KINETIC AND PRODUCTS OF C\textsubscript{3}H\textsubscript{3} AND C\textsubscript{4}H\textsubscript{2} REACTION: THEORETICAL AND COMPUTATIONAL STUDY

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Abstract

The formation of first aromatic ring was suggested to be a crucial step of the PAHs and soot growth mechanism. In general, four-, five-, six-, or seven-membered ring molecules could be formed by the addition reaction of two hydrocarbon molecules resulted from many different pathways. Small hydrocarbon molecules with numerous concentrations during combustion/pyrolysis are suspected to play an important role. Propargyl radical (\textbullet{}C\textsubscript{3}H\textsubscript{3}) and butadiene (C\textsubscript{4}H\textsubscript{2}) have been chosen as the initial reactants in this discussion, since they are found at relatively high concentrations in flame experiments to examine the above particular reaction. Following initial addition mechanisms, their adduct intermediate can form a ring molecule and undergo subsequent rearrangement. All possible molecular structures were considered and the viability of each channel was assessed through a “RRKM + master equation” kinetic study. This study is an attempt and example to develop and apply molecular computational method for solving problems in the chemical engineering.

Keywords: reaction kinetic, ab-initio calculation, RRKM theory, unimolecular reaction, propargyl, butadiene.

Abstrak

Reaksi pembentukan cincin aromatic pada senyawa hidrokarbon merupakan mekanisme awal terpenting dari pembentukan Polisiklik Aromatik Hidrokarbon (PAH) dan jelaga karbon. Secara umum, senyawa hidrokarbon dengan cincin berjumlah empat, lima, enam, atau tujuh dapat dibentuk oleh reaksi gabungan dua molekul hidrokarbon. Molekul hidrokarbon dengan jumlah atom karbon rendah akan memainkan peranan penting ditinjau dari besarnya konsentrasi senyawa ini saat pembakaran/pirolisis. Dalam diskusi ini, reaksi propargil radikal (\textbullet{}C\textsubscript{3}H\textsubscript{3}) dan butadiena (C\textsubscript{4}H\textsubscript{2}) digunakan sebagai studi kasus karena konsentrasi mereka yang relatif tinggi dalam percobaan laboratorium dengan menggunakan bunsen. Secara garis besar, reaksi pembentukan rantai lingkar (cincin) dapat tercapai baik secara langsung setelah reaksi adisi atau melalui penataan ulang molekul. Berbagai struktur molekul dan mekanisme yang mungkin ada dalam reaksi ini akan dianalisis melalui studi kinetika "RRKM + persamaan master (master equation)". Studi ini juga ditujukan sebagai usaha dan contoh untuk memperkenalkan penggunaan kimia komputasi molekuler dalam menyelesaikan berbagai problem di bidang teknik kimia.

Kata kunci: kinetika reaksi, perhitungan ab-initio, teori RRKM, reaksi unimolekular, propargil, butadiena.
1. Introduction

During the last decade, the speed of the computers has grown considerably and the computational investigation of realistic models of molecular compounds is becoming a standard practice, including in the field of Chemical Engineering (National Research Council, 2003). Current applications range from the investigation of the mechanism of synthetically useful reactions to the study of short lived intermediates, e.g., intermediates in thermal chloroform decomposition (Indarto et al., 2009a), until the catalytic surface reactions, e.g., polycyclic aromatic hydrocarbons formation in the presence of carbonaceous surface (Indarto et al., 2010). For thermal reactions, standard state-of-the-art ab-initio quantum chemical methods are already capable of providing a complete description of what happens at the molecular level during bond-breaking and bond-forming processes.

In this discussion, we would like to address the advance of theoretical computational science to understand complex reaction, i.e. 'fast' reaction with numerous intermediates. A detailed understanding of the 'fast' reaction pathway in the presence numerous intermediates will boost our ability to design new and to control known reactions, e.g., combustion/pyrolysis condition. As an example, the cyclic molecule formation involves the 1-butene-3-ene-1-yl radical and 3-methylidenecyclopropene radical from the addition of small aliphatics known as rate-determining step of soot growth (Indarto, 2009; Frenklach et al., 1986; Frenklach and Warnatz, 1987; Homman and Wagner, 1967). The identification of the elementary reactions leading to the first aromatic compound consequently is of great importance. In addition, ring molecules are themselves toxic and subject to environmental regulations (Dockery, 2001; Pope et al., 2002).

