

A density functional theory study of phenyl formation initiated by ethynyl radical (C₂H•) and ethyne (C₂H₂)

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Abstract An ab initio computational density functional theory (DFT) was used to study the formation of the first cyclic molecule (phenyl) initiated by the ethynyl radical (C₂H•). The study covers a competition reaction between the addition reactions of C₂H• with ethyne (C₂H₂) and some molecular re-arrangement schemes. The minimum energy paths of the preferred cyclic formation route were characterized. A thorough thermochemical analysis was performed by evaluating the differences in the energy of activation (ΔE), enthalpy (ΔH), and Gibb's free energy (ΔG) of the optimized stable and transition state (TS) molecules. The reaction temperatures were set to normal (T=298 K) and combustion (T=1,200 K) conditions.

Keywords Density functional theory · Ethyne · Ethynyl radical · Phenyl · Reaction mechanism

Introduction

The ethynyl radical (CH≡C), a simple open-shell olefinic species, plays an important role in combustion chemistry, low temperature extraterrestrial atmospheres, and air-pollution. C₂H is also known as an intermediate in chemical reactions, e.g., in the polymerization of acetylenic bonds and the formation of some cyclic compounds [1]. This becomes important from the point of view of environmental concerns regarding the polluting emissions of combustion processes due to the formation of poly-aromatic hydro-

carbons (PAHs) and/or poly-aromatic compounds (PACs). Some PAHs, e.g. benzo-a-pyrene (BaP), are known to be toxic and carcinogenic, and have become targets for elimination. Nowadays, the chemistry surrounding the formation and growth of aromatics at either normal or combustion temperatures is receiving much attention. The primary focus is on first ring formation from small aliphatics as the initiator species.

A series of papers by Howart and co-workers [2–5] reported the existence of intermediate radicals (C₂H and C₄H₃) in premixed flat flames at reduced pressure using mixtures of the following fuels with oxygen: C₂H₂, C₂H₄, C₃H₈, C₆H₆ and C₂H₅OH. Colket [6], in agreement with Frenklach et al. [7, 8], mentioned that addition of acetylene to n-C₄H₃ is the major pathway leading to cyclic compounds. n-C₄H₃ is formed by the reaction C₂H₂+C₂H, which is consistent with the analysis of Frenklach and Warnatz [7] for the post-flame zone, where the concentration of oxygen was very low, or to pyrolytic conditions. The proposed mechanism follows the sequence:



The formation of compound C₄H₃ in the reaction shown in Eq. 1 is still mysterious since C₄H₃ can form in many structures, for instance n-C₄H₃, iso-C₄H₃, or 3-methylidene-cyclopropene radical. The presence of such compounds could not easily be distinguished using the online infrared analysis instruments usually employed in this type of experiment. Despite its controversy [9], few papers (possibly

