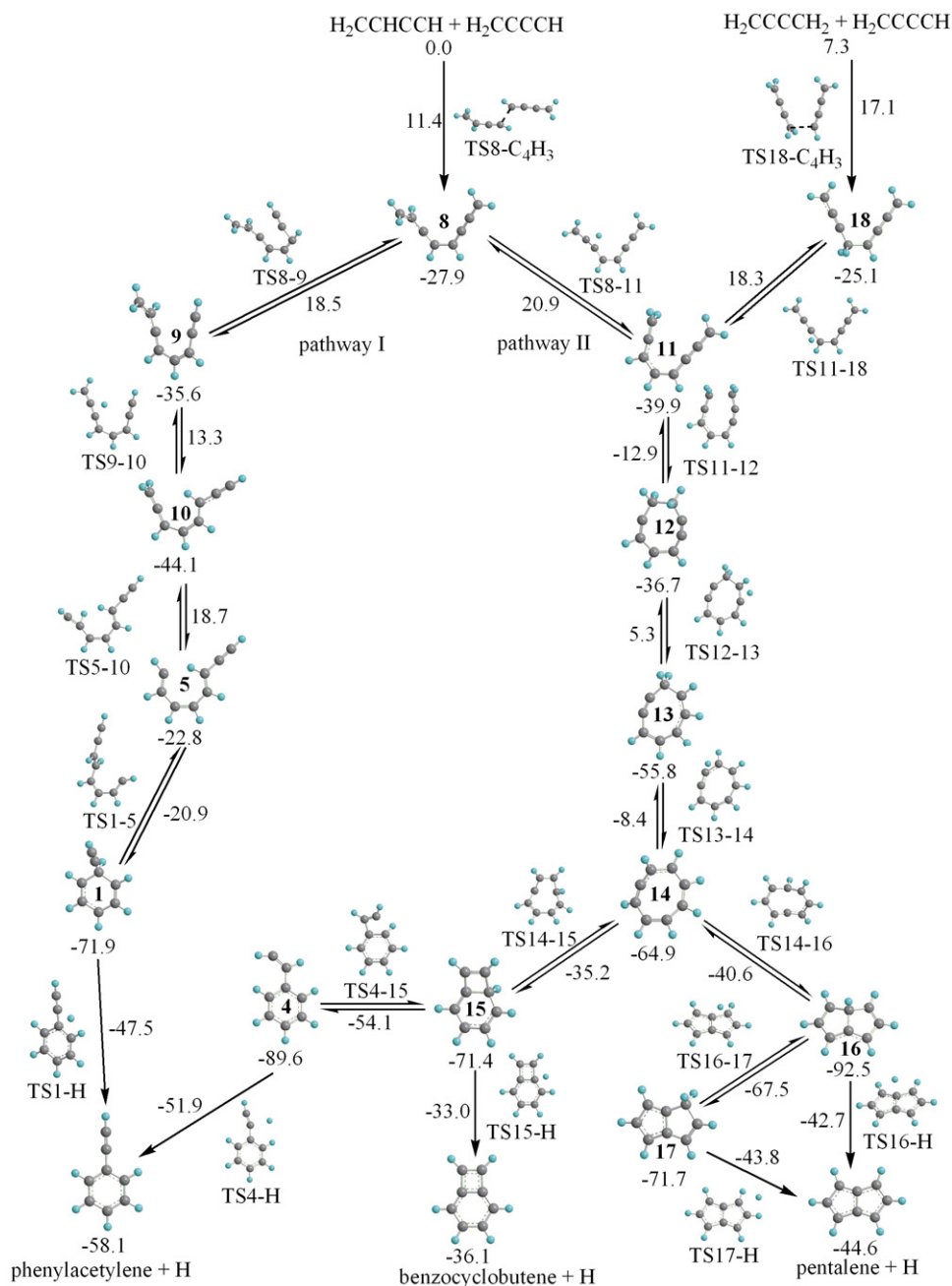
Fig. 2. Potential energy diagram for the $H_2CCHCCH + i\text{-}C_4H_3$ and $H_2CCCCH_2 + i\text{-}C_4H_3$ reactions calculated at the G3(MP2,CC)//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory. All energies are given in kcal/mol.