There are many general schemes leading to cyclization (ring formation) have been proposed and studied (eg: Romero and Indarto, 2008; Indarto et al., 2009b; 2010). At low temperature reaction, Bittner and Howard (1981) suggested the formation of benzene via butadienyl and acetylene reaction. This idea then partly supported by Cole at al.'s experiment (Cole et al., 1984) showing the formation butadienyl in 1,3 butadiene flame. In 1986, Frenklach et al. proposed the similar mechanism in their mechanism sequence.

\[ C_2H_5 + C_2H_2 \rightarrow n-C_6H_5 \]  
\[ n-C_6H_5 + C_3H_2 \rightarrow n-C_6H_7 \]  
\[ n-C_6H_7 \rightarrow \text{benzene + H} \]

The second most cited reaction is by the reaction between n-C_6H_2 and C_2H_2 which end up with phenyl (C_6H_5) (Frenklach and Warnatz, 1987). These reaction steps were believed as the dominant in the first part of the main oxidation zone. Unfortunately, there has been a longstanding debate regarding the possible importance of even-carbon pathways involving the reaction. (1) Both n-C_6H_2 and n-C_6H_5 have isomers, i-C_6H_2 and i-C_6H_5, that are more stable than long carbon chain (Miller and Melius, 1992), and distinguishing between the isomers on a current mass spectrometer technique is rather impossible. Although, later on, Walch (1995) mentioned that the both normal and iso molecules can react easily to form phenyl as the barriers are low. (2) First ring formation by these mechanisms does not occur in single step reaction. A stepwise reaction can make the global reaction very slow.

The recombination of hydrogen-deficient propargyl radicals (C_3H_3) appears to provide the dominant pathway in most flames (Westmoreland et al., 1989). The recombination of two propargyl radicals is already becoming a pivotal reaction subject for direct aromatic molecule both for experimentalists and theoreticians (Melius et al., 1992; Alkemade and Homann, 1989; Marinov et al., 1997). Miller and Melius (1992; Melius et al., 1992) showed that the reaction of two propargyl radicals is a much better candidate for forming the first ring molecule.

\[ C_3H_3 + C_3H_3 \rightarrow C_6H_5 + H \]  
\[ C_3H_3 + C_3H_3 \rightarrow C_6H_6 \]

Later on Miller and Klipenstain (2003) reconsidered that the above mechanism has serious deficiencies as they did not consider the reaction pathway of fulvene formation. Following the Stein et al.'s (1990) experiment.
result (see Figure 1). 1,2-dimethylenecyclobutene and fulvene should be the major products of 1,5-hexadiyne’s flame at two different temperature regions ($T=460-470^\circ C$ and $500-550^\circ C$, respectively. Moreover, Westmoreland et al. (1989) found insufficient $C_2H_3$ to account for soot formation in 1,2-butadiene flames. Therefore, propargyl recombination is almost certainly not the only reaction creating ring molecules in flames.

Apart from above discussion, other reactions between propargyl and polyynes are likely to play an important role in the hydrocarbon growth process. Propargyl and some polyynes have been reported to reach rather high concentrations in the oxidation zone of premixed acetylene (Westmoreland et al., 1989; Yang et al., 2007; Indarto, 2009) and benzene (Li et al., 2009) flames. This comes to our mind that the adduct between two moieties is relative ease formation and stable. In oxidizing atmosphere, propargyl may be readily formed by methylene with acetylene or some H abstraction mechanism. In the case of polyyne molecules, butadiene ($C_4H_2$) has been detected as the highest concentration of polyynes molecules in pyrolysis or combustion. In this present study, we would like to address the issue of ‘early-stage’ PAH growing reactions, first ring formation, as a product of propargyl addition to butadiene.

2. Methodology

2.1 Kinetic and thermochemistry calculation method: Quantum analysis

In this study, the thermochemistry properties of the molecules and reactions were calculated by using ab-initio simulation employing density functional theory (DFT). Numerous references on the application of ab-initio simulation in the field of Chemistry and Chemical Engineering have been published. However, a brief explanation of the model methodology will be explained below. Density functional theory (DFT) (Parr and Yang, 1989; Becke, 1988) theory is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry. The main idea of DFT is to describe an interacting system via its electron density and not by a many-body wave function. Hence the name density functional theory comes from the use of functionals of the electron density. Compared to ab initio methods, such as post-Self Consistency Field (post-SCF) methods based on a Hartree-Fock (Levine, 1991) calculation (as Møller-Plesset perturbation theory, configuration interaction, or coupled cluster (Cramer, 2002)), the computational costs of the DFT method are relatively low and quite satisfactory for large computational model. In this investigation, the DFT methods were employed for most investigations of the PAHs growth models, especially in the first part of the study where large molecular structures were used as computational models.
2.2 Rice Ramsperger Kassel Marcus (RRKM) theory and master equation

One the thermochemistry data, including low-frequency rotation and translation vibrations, were obtained, the RRKM combined with Master equation analysis was constructed to analyze the unimolecular kinetic. The Rice Ramsperger Kassel Marcus (RRKM) theory (Holbrook et al., 1996) is widely used to interpret the behavior of thermal and photochemical reactions (Gilbert and Smith, 1990). RRKM is one of the fundamental development of unimolecular kinetic based of the Lindemann mechanism (Lindemann, 1922) and its development by Hinshelwood (Hinshelwood, 1927). Treatment of molecular vibrations and rotations are the key point in this theory.

