Environ. Eng. Res. Vol. 12, No. 5, pp. 211～217, 2007
Korean Society of Environmental Engineers

Thermal Formation of Polycyclic Aromatic Hydrocarbons from Cyclopentadiene (CPD)

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Received April 2007, accepted October 2007

Abstract

Polycyclic aromatic hydrocarbon growth from cyclopentadiene (CPD) pyrolysis was investigated using a laminar flow reactor operating in a temperature range of 600 to 950°C. Major products from CPD pyrolysis are benzene, indene and naphthalene. Formation of observed products from CPD is explained as follows. Addition of the cyclopentadienyl radical to a CPD π-bond produces a resonance-stabilized radical, which further reacts by one of three unimolecular channels: intramolecular addition, C-H bond β-scission, or C-C bond β-scission. The intramolecular addition pathway produces a 7-norbornenyl radical, which then decomposes to indene. Decomposition by C-H bond β-scission produces a biaryl intermediate, which then undergoes a ring fusion sequence that has been proposed for dihydrofulvalene-to-naphthalene conversion. In this study, we propose C-C bond β-scission pathway as an alternative reaction channel to naphthalene from CPD. As preliminary computational analysis, Parametric Method 3 (PM3) molecular calculation suggests that intramolecular addition to form indene is favored at low temperatures and C-C bond β-scission leading to naphthalene is predominant at high temperatures.

Keywords: PAH (Polycyclic aromatic hydrocarbon), CPD (Cyclopentadiene), Thermal formation

1. Introduction

Improved chemical mechanisms for the formation and growth of polycyclic aromatic hydrocarbons (PAHs) in combustion are needed to predict and control emissions of toxic air pollutants and soot. Several PAHs formed from incomplete combustion are known to be mutagenic or carcinogenic. Under fuel-rich conditions, aromatic ring formation is driven mainly by hydrogen abstraction and acetylene addition route known as HACA mechanism.[1-5] However, the HACA mechanism seems to be too slow to kinetically explain the formation of large PAHs and at the same time its reaction steps were not thermodynamically favorable.[6] To account for that, the potential importance of resonantly stable free radicals in forming aromatics and PAH in flames was emphasized.[7]

The importance of resonantly stable free radicals such as propargyl and cyclopentadienyl (CPDyl) radicals in forming aromatics and PAH in flames has been emphasized because they can achieve high concentrations in thermal systems.[6-8] Studies reported by Violi and co-workers[9-12] show that key reactions in the formation of high molecular mass aromatics in flames are the combinations of resonance-stabilized radicals, including cyclopentadienyl self-combination, propargyl addition to benzyl radicals, and the sequential addition of propargyl radicals to aromatic rings.[13,14] The authors also showed that the total organic material collected in the flame is the result of a fast reactive coagulation of these small aromatics, forming structures of high molecular mass. Soot formation occurs through a slow process of dehydrogenation and aromatization of the high molecular mass compounds. This process seems to be the controlling step under slightly sooting conditions, which are of practical interest in diffusion flames.[9] Because these resonance-stabilized radicals are reactive at multiple sites, they can add to PAHs via several reaction channels to form larger, fused PAHs.[15-17]

The CPDyl radical is considered to be an important intermediate in PAH formation due to its ability to undergo self-recombination[6,18] and form aromatic products.[19] Recombination and rearrangement of CPDyl radicals have been recognized as

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important routes to naphthalene formation in flames,[20-23] and the pathways have been included in several kinetic models describing PAH growth.[7,20-22] Based on a theoretical approach, Melius and co-workers[21] proposed the formation of naphthalene from the self-recombination of CPDyl radicals to form 9,10-dihydrofulvalene (radical-radical pathway), followed by conversion of five-member rings to six-member rings. Ritcher et al.[22] confirmed that CPDyl radical self-recombination was the major pathway to naphthalene in benzene premixed flame. Furthermore, the recent observation of 9,10-dihydrofulvalene formation from anisole[19] provides additional support for the recombination route of CPDyl radicals to naphthalene.

