

Aromatic Formation from Vinyl Radical and Acetylene. A Mechanistic Study

Debby Natalia[†] and Antonius Indarto^{**}

[†]Clean Energy Research Center, Korea Institute of Science and Technology, PO BOX 131, Cheongryang, Seoul 136-791, Korea
 Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino, Corso Massimo D'Azeglio 48, 10125 Torino, Italy

*E-mail: indarto_antonius@yahoo.com

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The viability of acetylene addition in each step of aromatic formation initiated by vinyl radical and acetylene also with its competition with structure rearrangement is investigated by determining optimal geometries and barrier and reaction energies using quantum mechanical methods. In principle, the addition reaction has more difficult in term of free energy and enthalpy compared to geometry arrangement. Under combustion conditions, *i.e.* T = 1200 K, acetylene addition is unfavorable mechanism as the barrier energy values rise much higher than that of geometry arrangement. However, in longer chain hydrocarbon case, *e.g.* $n\text{-C}_x\text{H}_{x-1}$ where $x \geq 8$, C-C bond rotation is rather difficult and requires high energy to form a ring structure, elongation chain is preferable.

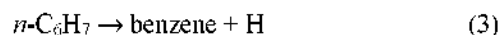
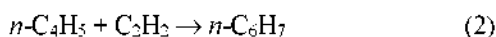
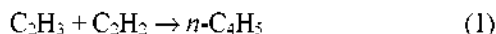
Key Words : Vinyl radical, Acetylene, Aromatic, Ring closure, Chain elongation

Introduction

Aromatic compounds, in particular polycyclic aromatic hydrocarbons (PAHs) and their derivatives (PACs, polycyclic aromatic compounds), are ubiquitous species, introduced in the urban air by incomplete combustion processes. Their presence is widespread and they are known as primary and secondary tropospheric pollutants. Many PAHs present in aerosols have been found to be mutagenic or tumorigenic¹⁻⁵ and a molecular biological pathway linking one of them-benzo[a]pyrene-to human lung cancer has been established.⁶ This is becoming an interesting subject of research activities among experimental, theoretical, and computational to collect the information about its formation and growth. A significant research effort on PAH and soot has been undertaken during recent years.

The formation and growth of aromatic species bridges the main combustion zone chemistry and soot formation. In addition, aromatic molecules are themselves toxic and subject to environmental regulations. Nowadays, the chemistry of aromatics either at normal temperature or at combustion temperature has received attentions. The primary focus is on the formation of the first aromatic ring from small aliphatics as soot growth initiator species.

There are many general schemes of first aromatic formation have been proposed and studied. At low temperature reaction, Bittner and Howard⁷ suggested the formation of benzene via butadienyl and acetylene reaction. This idea then supported by Cole *et al.*⁸ by showing the formation of butadienyl in 1,3 butadiene flame. Moreover, Frenklach *et al.*⁹ proposed the similar mechanism in their mechanism sequence



This reaction steps were believed as the dominant in the first part of the main oxidation zone. Instead of its controversy,¹⁰ few papers (and probably none of them) discussed about the competition reaction between the ring formation following above mechanism and the isomerisation (chain elongation) due to acetylene attack. It should be taken in account as each sequence of the above mechanism does not occur in a single step reaction. There are some structure rearrangements, for example bond rotation and conformation, before it goes to the next step. In this study, we try to address this issue by limiting the case only for first aromatic ring formation initiated by vinyl radical and acetylene reaction. We believe that other species, such as oxygen, nitrogen, or even other radical hydrocarbons, are existed in the real condition in the atmosphere and affect the reaction by another 'type' of competition reaction. However, this is in order to focus the analysis not to be broadening which can make ambiguous and diffused explanations. All studies were performed by computational *ab initio* DFT (density functional theory) method.