When a molecule reacts via a unimolecular reaction to form an intermediate, this intermediate could have an excess of rovibrational energy \( E^* \). By collisions with buffer gas, part of \( E^* \) is dispersed and after an adequate number of collisions, a thermal energy distribution (Boltzmann’s distribution, thermal equilibrium) is reached. At transition state, the excess of energy becomes \( E = E^* + E_0 \), where \( E_0 \) is the energy barrier. Conventionally, all the energies include the zero point corrections.

The rate constant to overcome the \( E_0 \) barrier is function of the energy \( E^* \) of the system: at high energy reaction is fast, and when \( E^* \) is below \( E_0 \), rate constant is zero by definition. RRKM theory describes the changes of the rate constant with the energy. It is possible to demonstrate that (Holbrook et al., 1996):

\[
k(E^*) = \frac{W(E^*)}{\hbar \rho(E^*)} = \frac{1}{\hbar} \frac{W(E^* - E_0)}{\rho(E^*)}
\]

where \( k(E^*) \) is the rate constant for the unimolecular process, in \( s^{-1} \). \( W(E) \) is the sum of the states: the total number of the states between 0 and \( E^* \). \( \rho(E) \) is the density of states: the number of the states between \( E^* \) and \( E^* + \delta \). The relation between \( W(E) \) and \( \rho(E) \) is:

\[
\rho(E^*) = \frac{\partial W(E^*)}{E^*}
\]

\( E^* \) or \( E^* \) can be partitioned into vibrational \( (E_v) \) and rotational \( (E_r) \) energies, and \( W(E) \) and \( \rho(E) \) are calculated from vibrational frequencies and moments of inertia, by using exact states count algorithms (Holbrook et al., 1996):

\[
W(E) = \sum_{E_v, E_r} P(E_v) = \sum_{E_v, E_r} P(E_v) \sum_{E_r} P(E_r)
\]

\[
\rho(E) = \sum_{E_v, E_r} P(E_v) \rho, (E_v - E_r)
\]

where \( P(E_v) \) is the number of vibrational states with vibrational energy of \( E_v \) and \( P(E_r) \) is the number of rotational states with rotational energy of \( E_r \). RRKM only shows how the rate constant changes with the
energy, but during the reaction the excited species could also collide with the buffer gas. Master equation is a complex system of equations which calculates the probability of the energy loss and gain at every collision with the buffer and the probability of competition among the reactions through the rate constant $k(E)$ and energy loss and gain at every collision with the buffer gas.

$$\frac{dA_i}{dt} = \omega \left( \sum_j P_{ij} A_j \right) - \omega A_i - k_i A_i \quad (10)$$

where $A_i$ is the concentration of reactant (A) in state number i (which has energy $E_i$), $\omega$ is the collision frequency, $P_{ij}$ is the probability that a molecule that is in its state j before collision is in state i after a collision, and $k_i$ is the rate constant for decomposition of $A_i$ to give products ($k_i = k(E_i)$).

Knowing the initial $E^*$ energy, the pressure of the buffer gas (usually $N_2$, He, Ar, $O_2$, etc), the type of the gas, it is possible to estimate the collision frequency ($\omega$) between the buffer gas and the molecule and numerically solve the Master Equation. The result is the concentration of A in function of the time $t$ (proportional to the number of collisions). At large $t$, collisions with buffer gas dissipate the excess of rovibrational energy and the system reaches the thermal equilibrium: in this borderline case, $k(E)$ coincides with the rate constant calculated by transition state theory (TST) (Holbrook et al., 1996):

$$k = \frac{1}{\hbar} \frac{Q^*}{Q} e^{E_i/\hbar kT} \quad (11)$$

where $Q$ and $Q^*$ are the partition functions for the intermediate and the transition structure, respectively.

2.3 Simulation strategy and method comparison

A preliminary exploration was devoted to find a proper DFT functional able to produce energetic close to benchmark calculations by CCSD(T) (Cramer, 2002) method. For this work, a published CCSD(T)'s computational model of ethynyl radical, $^1\text{C}_2\text{H}_2$, and butadiene reaction, which appears to be close to our model: propargyl + butadiene, by Landera et al. (2008) has been chosen. Here, we compared the computed energy of four different functionals, i.e. B3LYP (Becke, 1993; Lee et al., 1988), mPW1K (Meijer and Sprik, 1996), M05 (Zhao et al., 2006), and M05-2X (Zhao et al., 2006), and the results are presented in Table 1 below. It seems that the newly density functional proposed by Thrular’s group, M05-2X functional produces closer results to the CCSD(T) values, compared to others. Following this result, all further computations were carried out by using M052X functional.