In previous experimental work,[23-25] we investigated the growth of PAH from cyclopentadiene and indene, the latter being a benzoderivative of cyclopentadiene, in postflame conditions. Reaction pathways for the formation of chrysene, benz[a]anthracene and benzo[c]phenanthrene from indene were proposed in analogy to the dihydrofulvalene-to-naphthalene mechanism proposed by Melius et al.[21] We also highlighted a possible reaction pathway for the formation of benzofluorenes ([a] and [b] isomers) from indene and a pathway for the formation of indene from cyclopentadiene involving a bridged intermediate.

Drawing on this work, in this paper we report on a detailed study for the formation of PAH from cyclopentadiene in pyrolytic conditions using a laminar flow reactor. Preliminary computational results using semi-empirical molecular orbital methods are presented to describe the reaction pathways for the addition of cyclopentadienyl radical to cyclopentadiene.

2. Experimental and Computational Methods

A laminar flow reactor system with an isothermal quartz tube reactor (40 cm in length and 1.7 cm in diameter) used for the pyrolysis of CPD is shown in Figure 1. Due to the instability of cyclopentadiene (CPD) at room temperature, commercially available dicyclopentadiene ($C_{10}H_{12}$), dimer of CPD, was used as a reactant. Dicyclopentadiene (DCPD) was converted into CPD

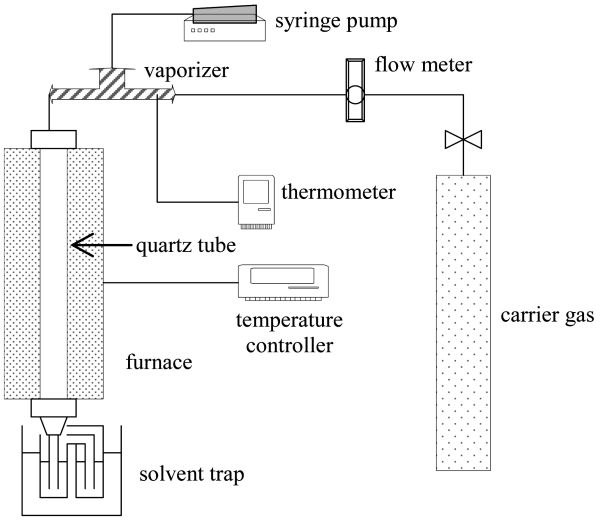

Fig. 1. A schematic diagram of the experimental apparatus of CPD pyrolysis.

when heated beyond its boiling point of 175°C.[26] DCPD was heated to liquid form (34°C) and fed by a syringe pump into a heated glass vessel where the reactant was vaporized and mixed with a nitrogen gas stream. The gas stream entering the reactor consisted of 0.7% molar CPD vapor in nitrogen. Experiments were conducted at temperatures ranging from 600 to 950°C. A reactor residence time of 2 to 3 sec was maintained. The product stream was quenched at the outlet of the reactor and collected in a dual ice-cooled dichloromethane trap. Soot, defined as the dichloromethane insoluble fraction, was separated by vacuum filtration and measured gravimetrically.

Filtered samples were analyzed using by Hewlett Packard GC/MS with HP5-ms column. Due to the high volatility of CPD and its co-elution with the solvent, CPD concentrations were separately measured from gas sample with direct injection of the gas samples into the GC-MS column. Aromatic products were identified and quantified using chemical standards, which included benzene, indene, naphthalene, toluene, styrene, fluorene, phenanthrene, anthracene, 2-methyl indene, and 1,2-dihydronaphthalene.

Heats of formation, $\triangle H_f$, for the intermediate and the transition state species for the dihydrofulvalene-to-naphthalene mechanism of Melius et al.[21] were calculated using the Parametric Method 3 (PM3)[27] semi-empirical quantum method in the MOPAC version 6.0 suite of codes to test its suitability as a screening tool for reaction pathway analysis. Thermodynamic properties of reactant and transition states for alternative CPDyl-CPD product rearrangements were calculated and used to obtain the kinetic constants. The transition state theory expression used to determine the rate constant is

$$k(T) = \frac{k_B T}{h} \exp(\Delta S^t / R) \exp(-\Delta H^t / RT)$$

where k_B is Boltzmann's constant, h is Planck's constant, ΔH^t and ΔS^t are the differences in enthalpy and entropy, respectively, between the transition state and the reactant, R is the universal gas constant and T is the absolute temperature.