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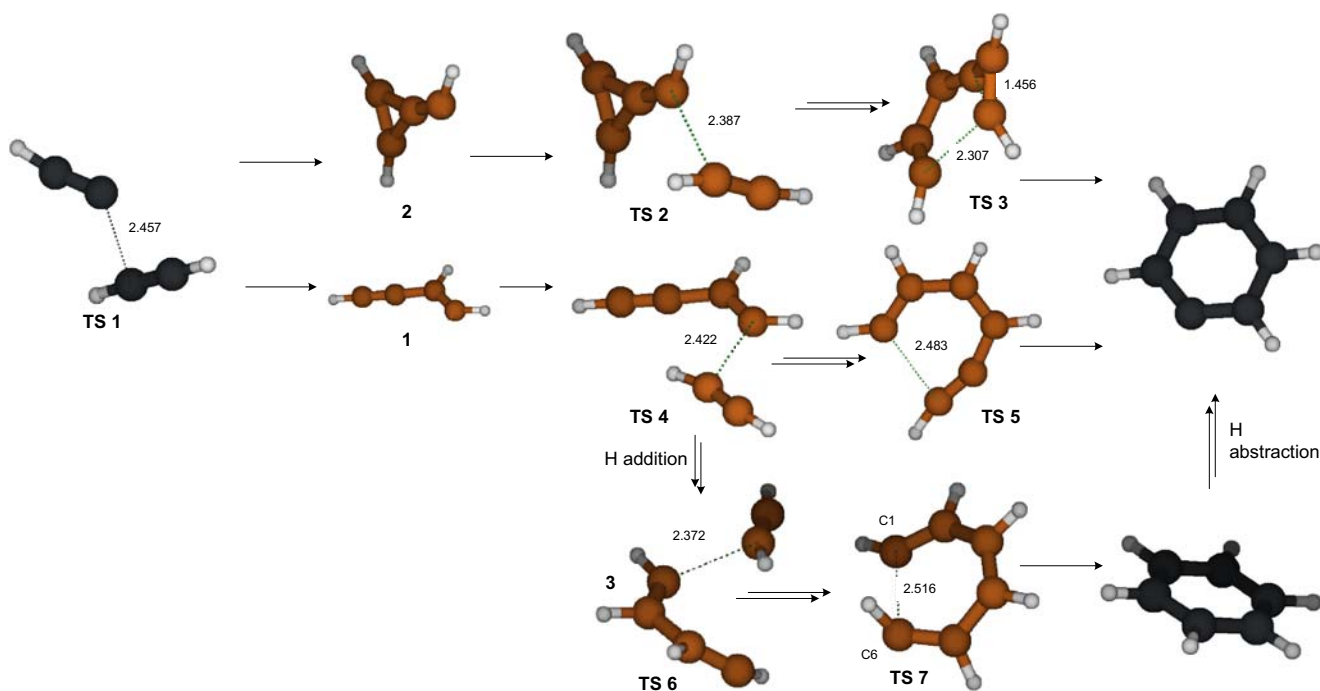


Fig. 1 The transition state (TS) scheme of first aromatic ring formation initiated by ethyne (C_2H_2) and ethynyl radical ($C_2H\cdot$). All values are in Angstrom units (\AA)

none) have discussed the competition reaction between ring formation according to the above mechanism and isomerization (chain elongation) due to continuous ethyne attack of growing molecules. This latter scheme is thought very likely to occur under conditions of high ethyne concentrations, e.g., in petrochemical-flare combustion where the concentration of ethyne reaches ca. 53.7 mg m^{-3} [10]. Structural rearrangements, for example bond rotation and hydrogen conformation, are required to orientate the structure in order to favor ring closure. In this study, we try to address this issue by limiting the case only to the first cyclic ring formation initiated by the ethynyl radical and the ethyne reaction. Obviously, other species such as oxygen, nitrogen or even other radical hydrocarbons, exist under real conditions in the atmosphere, and will affect the reaction by introducing other types of competition reaction. However, by considering first cyclic ring formation only, we hope to focus our analysis, rather than attempting a broad coverage that could lead to several ambiguous and unclear explanations. All simulations were performed using a computational DFT–B3LYP (density functional theory–Becke three-parameter Lee–Yang–Parr)-based method.

Computational methods

All molecular calculations were carried out using Gaussian 03 software [11]. The stable and transition state (TS) structures were determined by gradient procedures [12–15]

within the DFT and employing the B3LYP functional [16–20]. This function is well known and widely used, and even if it tends to underestimate some reaction barriers, in general the performance is acceptable regarding geometries and energetics [21]¹. Moriarty [22] also obtained reliable results for structure rearrangement. Inspection of the normal mode related to the single imaginary frequency was sufficient to confidently establish TS structures. The reaction pathways connecting TS structures and the corresponding equilibrium structures were followed by the intrinsic reaction coordinate (IRC) procedure. The selected TS of some geometries are shown in Fig. 1. The geometry scheme will be explained in the **Results and discussion** section. For all possible pathway, the energy evaluations were calculated by the 6–31G(d) level of theory [23–26]. Activation energies, reaction enthalpies, and free energy were obtained by thermochemical calculation from vibrational analysis².