All optimization and thermochemistry calculations were done at cc-pVTZ level of basis set, and energy was reassessed by single point cc-pVQZ calculation. The complete basis set (CBS) limit was then approached by the Halkier's extrapolation formula (Halkier et al., 1998). In order to obtain the distribution of reaction products, a RRKM + Master Equation kinetic study was finally conducted. For this purpose, Barker’s Multiwell software was exploited (Barker 2001; Barker et al., 2009).

The reported yield of each exit channel or well is the average of $10^6$ simulations and has an uncertainty $\leq \pm 3\%$. Details on the choice of various parameters and other considerations for the kinetic calculation of propargyl radical + butadiene, as well as the steps in the computational procedure, will be better explained in Result and discussion section.

3. Result and Discussion

Propargyl is a unique molecule with reasonably stabilized radical of two structures, as shown in Figure 3.

![Figure 3. Propargyl molecules (A) two hydrogens at C-radical center; and (B) one hydrogen at C-radical center](image)

If we refer to the radical position in propargyl, there will be four possibilities for the opening reactions between butadiene+propargyl. Two possibilities are resulted from propargyl A attacks butadiene at the terminal and the middle carbon chain and the remaining possibilities come similarly from B bounds with two carbon positions of butadiene. The overall reactions are shown in Figure 4.
Table 1. Preliminary (comparison of the potential-energy) study of DFT functionals

|                  | B3LYP/CBS | mPW1K/CBS | M05/CBS | M052X/CBS | CCSD(T)/CBS |
|------------------|-----------|-----------|---------|-----------|-------------|
| C₂H + C₄H₂       | 0.00      | 0.00      | 0.00    | 0.00      | 0.00        |
| C₆H₃             | -72.27    | -77.54    | -74.63  | -75.19    | -70.20      |
| TS ring closure  | 40.66     | 40.35     | 39.79   | 38.62     | 37.60       |
| cyclo-C₆H₃       | 1.33      | -7.58     | -1.72   | -4.65     | -4.90       |
| C₆H₃             | 0.00      | 0.00      | 0.00    | 0.00      | 0.00        |
| TS H loss        | 44.03     | 48.82     | 50.67   | 47.32     | 45.80       |
| Product          | 40.30     | 44.02     | 43.71   | 39.70     | 40.50       |

Note: All values are in kcal/mol. ¹CCSD(T)/CBS results are from reference Landera et al. (2008).

Figure 4. The overall scheme of propargy (C₃H₃) + butadiene (C₄H₂) reaction
Note: all mentioned molecule numbers (bold numbers) in the text will refer to this figure.

3.1 Entrance reactions
In accordance with above explanation, there are four possibilities of addition reactions. These reactions are slightly exoergic and have to overcome the barrier ca. 9-17 kcal/mol, giving central carbon attack shows to be more difficult compared to the terminal one. Although it looks easy to be occurred, the situation is changed in higher temperature condition, e.g.,
combustion/pyrolysis. Take an example at 1900 K, the Gibbs's assessment shows that the reaction barrier goes up to 67-74 kcal/mol and the products are highly endoergic in all cases. This situation could drive the reactions back to the reactants in high temperatures.

A schematic diagram of potential energy surface obtained for 4 entrance points of CCH$_3$ + C$_4$H$_2$ addition is provided in Figure 5-8. In this case, we chose four possible reaction pathways corresponding to the lowest activation energies. The TS Add1 – TS Add4 relate to the C-to-C attack positions whether it is carbon's head/tail of CCH$_3$ to C$_1$ (terminal) or C$_2$ (middle) of C$_4$H$_2$. At low temperature, 298K, it seems only TS Add1 and TS Add4 to be the most possible entrance channels ($k_{TS \text{Add1/TS Add2}} \approx 1.5 \times 10^5$; $k_{TS \text{Add1/TS Add3}} \approx 2.5 \times 10^6$; $k_{TS \text{Add1/TS Add4}} \approx 0.8$). In high temperatures, e.g., 1900K, the k difference these four channels are smaller than before, $k_{TS \text{Add1/TS Add2}} \approx 12$; $k_{TS \text{Add1/TS Add3}} \approx 7.5$, and the addition reaction could come from any channels.