3. Results and Discussion

3.1. Pyrolytic Product Yields

The yields of total carbon recovery, aromatic compounds, CPD and soot over the temperature range of 600 to 950°C are shown in Figure 2 expressed as a percent of carbon fed to the reactor. Soot was assumed to be pure carbon. Carbon recoveries of 80% and above were obtained for temperatures up to 850°C. Lower carbon recoveries for temperatures higher than 875°C are primarily attributed to unrecovered soot that could not be rinsed from the quartz tube wall. PAH product yields ranged from 2.7% of carbon input at 600°C to 82% at 850°C. The yields of CPD were greater than 90% up to 700°C. DCPD was below detection. Above 700°C, CPD began to react in significant amounts with more than 99% of the CPD reacted at 825°C. Soot formation was observed starting at 850°C and increasing

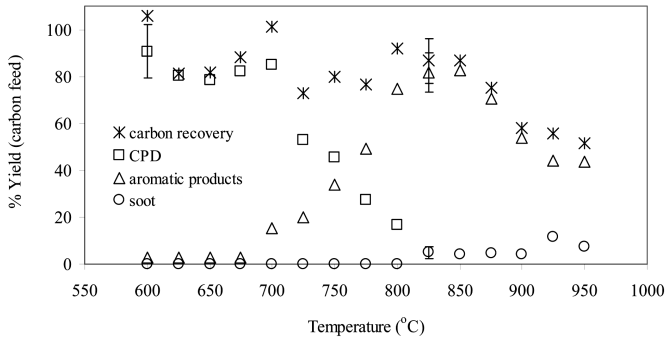

Fig. 2. Total carbon recovery and yields of CPD, total aromatic compounds and soot from CPD pyrolysis.

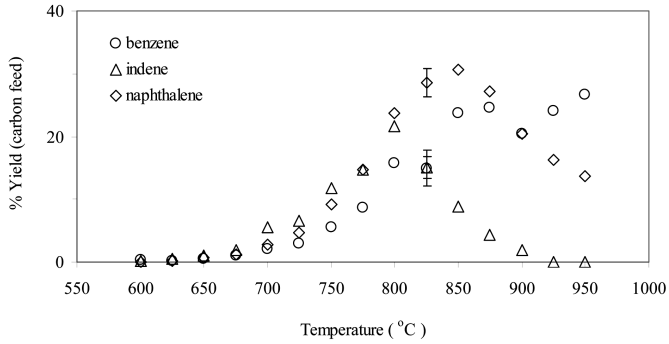

Fig. 3. Yields of indene, benzene and naphthalene from CPD pyrolysis.

with temperature.

The major products from CPD pyrolysis were benzene, indene and naphthalene, and their yields are shown in Figure 3. The amount of indene produced exceeded that of naphthalene and benzene for temperatures lower than 775°C. Between 775°C and 900°C, naphthalene was the main product, and above 900°C, benzene formation became predominant. The high conversion of CPD to these products (more than 90% of the total product yield) indicated high selectivity of product from CPD. Both high yields of benzene, indene, and naphthalene and low yields of aliphatic compounds suggested that the major products were not formed from the addition of C_2 or/and C_3 species, but more likely from CPD; therefore, the CPD-CPD reaction was the dominant reaction channel until 850°C which is consistent with the published experimental analysis of aromatic hydrocarbon growth from CPD and indene both individually and as a mixture in a laminar flow reactor.[23-25)]