Computational Methods

All molecular calculations were carried out by using the Gaussian 03¹¹ system of programs. The stable and transition structure (TS) were determined by gradient procedures¹² within the density functional theory (DFT) and employing the B3LYP functional.¹³ This function is of widespread used and, even if it tends to underestimate some reaction barriers, has generally performed well regarding geometries and energetics.¹⁴ In the case of transition structures, inspection of the normal mode related to the imaginary frequency was sufficient to confidently establish its connection with the initial and final energy minima. The selected TS of some geometry are shown in Figure 1 and explained later on the discussion section. For all possible pathway, the energy evaluations

[†]Present address: Energy & Environment Division, Korea Institute of Science and Technology, PO Box 31, Cheongryang, Seoul 136-791, Korea

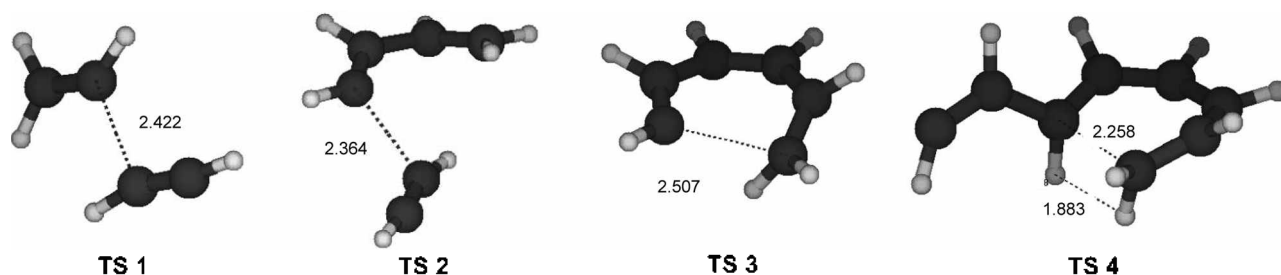


Figure 1. Selected geometry of transition structure (TS). TS1 = C₂H₂ addition on vinyl radical; TS2 = C₂H₂ addition on butadienyl; TS3 = TS of ring closure; TS4 = TS formation of phenylvinyl radical. All values are in Angstrom unit (Å).

were calculated by the 6-31G(d)¹⁵ level of theory. The activation, reaction enthalpies, and free energy were obtained by thermochemical calculation from the vibrational analysis.¹⁵

Results and Discussion

In order to find the best method and basis set applied for the system, acetylene and benzene have been chosen as the model for geometry and surface energy fitting. This choice is realistic since the study will deal with these molecules. Table 1 shows the result of computational using some method and basis set compared to the result from experimental. We observed few differences but generally it was found that the optimized geometry was fairly reasonable to be used as a fundamental structure for the next calculation. For the case of B3LYP/6-31G(d), which will be used in this study, it has a significant geometry similarity with result of experiment, at least up to two decimal digits. Although this simple study and analysis could not be said exactly correct, the general result of the simulation and model could well enough to describe the phenomena.

Following the schematic mechanism, the reaction is initiated *via* vinyl radical and acetylene. We find that this reaction is very exoergic in term of free energy and activation energy (by $\Delta G = -33.8$ kcal/mol, $\Delta E = -48.1$ kcal/mol, at $T = 298.15$ K, 298 for short in the following). This reaction has to surmount the transition energy which is around 3.17 kcal/mol with respects to the enthalpy difference and 10.6 kcal/mol for free energy barrier (ΔG^\ddagger) at room temperature. The straight-forward estimation of the TS geometry is verified by means of a couple of constrained

Table 2. Transition geometry steps from vinyl and acetylene to cyclohexadienyl

Transition Structure (TS) ^a	ΔE^b	ΔG^b		
		T = 298 K	T = 298 K	T = 1200 K
vinyl + C ₂ H ₂ adduct	2.7	3.2	10.6	40.8
H conformation of butadienyl 1 → 2 ^c	4.8	3.5	3.6	4.7
- C ₂ H ₂ adduct A1	2.6	2.3	11.8	41.1
C-C bond rotation 2 → 3	7.3	6.4	7.0	11.8
- C ₂ H ₂ adduct A2	6.0	6.4	13.2	44.9
C ₂ H ₂ addition of butadienyl 3 → 4	2.2	2.7	12.8	47.8
H conformation of hexadienyl 4 → 5	6.4	5.6	5.8	9.7
- C ₂ H ₂ adduct A4	2.6	2.9	10.3	38.2
C-C bond rotation 5 → 6	3.7	2.4	2.8	5.4
- C ₂ H ₂ adduct A5	4.0	3.5	12.4	42.7
Ring closure 6 → 7	1.5	0.6	2.2	9.8