In all figures, it illustrates that 1-ethynylcyclopentadienyl, 18, is found in all cases with lower wells and saddlepoints compared to others. The presence of resonance phenomenon occurred in 1-ethynylcyclopentadienyl has been mentioned by da Silva and Bozzelli (2009) as the major reason for molecular stability. The resonance stabilization energy of cyclopentadienyl is considerably greater than that of propargyl.

![Figure 5](image1.png)

**Figure 5. The potential energy charts of the most probable entrance reactions from TS Add 1. The TS Add 1 is shown in the left picture**

![Figure 6](image2.png)

**Figure 6. The potential energy charts of the most probable entrance reactions from TS Add 2. The TS Add 2 is shown in the left picture**
4- and 7-membered rings are also found to be possible in some cases while, interestingly, 6-membered ring is hardly produce. Only TS Add 4 result molecule 4a with barrier ca. 30 kcal/mol respects to 9 (intermediate product of TS Add 4).

The ring closure mechanism for 5-membered ring (cyclopentadiene) shows to be in a range of 11 to 21 kcal/mol, except for TS 1-15 (\(\Delta E^t = 63.5\) kcal/mol). This exception case occurs because the closure mechanism did not involve the radical carbon and result new two radical points (radical breeding) as the product.

Four-membered ring formation proceeds in slightly higher barrier energy than cyclization to cyclopentadiene, 1-2 kcal/mol higher respect to the cyclizations of 5-ring formation. Surprisingly, the formation of 7-membered ring is shown to be easier than cyclization to 6-membered (benzene-like) molecules. When we analyze carefully to the long chain structure, 7-ring molecules could be obtained simply by terminal-terminal carbon bonding of two end-sides of the chain. The only barrier that has to be overcome is the distance between the 2 carbons which usually quite far (ca. 4.7 \(\text{Å}\)).

![Figure 7](image1.png)

Figure 7. The potential energy charts of the most probable entrance reactions from TS Add 3. The TS Add 3 is shown in the left picture.

![Figure 8](image2.png)

Figure 8. The potential energy charts of the most probable entrance reactions from TS Add 4. The TS Add 4 is shown in the left picture.
3.2 Ring transformation reactions

Figure 9 illustrates the possible pathways for the transformation from cyclo-
C₆,₅,₆,7 to 6-membered ring molecules. In general, this way for 6-ring molecules
generation is hardly visible as the barrier is
very high with endoergic products. Taking an
element of direct transformation of 1-
ethylcyclopentadienyl into fulvene-like
molecule, H₂C-C₆H₃, this reaction has to
overcome the barrier of ΔE₁₂₀₀₀K = 86.5
kcal/mol. Temperature increment did not
help much as the free energy barrier is still
relatively high, e.g., ΔG₁₉₀₀₀K = 51.8 kcal/mol.

A similar pattern of high-energetical
hills and wells of fulvene to benzene
transformation was reported before by Miller
and Klippenstein (2003). The barriers of this
molecular rearrangement were laid above 60
cal/mol. Although the above routes are
shown in Figure 9 are rarely possible, these
path ways were explicitly included in the
kinetic calculation.

3.3 Uni-molecular rearrangements

In order to obtain stability, some
molecules could perform molecular
rearrangements either by transferring one H
to another positions (including direct H-loss)
or forming/breaking a bond. Some
mechanisms of new ring formation could end
up with the formation of high energetic
intermediate product, e.g., 3 (+17 kcal/mol
higher than 1 due to radical-breeding).
Taking intermediate 3 as an example, to
reduce the potential energy, 3 could transfer
1 H (a) to allow the radical to be more
delocalized, e.g., 3a, or (b) to form of new σ-
band with another radical, e.g., 3a. For these
two H-transfers, the barriers are ca. 42-49
kcal/mol. Another possible way of
rearrangement is by forming a new σ-band
between the two radical sites, e.g., 22. This
way could be more favorable than the
previous way, with giving barrier only 13
kcal/mol than ΔE₁ of TS H-transfer. In some
cases, i.e. TS 3a-19, the barrier is even
smaller (less than 1 kcal/mol). Bicyclic
products, such as 11 and 19, could one of the
favorable products as these molecules are
thermodynamically stable as far as it contains
aromaticity. Kaiser et al. (2003) also
mentioned the presence of 19 as the most
stable isomers in binary collisions between
carbon atom, C(14P), with benzene.

3.4 Kinetic of RRKM and master equation

Kinetic parameters

In order to obtain product distribution
of propargy and butadiene reaction,
MultiWell (Barker 2001; Barker et al., 2009)
program suite was employed. This software
enables us to parameterize hindered
rotations, calculating sum and densities of
states, and obtaining microcanonical RRKM
rate coefficients from properties of the
potential energy surfaces. In this kinetic
studies, 36 species, either intermediates,
reagents, and products, were identified. 54
transition states were also included in the
mechanism and the simulation was
conducted at atmospheric pressure (1 atm).

