KINETIC AND PRODUCTS OF C_3H_3 AND C_4H_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 ($\cdot C_3H_3$) and butadiene (C_4H_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 ($\cdot C_3H_3$) dan butadiena (C_4H_2) digunakan sebagai studi kasus karena konsentrasinya yang relatif tinggi dalam percobaan laboratorium dengan menggunakan bunsen. Secara garis besar, reaksi pembentukan rantai lingkaran (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, ie. '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-buten-3-yne-1-yl radical and 3-methylidenecyclopropene radical from the addition of small aliphatics ethynyl radical and ethyne (Romero and Indarto, 2008). The formation and growth of ring-containing species bridges the main combustion zone chemistry and soot formation. The formation of the first ring molecule from 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.

The second most cited reaction is by the reaction between n-C₄H₃ and C₂H₂ which end up with phenyl (C₆H₅) (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-C₄H₃ and n-C₄H₅ have isomers, i-C₄H₃ and i-C₄H₅, 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 (C₃H₃) 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.

Later on Miller and Klipenstein (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

Figure 1. Product distributions in atmosphere pressure flow experiment of 1,5-hexadiyne flame (Stein et al., 1990)

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 ($T=460-470^{\circ}\text{C}$ and $500-550^{\circ}\text{C}$, respectively). Moreover, Westmoreland et al. (1989) found insufficient C_3H_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):

$$k(E^*) = \frac{W(E^*)}{h \rho(E^*)} = \frac{1}{h} \frac{W(E^* - E_0)}{\rho(E^*)} \quad (6)$$

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:

$$\rho(E^*) = \frac{\partial W(E^*)}{\partial E^*} \quad (7)$$

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):

$$W(E) = \sum_{E_v=0}^{E_v} P(E_v) = \sum_{E_v=0}^{E_v} P(E_v) \sum_{E_r=0}^{E_r-E_v} P(E_r) \quad (8)$$

$$\rho(E) = \sum_{E_v=0}^{E_v} P(E_v) \rho_r(E_v - E_v) \quad (9)$$

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

Figure 2. Illustration of potential-energy surface for unimolecular reaction

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), ω 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 (ω) 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):

$$k = \frac{1}{h} \frac{Q^\ddagger}{Q} e^{-E_0/RT} \quad (11)$$

where Q and $Q^\ddagger$ 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, $\cdot C_2H$, 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 $\leq \pm 10^{-3}$. 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

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 ¹
C ₂ H + C ₄ H ₂	0.00	0.00	0.00	0.00	0.00
C ₆ H ₃	-72.27	-77.54	-74.63	-75.19	-70.20
C ₆ H ₃	0.00	0.00	0.00	0.00	0.00
TS ring closure	40.66	40.35	39.79	38.62	37.60
cyclo-C ₆ H ₃	1.33	-7.58	-1.72	-4.65	-4.90
C ₆ H ₃	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 $C_2H_3 + C_4H_2$ 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 C_2H_3 to C_1 (terminal) or C_2 (middle) of C_4H_2 . At low temperature, 298K, it seems only TS Add1 and TS Add4 to be the most possible entrance

channels ($k_{TS\text{ Add1}/TS\text{ Add2}} \approx 1.5 \times 10^5$; $k_{TS\text{ Add1}/TS\text{ Add3}} \approx 2.5 \times 10^6$; $k_{TS\text{ Add1}/TS\text{ Add4}} \approx 0.8$). In high temperatures, e.g., 1900K, the k difference these four channels are smaller than before, $k_{TS\text{ Add1}/TS\text{ Add2}} \approx 12$; $k_{TS\text{ Add1}/TS\text{ Add3}} \approx 7.5$, 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. 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. 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** ($\Delta E^\ddagger = 63.5$ 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 Å). Different cases for the cyclization of 6-membered ring were found. In order to construct 6-membered ring: (1) Straight-line carbon chain has to bend in a certain way to enable an attack to a sp² carbon's radical side, for example TS **1-4** with $\Delta E^\ddagger = 40.8$ kcal/mol; or (2) Connecting the 2 carbons which don't have any free electron radical, for example TS **1-3** with $\Delta E^\ddagger = 40.7$ kcal/mol. In the latter case, the product, **3**, will contain new two

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

radical centers. Only one case where we found relatively easy cyclization, TS **9-4a**, with $\Delta E^\ddagger = 22.7$ kcal/mol (see Figure 8) as this TS performs by the attack of free radical sp^2 carbon.

Instead of ring closure mechanism, the abstraction or losing of one hydrogen from the molecule should be considered as one of the competitor in combustion or pyrolysis condition. H loss goes with potential energy barrier of 48-49 kcal/mol which simply considered 'not important' mechanism in ambient temperature. Moreover, the product is endoergic by 42-44 kcal/mol compared to the reactant. However, this condition is dramatically changing at higher temperatures. Take an example at $T=1900$ K, the free energy barrier of H loss from is only slightly higher than cyclization of 5-membered ring (37 kcal/mol for $\Delta G^\ddagger$ of TS 5-ring cyclization (**1-14**) vs. 45 kcal/mol for $\Delta G^\ddagger$ H-loss (**1-5**)). At the end, at similar temperature, the H-abstraction product is exoergic by -5 kcal/mol.

3.2 Ring transformation reactions

Figure 9 illustrates the possible pathways for the transformation from cyclo- $C_{4,5, \text{or } 7}$ to 6-membered ring molecules. In general words, this way for 6-ring molecules generation is hardly visible as the barrier is very high with endoergic products. Taking an example of direct transformation of 1-ethynylcyclopentadienyl into fulvene-like molecule, $H_2C^+-C_6H_3$, this reaction has to overcome the barrier of $\Delta E^\ddagger_{298K} = 86.5$ kcal/mol. Temperature increment did not help much as the free energy barrier is still relatively high, e.g., $\Delta G^\ddagger_{1900K} = 51.8$ 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 kcal/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 -bond 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 -bond 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 $\Delta E^\ddagger$ 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, $C(^3P)$, 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

σ (Å) for collider	3.74
ε/k_B (K) for collider	82.0
MW (g/mol) of collider	28.0
σ (Å) for well	6.0
ε/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

Figure 9. The potential energy charts of ring transformation to 6-membered ring molecules

Figure 10. The selectivity of 2 major products at different coefficient α energy transfers. The data are obtained at T=1900K

to the others. Special for energy transfer coefficient (α), 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-triynyl (**5**) + H, in this case, are only slightly affected by the variation of energy transfer coefficients (α). Later, the value of $\alpha = 2800 \text{ cm}^{-1}$ will be used 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 propargyl radical with butadiene from TS Add-1 (Figure 1), at low temperatures ($\leq 700\text{K}$), the dominant reaction is the formation of adduct **1**. In this stage, 5-membered ring molecules, **14** and **18**, are starting to be formed; however, the

Figure 11. Product distribution of the propargyl radical + butadiene from channel TS Add-1

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-membred 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-triyn, **5**, + H. Another possible channel of H loss comes from molecule **9** into epta-5,6-dien-1,3-dino, **9a**.

Figure 12. Product distribution of the propargyl radical + butadiene from channel TS Add-4

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** → **30** → **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.

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