^aEnergy different was calculated refers to the previous stable structure.
^bUnits: kcal/mol. ^cThis column is referring to Figure 2 to see the structure evolution.

optimizations at shorter and larger C-C distance between vinyl radical and acetylene. This confirms the geometrical location of the maximum along the G profile in correspondence to the TS on the E surface, and yields the values reported in Table 2. The acetylene attacks on vinyl radical will result 1 which is unfavorable geometry for the formation aromatic and for closing-ring reaction. This results from the position of radical on the vinyl and effects on the acetylene bond bending of C-H. From this point, the rearrangement of adduct molecule is required by two ways: (1) H conformation to form 2 and continued by C-C single bond rotation to form 3 or (2) C-C single bond rotation and

Table 1. Calculated and experimental data of the optimized geometry of acetylene and benzene in ground state

	HF		B3LYP		PW91	MP2		Experimental
	6-31G(d)	6-311G(2d,p)	6-31G(d)	6-311G(2d,p)	6-31G(d)	6-31G(d)	6-311G(2d,p)	
Acetylene								
C-C	1.1855	1.1781	1.2050	1.1944	1.2142	1.2177	1.2095	1.2024 ¹⁷
C-H	1.0567	1.0550	1.0666	1.0630	1.0727	1.0662	1.0643	1.0625 ¹⁷
Benzene								
C-C	1.3862	1.3821	1.3966	1.3913	1.4015	1.3966	1.3954	1.397 ¹³
C-H	1.0756	1.0748	1.0870	1.0829	1.0934	1.0870	1.0854	1.084 ¹³

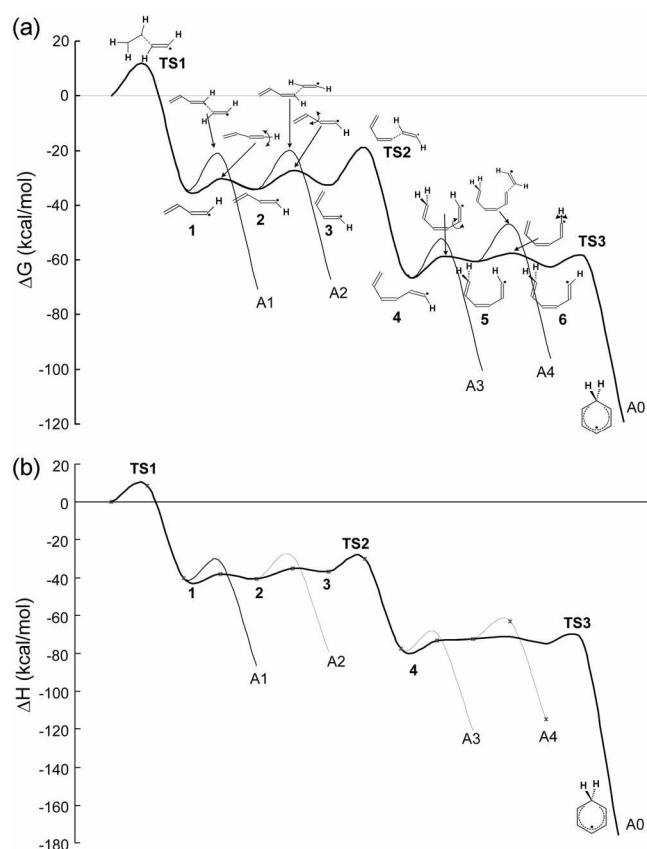


Figure 2. The energy profile for the structure evolution from vinyl + acetylene to cyclohexadienyl: (a) the Gibbs energy at 298 K and (b) the Enthalpy at 1200 K.

continued by H conformation to form **3**. Without this rearrangement scheme, the further adduct reaction with acetylene will produce chain elongation, such an isomerisation, that we will not address in this study. However, we will also discuss the probability of long chain rearrangement steps to achieve ring closure, *e.g.* *n*-C₈H₉ (the Gibbs energy profile is shown in Figure 3).