lier as the product of ring opening of **1** (Fig. 1). The ring-closure barrier in **5** is only 1.9 kcal/mol and thus the six-member ring structure **1** can be easily produced once the series of H migrations rearranges hydrogen atoms in the appropriate way. The final step is H elimination from **1** giving phenylacetylene. The overall exothermicity of the $H_2CCCCH + H_2CCHCCH \rightarrow 8 \rightarrow 9 \rightarrow 10 \rightarrow 5 \rightarrow 1 \rightarrow PA + H$ reaction sequence is 58.1 kcal/mol and the highest barrier, 18.7 kcal/mol relative to the initial reactants, is found at TS5-10.

Pathway II starts with 1,2-H shift from the CH group on the left-hand side of intermediate **8** (Fig. 2), which results in structure **11**, $H_2CCCHCHCHCCCH_2$. The barrier at TS8-11 is 48.8 kcal/mol, 2.4 kcal/mol higher than that at TS8-9 in pathway I. Compound **11** can undergo eight-member ring closure by the formation of a new C–C bond connecting two terminal CH_2 fragments. As a result,

a cyclic intermediate **12** is produced overcoming a barrier of 27.0 kcal/mol at TS11-12. The next two reaction steps, **12** → **13** → **14**, involve 1,2-H migration in the eight-member ring from CH_2 group to the neighboring hydrogen-less carbon atoms, which exhibit barriers of 42.0 and 47.4 kcal/mol. In the resulting isomer **14**, all except one C atoms of the ring are linked to an H atom. Intermediate **14** is the most stable of the three eight-member cyclic intermediates and lies 64.9 kcal/mol below the reactants. Starting from **14**, two different reaction scenarios are possible. In the first one, the eight-member ring undergoes ring contraction producing a bicyclic intermediate **15** consisting of a six- and a four-member ring via a barrier of 29.7 kcal/mol. On one hand, **15** is a precursor of benzocyclobutene, which can be produced from the former by H elimination through a barrier of 38.4 kcal/mol. On the other hand, four-member ring opening in **15** gives the six-member ring struc-

ture **4**, C_6H_5CHCH, via a lower barrier of 17.3 kcal/mol. Intermediate **4** is the initial intermediate in the reaction of phenyl radical with acetylene and the C_8H_7 PES in its vicinity was carefully studied by Tokmakov and Lin [23]. The most favorable channel for the further development of **4** is H elimination from the non-terminal side-chain CH group producing PA after overcoming a 37.7 kcal/mol barrier. Note that PA is 22.0 kcal/mol more stable than benzocyclobutene and, as a result, the **15** → **4** → PA + H sequence is preferable energetically as compared to **15** → benzocyclobutene + H. The second pathway starting from **14** involves eight-member ring contraction to two five-member rings in intermediate **16**. The barrier at TS14-16 is 5.4 kcal/mol lower than that at TS14-15, hence the 5 + 5 ring contraction is energetically more favorable than 6 + 4; note that **16** is also 21.4 kcal/mol more stable than **15**. Structure **16** is a precursor of pentalene, which can be produced either by immediate H loss or via a two-step mechanism via **17** including H migration followed by H elimination. In terms of the height of the largest barrier, the two-step mechanism is slightly preferable. Pentalene is calculated to be 13.5 kcal/mol less stable than PA, but 8.5 kcal/mol more stable than benzocyclobutene.

The highest barrier on the reaction pathway leading from *i*-C_4H_3 + vinylacetylene to either phenylacetylene, pentalene, or benzocyclobutene via eight-member cyclization is 20.9 kcal/mol with respect to the reactants occurring at TS8-11, which makes this mechanism slightly less favorable than the six-member cyclization pathway via TS8-9. According to the calculated energetics, PA + H appears to be the most likely reaction product, however, the formation of pentalene and benzocyclobutene cannot be ruled out. Note that other possible C_8H_6 isomers, including open-chain structures and eight-member rings, lie at least 56 kcal/mol higher than PA and cannot be competitive products. The relative yields of PA, pentalene, and benzocyclobutene depending on the temperature and pressure under real combustion conditions can be evaluated in future by RRKM and master equation calculations.