The formation of benzene and indene supported the existence of the CPDyl-CPD addition pathway.[24)] Naphthalene could be formed through the CPDyl-CPD addition pathway or the CPDyl-CPDyl recombination pathway.[21)] Intermediates with molecular formula of $C_{10}H_{10}$ were detected among the products and the yields of two methyl indenes, dihydronaphthalene, and an unidentified $C_{10}H_{10}$ intermediate, are shown in Figure 4. Based on the mass spectrum of the unidentified $C_{10}H_{10}$ compound, we believed that this hydrocarbon was either methyl indene or dihydronaphthalene. The order of principal m/z peaks associated with this hydrocarbon (130, 129, and 115) was not consistent with the published order of principal m/z peaks in a dihydrofulvalene (129 and 130).[28)] Moreover, this hydrocarbon does

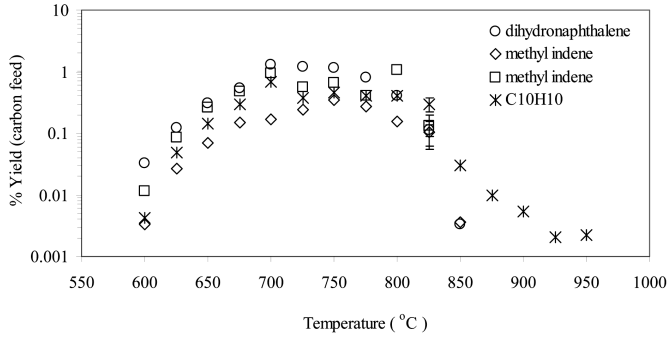

Fig. 4. Yields of $C_{10}H_{10}$ products from CPD pyrolysis.

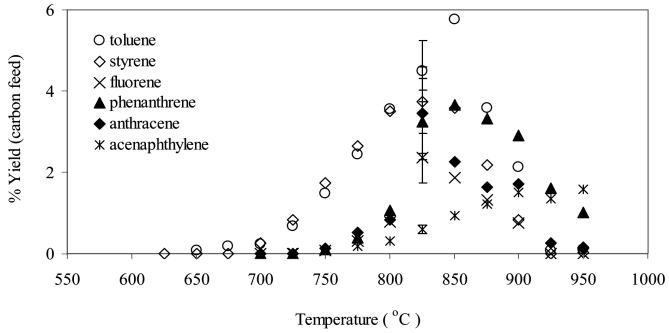

Fig. 5. Yields of other aromatic products from CPD pyrolysis.

not have a big half-ion peak at 65 m/z whereas both 1,1- and 1,2-biindenyl containing a dihydrofulvalene moiety have a distinguished half-ion peak at 115 m/z. Formation pathways involving these intermediates will be discussed later.

Other aromatic products were toluene, styrene, fluorene, phenanthrene and anthracene, and their yields are shown in Figure 5. Fluorene, phenanthrene and anthracene can be formed from the reaction between CPD and indene, consistent with previous studies.[23-25)] Toluene and styrene are likely formed from the reactions involving CPD, benzene and acyclic fragments.

3.2. Pathways of PAH Growth from CPD.

In order to explain the observed major product formation from CPD pyrolysis, possible reaction pathways are proposed in Figure 6. The proposed pathways are based on the published mechanisms: the radical-radical (CPDyl-CPDyl) pathway by Melius and co-workers[21)], and the radical-molecule (CPDyl-CPD) pathway by Mulholland and co-workers.[23-25)]

All of the routes begin with the addition of CPDyl to CPD to form intermediate I1. Alternative intramolecular rearrangements lead to the major products via this intermediate. In Figure 6, the intramolecular addition reactions (R1 and R2) lead to the formation of bridged intermediates. Bridge opening and loss of H atom produce 4-methyl indene or 7-methyl indene; subsequent loss of methyl radical produces indene. Methyl radical produced by this pathway can react with CPD to form fulvene, which can isomerize to benzene.[29)] Our experimental observation of two methyl-indenes and indene is consistent with the intramolecular addition pathways R1 and R2.