Collision frequencies were calculated
by using the Lennard-Jones parameters given
in Table 2.

Table 2. Lennard-Jones parameters

| Parameter | Value   |
|-----------|---------|
| α (A) for collider | 3.74    |
| ω/k_B (K) for collider | 820     |
| MW (g/mol) of collider | 28.0    |
| α (A) for well | 6.0     |
| ω/k_B (K) for well | 450.0   |
| coeff. α (cm⁻¹) energy transfer | 2800    |

For the collider, the Lennard-Jones
parameters were set similar as nitrogen gas
while for all the intermediates (“wells”),
the parameters were assumed to be the same one.
to the others. Special for energy transfer coefficient ($\alpha$), we did a test to analyze the effect to the global products distribution and the result is shown in Figure 10.

As shown in Figure 10, the selectivities of product, i.e. two products, 1-ethynylcyclopentadienyl (18) and 1,4,6-triyne (5) + H, in this case, are only slightly affected by the variation of energy transfer coefficients ($\alpha$). Later, the value of $\alpha = 2800$ cm$^{-1}$ will be use for further kinetic simulation.

3.5 Kinetic result and discussion

As it was mentioned above, the most favorable two channels for the propargyl radical + butadiene addition are TS Add1 and TS Add4. For this reason, we consider two kinetic models starting from: (1) the intermediate 1, as adduct of TS Add1, and (2) 9 as intermediate adduct of TS Add4. In order to access wide ranges of combustion or pyrolysis temperatures, the kinetic simulation was done at temperatures varied between 300 and 3000 K.

For the reaction of propargy radical with butadiene from TS Add-1 (Figure 1), at low temperatures ($\leq 700$K), the dominant reactions is the formation of adduct 1. In this stage, 5-membered ring molecules, 14 and 18, are starting to be formed; however, the
selectivities of those molecules are too small to be considered significant. Above 700K, the formation of 18 is growing fast and at 900K, the selectivity of 18 surpasses the selectivity of production 1. As 18 is produced through stepwise mechanism of $1 \rightarrow 14 \rightarrow 18$, increasing temperatures has shifted the reaction and drive 1 to form 5-membered ring 14 and end with formation 18. As shown in Figure 4, the transition structure of ring closure is sufficiently low in energy (ca. 17 kcal/mol respects to 1) and could be the lowest among other TS. The bottleneck of the stepwise reaction of formation 1 could be the H transfer to allow one radical more delocalized inside the ring which lies about 26 kcal/mol from 14. However, increasing temperatures will raise the free energy of TS addition and intermediate 1 to be more endoergic. This situation drives the reaction back to reactant side instead going through to the next reactions. At 900K, the total yield of products is only 55%. At higher temperatures, this value continuously decreases and approaches 0% at very high temperature, e.g., at 3000K, the product yield is only 4%. The selectivity of 18 reaches maximum at 1400K which shows almost all of reactions (~99%) convert to this product. At more than 1500K, direct H loss becomes the dominant channel, mostly H loss from 1 to 1,4,6-triyne, 5, + H. Another possible channel of H loss comes from molecule 9 into epta-5,6-dien-1,3-dino, 9a.
Another favorable channel of addition obtained from addition of propargyl radical + butadiene is TS Add-4 (Figure 12). In general, the pattern of global reactions is not much different. At low temperatures (< 900K), the formation of adduct 9 is dominant. At > 900K, an analogous reaction of formation 18 is starting to be the major pathway. In this case the channel of formation 18 could come from a stepwise mechanism of $9 \rightarrow 30 \rightarrow 18$. The situation is exactly similar to the first case of TS Add-1, where the barriers lies about 21 kcal/mol respect to 9 for ring closure and 26 kcal/mol respect to 30 for H-transfer (see Figure 8). A product distribution with predominant H loss from 9 to 9a is found at high temperature conditions ($T > 2000K$). As it was predicted before, the production of 6-membered ring is hardly occurred due to high energy barrier. TS Add-4, the only channel shows the 6-ring molecules, produce 4a in very low selectivity (< 5%). Moreover, we can conclude that 6-membered ring formation could not be (minor importance) obtained from unimolecular mechanism of adduct between propargyl radical and butadiene.

4. Conclusions

To this end, we have explored several reaction pathways starting from the addition of the propargyl radical to butadiyne. Using a “RRKM + master equation” approach for kinetic simulation, it was found that that a cyclic-molecule, 1-ethynylcyclopentadienyl, was formed with high selectivity at intermediate temperatures (ca. 1000 < $T < 2000K$). For temperatures higher than 2000K, the reaction will be dominated by H loss. By contrast, the formation of an aromatic six-membered ring was found not to be significant.