Results and discussion

In order to find the best quantum mechanical method and basis set to apply to the system, ethyne (C_2H_2), ethynyl

¹ This theory level was tested on a model reaction and compared with more expensive ab initio methods [21], where it appeared to be a rather good compromise

² Reaction enthalpies and free energies were computed as outlined, for example, in [27]

radical (C_2H^\bullet), and benzene ($c-C_6H_6$) were chosen as model systems to compare geometry fitting between computational calculations and experimental data. This is reasonable since the study will deal with these molecules, especially ethyne and ethynyl radical, and benzene could be considered the best approach structure to represent phenyl ($c-C_6H_5^\bullet$). Table 1 compares the results of computation using several methods and basis sets with experimental results. Small differences were found but, in general, it appeared reasonable to use the optimized geometry as a fundamental structure in the calculation. Except in the case of ethynyl radical, the results computed with basis set B3LYP/6–31G(d) agreed with the experimental results to two decimal places, and thus gave the best optimization among all the methods and basis sets used. Although this simple study and analysis could not be called comprehensive, and others have suggested using multi-reference methods, the general results of the simulation and the model describe the phenomenon well enough.

Following the schematic mechanism, the reaction is initiated via ethynyl radical (C_2H^\bullet) and ethyne (C_2H_2). The adduct reaction will give two products: 1-buten-3-yne-1-yl radical (**1**) and 3-methylidenecyclopropene radical (**2**)—both of which are very exoergic. Product **1** is more stable than product **2**, as shown by its lower free energy and potential energy ($\Delta G = -71.7 \text{ kcal mol}^{-1}$, $\Delta E = -58.4 \text{ kcal mol}^{-1}$ for **1**, and $\Delta G = -53.6 \text{ kcal mol}^{-1}$, $\Delta E = -40.3 \text{ kcal mol}^{-1}$ for **2**, at $T = 298.15 \text{ K}$, hereafter 298 for short). These reactions have to surmount a similar transition energy, which is around $2.9 \text{ kcal mol}^{-1}$ for the free energy barrier (ΔG^\ddagger) at room temperature. The adduct reaction of the two moieties will not yield $i-C_4H_3$ (either 1-buten-3-yne-2-yl or 1,2,3-butatriene-4-yl radical) in a direct way. A previous numerical analysis by Miller and Melius [32] revealed that the iso-form is thermodynamically more stable (i.e., has

lower energy) than the normal-form. Our calculation using the B3LYP/6–31G(d) method resulted in a standard enthalpy difference, $\Delta_f H_{298}^\circ$, between the *n*- and iso-form of $17.8 \text{ kcal mol}^{-1}$. This is similar to previous calculations using the BAC-MP4 ([32]; 19 kcal mol^{-1}) and MP2/6–311G(d) ([33]; $20.9 \text{ kcal mol}^{-1}$) methods. Sticking to the above scheme, following Frenklach [9], the iso-formation cannot be obtained via a single step addition mechanism and requires further geometry rearrangement from **1** and **2**. *n*- C_4H_3 (isomer **1**) can undergo a 2,1 H shift to *i*- C_4H_3 with a free energy barrier of $46.9 \text{ kcal mol}^{-1}$. Even this value is overestimated—a prediction by Le et al. [33] using a more expensive method, G2M(RCC,MP2), resulted in a value of $32.3 \text{ kcal mol}^{-1}$. All these results tend to neglect the possibility of internal geometry rearrangements involving H shifts as they require a lot of energy. The most probable mechanism of geometry evolution is via H abstraction on C_2 followed by H addition to C_1 of *n*- C_4H_3 . H addition, for example, requires a lower energy barrier ($\Delta G^\ddagger \approx 9 \text{ kcal mol}^{-1}$). We are currently pursuing our study of this structural evolution mechanism and it will not be addressed further here.

The straightforward estimate of the TS geometry of addition is verified by means of a couple of constrained optimizations at shorter and larger C–C distance between the moiety and ethyne. This is applied to the TS of geometry rearrangements as performed by angle-constrain optimization of C–C rotation or C–H conformation. This confirms the geometric location of the maximum along the G profile corresponding to the TS on the E surface, and yields the values reported in Table 2.