Competing with the formation of the bridged compounds via

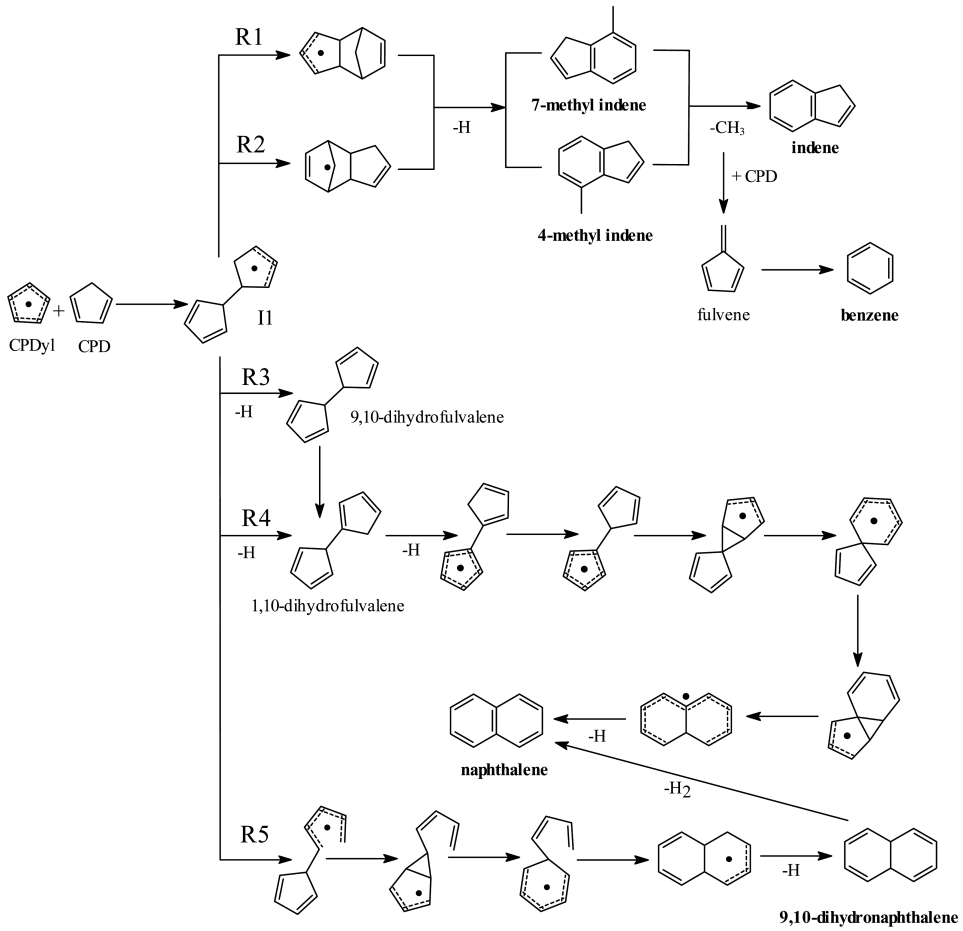

Fig. 6. Reaction pathways to indene, benzene and naphthalene from CPDyl-CPD (I1). Products observed in experiments are written in bold.

intramolecular addition is the formation of dihydrofulvalenes via beta-scission of H atom (R3 and R4, Figure 6). The reaction mechanism of the dihydrofulvalene-to-naphthalene has already been studied using the BAC-MP4 and BAC-MP2 methods.[21] The CPDyl-CPD intermediate (I1) undergoes C-H bond cleavage to form either 9,10-dihydrofulvalene (R3) or 1,10-dihydrofulvalene (R4). 9,10-dihydrofulvalene can form 1,10-dihydrofulvalene via H-atom shift.[21] As described elsewhere,[19,21] the fusion of the bicyclic dihydrofulvalene occurs by three-member ring closure and ring opening, resulting in naphthalene.

Another competing reaction channel is C-C β-scission, shown as R5 in Figure 6. Ring expansion of cyclopentadiene to a six-member ring via the formation of a three-member ring, analogous to the conversion of methylcyclopentadienyl radical to benzene,[29,30] leads to the formation of butyl-cyclohexadienyl radical. Cyclodehydrogenation leads to naphthalene. The experimental identification of dihydronaphthalene, which is not expected from the C-H β-scission routes (Figure 6), supports the proposed C-C β-scission route.