At this level, the relevant free energy barrier was in this following sequence: 3.6 kcal/mol for H conformation and 6.9 kcal/mol for bond rotation. These values are much preferable compared to the energy value of adduct reaction for each species with C₂H₂. At 298 K, the adduct reaction of **1** + C₂H₂ requires $\Delta G^\ddagger = 11.8$ kcal/mol and **2** + C₂H₂ needs $\Delta G^\ddagger = 13.2$ kcal/mol. From the enthalpy point of view, there was not much different between molecular structure rearrangements and adduct reactions with C₂H₂. Under the combustion conditions, say at 1200 K, the assessment of the free energy profile provides much higher barriers and, consistently, maxima located at shorter intermolecular distances. The barrier height of **1** + C₂H₂ is 41.1 kcal/mol and 44.9 kcal/mol for **2** + C₂H₂. The similar condition was found for the enthalpy calculation which the enthalpy barrier difference between reactants and TS jumped to 8-11 kcal/mol. These data seem to minimize the possibility of chain elongation, but we have to consider that rearrangement reaction is reversible reaction. The enthalpy energy differences are

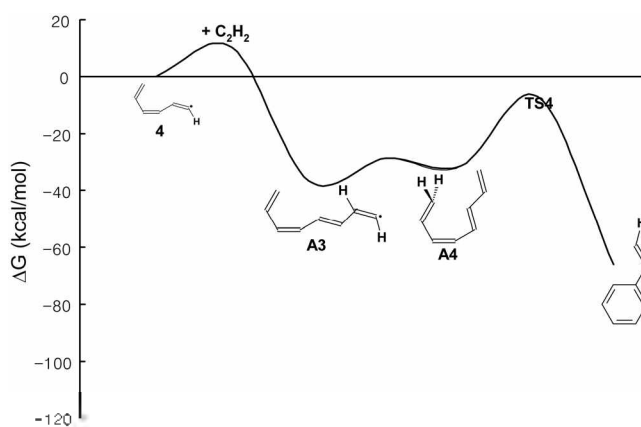


Figure 3. Free energy profile (T = 298 K) of ring closer mechanism for long chain molecule, C₈H₉, by forming phenylvinyl radical.

only -0.51 kcal/mol between **1** and **2** and 2.9 kcal/mol for **2** to **3**. On the other hand, the adduct reaction is exoergic reaction which results stable compound. $\Delta H = -47.8$ kcal/mol for A1 and -43.2 kcal/mol for A2. Although the attack of C₂H₂ is more difficult than that of re-arrangement cases, 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_{12} (forward rate constant from **1** to **2**) to k_{A1} (rate constant for adduct reaction of **1**), $k_{12}/k_{A1} \approx 1.1 \times 10^6$. The lower value is found for the ratio of k_{23} (**2** to **3**) to k_{A2} (adduct of **2**) $\approx 4 \times 10^4$ (T = 298 K). As the rate for A1 and A2 is relative to the concentration of acetylene, $r_{A1} = k_{A1} [C_2H_2]$ and $r_{A2} = k_{A2} [C_2H_2]$, the adduct reaction rate will possibly surpass the rate of geometry rearrangement at high acetylene concentration.