The initiation reaction of ethyne attacks on ethynyl radical will result in **1** and **2** (**1** is more stable than **2**). The isomer **2** can undergo β -fragmentation via ring opening and one H atom migration to form **1**. However, it suffers from a

Table 1 Calculated and experimental data of the optimized ground-state geometry of ethyne (C_2H_2), ethynyl radical (C_2H^\bullet), and benzene ($c-C_6H_6$). All values are in Angstrom unit

	HF		B3LYP		PW91	MP2		Experimental
	6–31G(d)	6–311G(2d,p)	6–31G(d) ^a	6–311G(2d,p)		6–31G(d)	6–311G(2d,p)	
Ethyne								
C–C	1.1855	1.1781	1.2050	1.1944	1.2142	1.2177	1.2095	1.2024 [28]
C–H	1.0567	1.0550	1.0666	1.0630	1.0727	1.0662	1.0643	1.0625 [28]
Ethynyl radical								
C–C	1.2650	1.2646	1.2263	1.2305	1.2414	1.2428	1.2399	1.207 ^b [29] ^c
C–H	1.0620	1.0618	1.0700	1.0694	1.0779	1.0718	1.0688	1.069 ^b [29] ^c
Benzene								
C–C	1.3862	1.3821	1.3966	1.3913	1.4015	1.3966	1.3954	1.397 [30, 31]
C–H	1.0756	1.0748	1.0870	1.0829	1.0934	1.0870	1.0854	1.084 [30, 31]

^a Basis set used in this study

^b Determined by a mixed theoretical/experimental approach

^c And references therein

Table 2 Transition geometry calculation using B3LYP//6–31G(d). All values are in kcal mol⁻¹. Energies are calculated with respect to the previous structure

	ΔE	ΔH	ΔG (T=298 K)	ΔG (T=1,200 K)
1 +C ₂ H ₂ → c-C ₆ H ₅				
Reactant (C ₂ H+C ₂ H ₂)	0.0	0.0	0.0	0.0
TS C ₂ H ₂ addition (TS1)	-6.4	-5.0	2.1	30.6
TS H conformation	5.6	4.2	4.3	4.7
- TS C ₂ H ₂ Addition ^a	3.3 ^a	3.6 ^a	11.4 ^a	41.2 ^a
TS C ₂ H ₂ addition (TS4)	0.7	1.1	9.5	37.6
TS C-C rotation	7.6	6.7	7.4	11.2
- TS C ₂ H ₂ Addition ^a	2.4 ^a	2.7 ^a	10.1 ^a	39.4 ^a
TS H conformation	4.8	3.4	3.5	9.2
- TS C ₂ H ₂ Addition ^a	2.8 ^a	3.1 ^a	10.3 ^a	40.2 ^a
TS ring closure (TS5)	4.7	4.0	5.5	13.2
2 +C ₂ H ₂ → c-C ₆ H ₅				
Reactant (C ₂ H+C ₂ H ₂)	0.0	0.0	0.0	0.0
TS C ₂ H ₂ addition (TS1)	-6.4	-5.0	2.1	30.6
TS C ₂ H ₂ addition (TS2)	3.3	3.6	11.4	41.2
TS C-C rotation	6.7	5.9	6.7	9.3
TS H conformation	4.7	3.4	3.5	5.8
TS ring closure (TS3)	18.4	17.0	18.7	25.4
3 +C ₂ H ₂ → c-C ₆ H ₆				
Reactant (C ₂ H+C ₂ H ₂)	0.0	0.0	0.0	0.0
TS C ₂ H ₂ addition (TS1)	-6.4	-5.0	2.1	30.6
TS H addition	2.7	2.6	9.1	n.a
TS H conformation	4.6	3.3	3.0	5.8
- TS C ₂ H ₂ Addition ^a	45.4 ^a	2.7 ^a	10.1 ^a	38.9 ^a
TS C ₂ H ₂ addition (TS6)	2.0	2.5	12.6	50.4
TS H conformation	6.5	5.6	5.9	7.9
TS ring closure (TS7)	1.3	0.6	2.2	9.3