3.3. Preliminary Computational Analysis of Alternative CPDyl-CPD (I1) Reactions

The PM3 method was selected for preliminary analysis because it is efficient and more accurate for aromatic systems than the other semi-empirical methods.[27] In order to verify the accuracy of the PM3 method for our system, we compare PM3 results to BAC-MP2 method results[21] on the heats of formation for the intermediates and the transition states in the dihydrofulvalene-to-naphthalene mechanism (R4, Figure 6). The comparison is shown in Figure 7. The discrepancy between the two methods in the computed values for the heat of formation of the two three-member ring closing transition states is attributed to that the PM3 method employs the empirical data in its thermodynamic data calculation of compounds. It should be noted that the qualitative agreement between the two methods indicates that the PM3 method can be used as a screening tool for preliminary computational study of this system.

The relative energies of the reactant (I1), transition states and products of the alternative reaction steps in R1 through R5 are shown in Figure 8. The two intramolecular addition channels (R1 and R2) that form norborenyl structures are the lowest energy paths. The C-C bond β-scission reaction (R5) is lower in energy than the C-H bond β-scission reactions (R3 and R4). On the other hand, the formation of the nonborenyl structures by intramolecular addition is expected to be less favored over β-scission reactions based on entropy consideration.

Using the transition state theory, rate constants for the second-

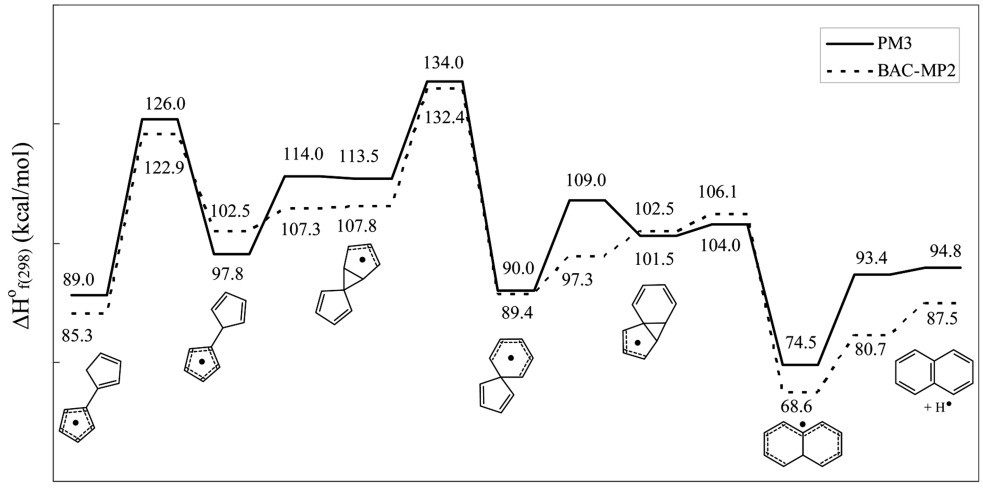

Fig. 7. Comparison between PM3 and BAC-MP2 methods for the dihydrofulvalene-to-naphthalene reaction pathway R4.