Another C_4H_4 isomer, butatriene H_2CCCCH_2, can also react with *i*-C_4H_3 overcoming a lower barrier of 9.8 kcal/mol to form intermediate **18**, $H_2CCCH_2CHCCCH_2$, lying 32.4 kcal/mol below the reactants. Next, **18** can rearrange to **11** by 1,2-H migration requiring a 11.0 kcal/mol barrier relative to H_2CCCCH_2 + *i*-C_4H_3. After that, the reaction pathways are the same as those described above for the vinylacetylene + *i*-C_4H_3 reaction leading either to PA + H via **8** and the six-member ring closure route with the highest in energy TS8-11 residing 13.6 kcal/mol above butatriene + *i*-C_4H_3 or to PA + H/pentalene + H/benzocyclobutene + H via the eight-member ring closure route with all TSs encountered after **11** residing below the reactants. We can conclude that butatriene should be more reactive toward *i*-C_4H_3 that vinylacetylene and its reaction is expected to produce higher yields of pentalene and benzocyclobutene as compared to those in the vinylacetylene reaction because the eight-member ring mechanism is more favorable for the H_2CCCCH_2 + *i*-C_4H_3 case.

4. Conclusions

High-level ab initio G3(MP2,CC)//B3LYP/6-311G** calculations demonstrate that ethynyl radical can recombine with benzene without a barrier to produce the $C_6H_6(C_2H)$ adduct **1** with exothermicity of 42.2 kcal/mol. The latter can lose the hydrogen atom from the $C(H)(C_2H)$ group to form phenylacetylene, which is predicted to be the exclusive reaction product unless **1** is collisionally stabilized. Overall, the $C_2H + C_6H_6 →$ PA + H reaction is computed to be 28.4 kcal/mol exothermic and to exhibit an exit barrier of 10.6 kcal/mol. Other reaction channels are not expected to be competitive. The direct H abstraction is unlikely because of the strongly attractive nature of the PES along the approach of C_2H toward car-

bon atoms of benzene. The $C_2H_2 + C_6H_5$ products can be in principle formed from **1** by the C_2H roaming mechanism, however, the barrier for this process is 44.0 kcal/mol, 19.6 and 1.8 kcal/mol higher than the energies required for the H and C_2H elimination from **1**, respectively.

Interestingly, the $C_2H_2 + C_6H_5$ reaction is known to be a major source of phenylacetylene in combustion, but this reaction should be slow in Titan's atmosphere, as it is hindered by a ~4 kcal/mol barrier. On Titan, the barrierless $C_2H + C_6H_6$ reaction can play the similar role and efficiently produce phenylacetylene. In the HACA mechanism of PAH formation and growth, PA is produced by hydrogen abstraction from benzene followed by acetylene addition and H loss. Here, this is replaced by ethynyl addition and H elimination. Since the HACA sequence is equivalent to ethynyl addition, which is very fast even at extremely low temperatures, one can expect that the C_2H addition mechanism may be a viable alternative to HACA in the environments where ethynyl radicals are readily available due to photochemical destruction of C_2H_2, but the temperature and/or concentration of H-abstracting radicals are too low to allow the HACA sequences to occur.

The reactions of vinylacetylene and butatriene with *i*-C_4H_3 can lead to the PA + H, pentalene + H, and benzocyclobutene + H products via pathways starting from addition of the radical to C_4H_4 to form chain intermediates, which then undergo hydrogen migrations followed by six- or eight-member ring closures, ring contractions, and H eliminations. The *i*-C_4H_3 + C_4H_4 reactions are unlikely to be important at low-temperature conditions of Titan's atmosphere because of the significant barriers of at least 10–11 kcal/mol for the initial association steps. However, these reactions may play a role under combustion conditions and may lead to the formation of the aromatic PA molecule bypassing benzene and therefore should be included into kinetic models for the PAH formation.

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