^a Competition reaction (C₂H₂ addition) with structural rearrangements of C–C rotation and/or H conformation

high free energy barrier ($\Delta G^\ddagger=44.7$ kcal mol⁻¹ compared to the previous structure). This means that isomer **2** is actually stable enough to exist, and has a high probability of being included in the reaction schemes of first aromatic ring formation. The free energy profile at T=298 K of the scheme is shown in Fig. 2. Rearrangement of the moiety resulting from adduct reaction of the two molecules is required to obtain the structure that is preferentially able to form a cyclic compound. In general, this evolution can be done in two ways: (1) H conformation (from cis- to trans- or vice versa) followed by C–C single bond rotation, or (2) C–C single bond rotation followed by H conformation (from cis- to trans- or vice versa). Our calculations suggest that, for hydrocarbon molecules with six C atoms or less, the results obtained with both mechanisms are almost the same. Without geometry rearrangement schemes, the further adduct reaction with ethyne produces chain elongation; this polymerization process will not be further addressed here. We discarded the possibility of H atom migration among C atoms at each step of the mechanism since this would require large amounts of energy, e.g., $\Delta G^\ddagger=44.7$ kcal mol⁻¹ for n-C₄H₃ (**1**). On the

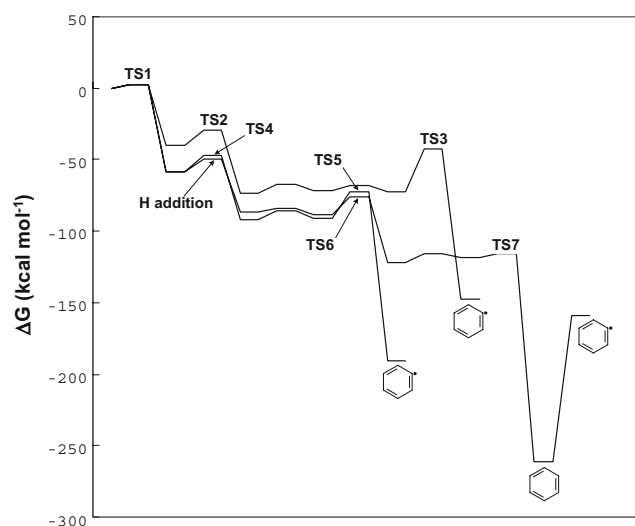


Fig. 2 Free energy profile calculations using the B3LYP//6–31G(d) basis set

other hand, we have to consider hydrogen addition as the energy barrier is smaller ($\Delta G^\ddagger=9.3$ kcal mol⁻¹). Addition of a hydrogen atom to isomer **1** is acceptable since there is no steric geometry hindrance. The adduct reaction will form an even molecule of C₄H₄ (**3**), which appears at lower temperature combustion of vinylacetylene [33], which has a triplet electronic state.

At this level, the relevant free energy barrier (ΔG^\ddagger) of geometry rearrangement of **1** (from a trans position between the radical and ethyne groups to a cis position by H conformation on C₁) is 4.3 kcal mol⁻¹. This value is far more preferable compared to the energy value of adduct reaction with C₂H₂. At 298 K, the adduct reaction of **1**+C₂H₂ requires $\Delta G^\ddagger=11.8$ kcal mol⁻¹. Under combustion conditions, say at 1,200 K, the assessment of the free energy profile reveals much higher barriers at shorter intermolecular distances. The barrier height of **1**+C₂H₂ is 40.2 kcal mol⁻¹. Similar results are found for the molecular rearrangements of **2** and **3**. The free energy barrier of H conformation is 4.3 kcal mol⁻¹ at T=298 K for **2** and 3.0 kcal mol⁻¹ for **3**. These values will rise when the temperature increases ($\Delta G^\ddagger=4.7$ kcal mol⁻¹ for **2** and 5.8 kcal mol⁻¹ for **3** at T=1,200 K). The adduct between two moieties, i.e., **2** and C₂H₂ or **3** and C₂H₂, also requires more energy than H conformation. At T=298, ethyne addition to **2** has a ΔG^\ddagger saddle point of 11.4 kcal mol⁻¹, while ethyne addition to **3** is 10.1 kcal mol⁻¹. These data seem to reject the possibility of chain elongation as geometry rearrangement is preferable, but we must bear in mind that rearrangement is usually a reversible reaction. The enthalpy energy differences between **1**, **2**, **3** and their H conformation products are only -0.1, 0.1, and -0.7 kcal mol⁻¹, respectively. On the other hand, the adduct reaction is an exoergic reaction, which results in a stable compound; $\Delta H=-46.9$ kcal mol⁻¹ for **1**+C₂H₂. Although the attack of C₂H₂ is more difficult than a geometry rearrangement, the rate of reaction will increase at higher concentration of C₂H₂. At T=298 K, roughly estimated from Table 2, the rate constant ratio of k_{A1} (forward rate constant of H conformation of **1**) to k_{B1} (rate constant for adduct reaction of **1**+C₂H₂), $k_{13}/k_{A1}\approx 3.4\times 10^5$ and rises to 2.9×10^6 at T=1,200 K. As the reaction rate for B1 depends on the concentration of ethyne, $r_{A1}/r_{B1}=k_{A1}/k_{B1}\times 1/[C_2H_2]$, the adduct rate will possibly surpass the rate of geometry rearrangement at high ethyne concentrations, which means that chain elongation would be the dominant reaction.