From the above example, a deeper and thorough exploration of reaction mechanism could obtain by using molecular computational method. It will allow us to investigate the presence of transition state molecules and intermediates in proper way that is difficult to distinguish in the real experimental condition. It means that the probability of the products and reaction mechanism can be evaluated based on energy profile (potential energy surface, enthalpy, etc.), molecular configuration (electron and bonding), and inter molecular interactions.

References

Adamson, J. D.; Morter, C. L.; DeSain, J. D.; Glass, G. P.; Curl, R. F. J. Propargyl from the reaction of singlet methylene with acetylene. *Phys. Chem.* 1996, 100(6), 2125-2128.

Alkemade, U.; Homann, K. H., Formation of C$_6$H$_6$ isomers by recombination of propynyl in the system sodium vapour/propynylhalide, *Z. Phys. Chem. NeueFolge.* 1989, 161, 19-34.

Barker, J. R. Multiple-well, multiple-path unimolecular reaction systems. I. MultiWell computer program suite. *Int. J. Chem. Kinetics.* 2001, 33(4), 232-245.

Barker, J.R.; Ortiz, N.F.; Preses, J.M.; Lohr, L.L.; Maranzana, A.; Stimac, P. J.; Nguyen, L. T. *MultiWell-2009 Software*; University of Michigan: Ann Arbor, MI, 2009.

Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 1993, 98, 5648-5652.

Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A.* 1988, 38(6), 3098–3100.

Bittner, J. D.; Howard, J. B. Composition profiles and reaction mechanisms in a near-sooting premixed benzene/oxygen/argon flame. *Proc. Combust. Inst.* 1981, 18(1), 1105-1116.

Cole, J. A.; Bittner, J. D.; Longwell, J. P.; Howard, J. B. Formation of aromatic compounds in aliphatic flame. *Combust. Flame.* 1984, 56(1), 51-70.

National Research Council, Committee on Challenges for the Chemical Science in the 21st Century.*Beyond the Molecular Frontier*; National Academies Press.: Washington, 2003; 71-94.

Cramer, C.J. *Essentials of Computational Chemistry*; John Wiley & Sons, Ltd.: Chichester, 2002; 191–232.

da Silva, G.; Bozzelli J. W., The C$_6$H$_5$ fulvenallenyl radical as a combustion intermediate: potential new pathways to two- and three-ring PAHs. *J. Phys. Chem. A.* 2009,
Dockery, W. D. Epidemiologic evidence of cardiovascular effects of particulate air pollution. *Environ. Health Perspect.* **2001**, 109(4), 483-486.

Frenklach, M.; Clary, D. W.; Yuan, T.; Gardiner, W. C., Jr.; Stein, S. E. Mechanism of soot formation in acetylene-oxygen mixtures. *Combust. Sci. & Technol.* **1986**, 50(1-3), 79–115.

Frenklach, M.; Warnatz, J. Detailed modeling of PAH profiles in a sooting low-pressure acetylene flame. *Combust. Sci. & Tech.* **1987**, 51(4-6), 265-283.

Gilbert, R. G.; Smith, S. C. Theory of unimolecular and recombination reactions. Blackwell Scientific, Oxford, 1990.

Hinselwood, C. N. On the theory of unimolecular reactions. *Proc. R. Soc. Lond. A* **192**, 113, 230-233.

Hippler, H.; Troe J.; Wendelken H. J. Collisional deactivation of vibrationally highly excited polyatomic molecules. II. Direct observations for excited toluene. *J. Chem. Phys.* **1983**, 78(11), 6709-6717.

Holbrook, K. A.; Pilling M. J.; Robertson S. H. *Unimolecular reactions*; John Wiley & Sons: Chichester, 1996.

Homann, K.; Wagner; H. G. Some new aspects of the mechanism of carbon formation in premixed flames. *Intl. Symp. Combust.* **1967**, 11(1), 371-379.

Indarto, A.; Giordana A.; Ghigo, G.; Maranzana, A.; Tonachini, G. Polycyclic aromatic hydrocarbon formation mechanism in the "particle phase". A theoretical study. *Phys. Chem. Chem. Phys.* **2010**, 12, 9429-9440.

Indarto, A. Soot growing mechanism from polyynes: A review. *Environ. Eng. Sci.* **2009**, 26(5), 251-257.

Indarto, A.; Choi, J. W.; Lee, H. Oxidation of chloroform in a gliding-arc plasma: observation of molecular vibrations. *IEEE Trans. Plasma Sci.* **2009a**, 37(8), 1526-1531.

Indarto, A.; Giordana, A.; Ghigo, G.; Tonachini, A. Formation of PAHs and soot platelets: multi configuration theoretical study of the key step in the ring closure–radical breeding polyyne-based mechanism. *J. Phys. Org. Chem.* **2009b**, 23(5), 400-410.