The addition of C₂H₂ to **3** results *n*-C₆H₇ that has a half circle geometry. The adduct reaction is exoergic with $\Delta H = -44.1$ kcal/mol and $\Delta G = -32.1$ kcal/mol at T = 298 K. These values will increase at higher temperature and the products will be less stable. *e.g.* at T = 1200 K, $\Delta H = -40.4$ kcal/mol and $\Delta G = 8.4$ kcal/mol. For this reaction, the activation energy of TS is 2.2 kcal/mol, slightly lower than TS of vinyl + C₂H₂ ($\Delta H^\ddagger = 2.74$), but relatively higher in Gibbs energy different 12.8 kcal/mol (*vs* $\Delta G^\ddagger = 10.6$ kcal/mol for TS vinyl + C₂H₂) at 298 K. Similar to the previous case, the adduct reaction of **3** will result **4** which has unfavorable geometry for cyclic formation. Again, the rearrangement is necessary and finalized by ring closure reaction.

Also similar to the previous energy profile, the TS of geometry transformation has lower Gibbs energy different than that of adduct reaction, for example $\Delta G^\ddagger = 5.8$ kcal/mol for **4** to **5** and 2.8 kcal/mol for **5** to **6** while $\Delta G^\ddagger = 10.3$ kcal/mol for A3 and 12.3 kcal/mol for A4 at T = 298 K. These values will rise at higher temperature that result much unpreferable reaction of C₂H₂ addition reaction. Later, the energy profile can be seen clearly in Table 2 and Figure 2a (for 298 K). We were failed to find the geometry of C₂H₂ addition to **6** as the geometry, shown in Figure 2, looks to give a hindrance. The optimization resulted something else which totally unreasonable geometry for this scheme.

We also calculated the possibility of hydrogen elimination from *c*-C₆H₇. In agreement with Richter and Howard paper,¹⁹ direct elimination of single H to form benzene or dihydrogen to form phenyl was required much energy. Elimination single H from *c*-C₆H₇ followed by spontaneous H loss results $\Delta G = 16.8$ kcal/mol and $\Delta H = 23.7$ kcal/mol and for dihydrogen elimination to form phenyl the energy different is much higher ($\Delta G = 21.7$ kcal/mol and $\Delta H = 35.5$ kcal/mol). We found that H abstraction by free radical H (forming H₂) is much easier which requires $\Delta G^\ddagger = 0$ kcal/mol (almost no barrier).

The long chain molecule, *n*-C₈H₉, produced by addition of C₂H₂ to *n*-C₆H₇ (could be from **4** and **5** shown in Figure 2), still has a probability to form a cyclic molecule. In this case we will only address the benzene-like geometry as *n*-C₈H₉ is also able to form 5 or 7 or even 8-membered ring molecule. The Gibbs energy profile is shown in Figure 3. To assess the closure ring reaction, the geometry re-arrangement is absolutely required, e.g. from A3 to A4. Different from the molecular rearrangement of lower C molecules, C_xH_{x+1} ($x \leq 6$), the required energy (ΔG^\ddagger) is much higher and equal to C₂H₂ addition, ca. 8-12 kcal/mol. It is more difficult to rearrange the structure when the molecule chain is longer. Further elongation is favorable and geometry rearrangement reaction is again reversible. As in the real condition, longer chain molecule of C_{2n}H_{2n-1} was rarely detected; there should be some reaction mechanisms tend to decompose this molecule or reform into more stable compounds. Ring closure reaction (to form phenylvinyl radical) is also less possible due to the effects of very high barrier energy (ΔG^\ddagger) which ca. 24.1 kcal/mol (T = 250 K) or 30.4 kcal/mol (T = 1200 K).

Conclusion

The formation of aromatic, initiated by vinyl radical and acetylene reaction, was studied by using computational quantum mechanics of B3LYP/6-31G(d). The calculation of the enthalpy and Gibbs energy shows that the addition reaction with acetylene is less favorable than molecular rearrangement, especially for high temperature reaction conditions; in this case 1200 K. The TS energy barrier of the adduct reaction is almost > 2 times of the re-arrangement geometry. Molecular arrangement step is required to result the structure which thermodynamically favors to form stable cyclic molecule or aromatic. Although cyclic molecule can be obtained from longer chain molecule, e.g. *n*-C₈H₉, but it shows higher barrier energy than shorter chain molecule, e.g. *n*-C₆H₇, for the ring closure reaction.

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