A further free energy profile can be seen clearly in Table 2 and Fig. 2 (for 298 K). As shown in Fig. 2, the energy profiles of the three starting species **1**, **2**, and **3** are similar. The main difference is in the final step of the ring closure reaction. If we maintain the spin contamination rules, addition of ethyne to **3** will result in C₆H₆ (see TS6 in Fig. 1, which has a triplet electronic state). As the radical is positioned on

C₁ and C₆ (see TS7 in Fig. 1), closure of the chain is easier (ΔG^\ddagger is only 2.2 kcal mol⁻¹) and results in singlet C₆H₆ (benzene) as the final product. Following the 'HACA mechanism' [9], the first step of H abstraction will result in C₆H₅ (phenyl radical) and a hydrogen atom, which is very endoergic in term of enthalpy. The opposite case was found for the 3-propylidenecyclopropene scheme (formed from **2**+ethyne, the TS addition is shown by TS2), in which the closure reaction requires higher energy ($\Delta G^\ddagger=18.7$ kcal mol⁻¹). Ring closure of TS3 was obtained by chain breaking (could be by elongation of the C–C bond) followed by a C₁ to C₆ closure step. We failed to find the geometry of C₂H₂ addition to C₆H₅ or C₆H₆ (the stable geometries before ring closure), shown in Fig. 1, as the geometry seems to impose a steric hindrance. The optimization results in something else that has a totally unreasonable geometry for this scheme.

Conclusions

The first aromatic (phenyl) formation mechanism, initiated by ethyne addition on ethynyl radical, has been studied using the B3LYP method with a 6–31G(d) basis set. The addition of ethyne has a small entrance channel barrier ($\Delta G^\ddagger=2.1$ kcal mol⁻¹ with respect to the reactants) and results in 1-buten-3-yne-1-yl radical (n-C₄H₃) and 3-methylidenecyclopropene. Further H addition on n-C₄H₃ will produce a triplet state of C₄H₄. In general, C–C bond rotation or H confirmation on C₁ or C₆ has lower barrier energies compared to ethyne addition (4.3 vs 11.8 for **1**, 4.3 vs 11.4 for **2**, 3.0 vs 10.1 for **3**, all values in kcal mol⁻¹). This suggests that molecular rearrangements are preferable although a reversible reaction could occur simultaneously. The closure step of triplet C₆H₆ leading to phenyl radical has the lowest free energy barrier value, see Figs. 1 and 2, ($\Delta G^\ddagger=2.2$ kcal mol⁻¹), and, conversely, 3-propylidenecyclopropene (from **2**+ethyne) has the highest closure energy barrier due to C–C bond elongation and C₁ to C₆ closure. Thus, since all these structural rearrangements have lower energy barriers than ethyne addition, the final product is expected to be phenyl radical (or benzene), although, in reality, other intermediates could affect the final product.

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