Kaiser, R. I.; Vereecken, L.; Peeters, J.; Bettinger, H. F.; Schleyer, P. v. R.; Schaefer, H. F. III. Elementary reactions of the phenyl radical, C₆H₆, with C₃H₄ isomers, and of benzene, C₆H₆, with atomic carbon in extraterrestrial environments. *Astro. & Astrophys.* **2003**, 406(2), 385-391.

Landera, A.; Krishtal, S. P.; Kislov, V. V.; Mebel, A. M.; Kaiser, R. I. Theoretical study of the C₆H₃ potential energy surface and rate constants and product branching ratios of the C₆H(2Σ⁺) + C₄H₄(1Σ(g)+) and C₆H(2Σ⁺) + C₄H₃(1Σ(g)+) reactions. *J. Chem. Phys.* **2008**, 128(21), 214301.

Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B.* **1988**, 37(2), 785-789.

Levine, I. N. *Quantum chemistry*; Prentice Hall: New Jersey, 1991; 455-544.

Li, Y.; Zhang, L.; Tian, Z.; Yuan, T.; Zhang, K.; Yang, B.; Fei. Q. Investigation of the rich premixed laminar acetylene/oxygen/argon flame: Comprehensive flame structure and special concerns of polyynes. *Proc. Combust. Inst.* **2009**, 32(1), 1293-1300.

Lindemann, F. A. Discussion on the radiation theory of chemical action. *Trans. Faraday Soc.* **1922**, 17, 598-606.

Marinov, N. M.; Castaldi, M. J.; Melius, C. F.; Tsang, W. Aromatic and polycyclic aromatic hydrocarbon formation in a premixed propane flame. *Combust. Sci. Technol.* **1997**, 128(1-6), 295-342.

Meijer, E. J.; Sprik, M. A density-functional study of the intermolecular interactions of benzene. *J. Chem. Phys.* **1996**, 105(19), 8684-8689.

Melius, C. F.; Miller, J. A.; Evleth, E. M. Unimolecular reaction mechanisms involving C₃H₆, C₄H₄, and C₆H₆ hydrocarbon species. *Proc. Combust. Inst.* **1992**, 24(1), 621-628.
Kinetic And Products Of C$_3$H$_3$ And C$_4$H$_2$ Reaction (A. Indarto)

Miller, J. A.; Klippenstein, S. J. The recombination of propargyl radicals and other reactions on a C$_6$H$_6$ potential. *J. Phys. Chem. A.** 2003, 107(39), 7783–7799.

Miller, J. A.; Melius, C. F. Kinetic and thermodynamic issues in the formation of aromatic compounds in flames of aliphatic fuels. *Combust. Flame.** 1992, 91(1), 21-39.

Parr, R.G.; Yang, W. Chapter 3. *Density functional theory of atoms and molecules*; Oxford University Press: New York, 1989.

Pope, C. A.; Burnett, R. T.; Thun, M. J.; Valle, E. E.; Krewski, D.; Ito, K.; Thurston, G. D. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *Amer. Med. Assoc. (JAMA).** 2002, 287(9), 1132-1141.

Santiago, R. M.; Indarto, A. A density functional theory study of phenyl formation initiated by ethynyl radical (C$_2$H$_3$) and ethyne (C$_2$H$_2$). *J. Mol. Model.** 2008, 14(12), 1203-1208.

Stein, S. E.; Walker, J. A.; Suryan, M. M.; Fahr, A. A new path to benzene in flames. *Intl. Symp. Combust.** 1990, 23(1), 85-90.

Walch, S. P. Characterization of the minimum energy paths for the ring closure reactions of C$_4$H$_3$ with acetylene. *J. Chem. Phys.** 1995, 103(19), 8544-8547.

Westmoreland, P. R.; Dean, A. M.; Howard, J. B.; Longwell, J. P. Forming benzene in flames by chemically activated isomerization. *J. Phys. Chem.** 1989, 93(25), 8171-8180.

Yang, B.; Li, Y.; Wei, L.; Huang, C.; Wang, J.; Tian, Z.; Yang, R.; Sheng, L.; Zhang, Y.; Qi, F. An experimental study of the premixed benzene/oxygen/argon flame with tunable synchrotron photoionization. *Proc. Combust. Inst.** 2007, 31(1), 555-563.

Zhao, Y.; Schultz, N. E.; Truhlar, D. G. Design of density functionals by combining the method of constraint satisfaction with parametrization for thermochemistry, thermochemical kinetics, and noncovalent interactions. *J. Chem. Theory Comput.** 2006, 2(2), 364-382.