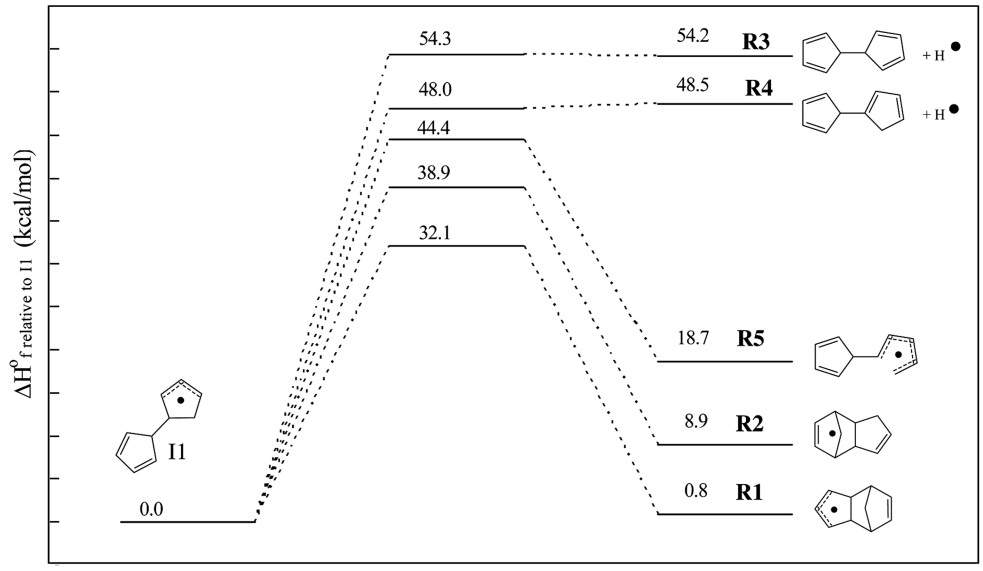

Fig. 8. PM3 energy diagrams for alternative unimolecular reactions of CPDyl-CPD (I1).

Table 1. Rate constants for the unimolecular reactions from CPDyl-CPD

Reaction	log k (s^{-1})
R1	11.53 - 7.12 × 10^3/T*
R2	11.65 - 8.62 × 10^3/T
R3	13.43 - 12.09 × 10^3/T
R4	12.79 - 10.41 × 10^3/T
R5	13.70 - 9.95 × 10^3/T

*T = absolute temperature.

steps in the radical-molecule pathways are calculated in Table 1, which are plotted in Figure 9 as a function of temperature. The results show that the rate constants for the five-unimole cular reactions are of comparable magnitudes at a temperature of about 1000 K (725°C). At lower temperatures, the intramolecular addition pathways (R1 and R2) are favored over the β-scission pathways due to lower transition state enthalpies. At high temperatures, the β-scission pathways (R3, R4 and R5) are favored due to higher transition state entropies. These results

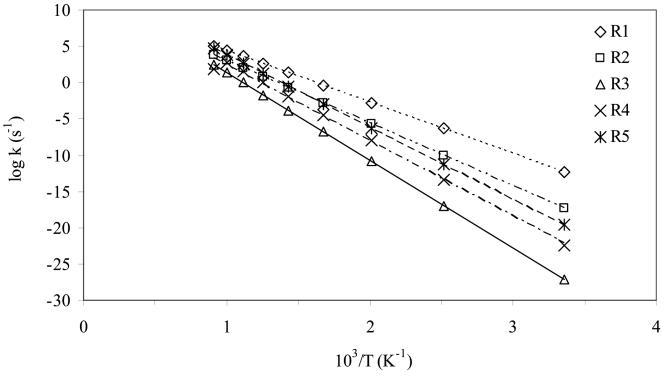

Fig. 9. Arrhenius plots for the alternative unimolecular reactions of CPDyl-CPD (I1).

are qualitatively consistent with the experimental observation that the intramolecular addition product, indene, was favored at temperatures below 750°C whereas the β-scission product, naphthalene, was favored at temperatures above 800°C.

It should be noted that these reaction pathways consist of a series of reaction steps. In order to determine overall reaction kinetics, complete energy profiles for each reaction channel need to be calculated. In addition, bimolecular reactions, such as H-atom abstraction by H atom, were not considered. Thus, the computational results are appropriate for H-atom poor conditions. A more detailed computational analysis is being performed on this system using higher-level molecular modeling methods.

4. Conclusions

Experimental study of PAH formation from CPD pyrolysis was carried out in a laminar flow tube reactor between 600 and 950°C. The main products identified were indene and benzene through the intramolecular addition routes (R1 and R2) and naphthalene via β-scission routes (R3, R4 and R5). Identification of stable intermediates supports the proposed formation routes. The intramolecular addition products were favored at low temperatures (below 750°C) whereas β-scission routes were favored at high temperatures. At temperatures above 850°C, the reaction between CPD and acyclic fragments appears to be dominant. Observation of fluorene, phenanthrene and anthracene indicates that the reaction of CPD with indene leads to the formation of other PAHs via similar reaction routes.

Preliminary computational study using PM3 was performed on the proposed radical-molecule pathways. Comparison of PM3 results with BAC-MP2 method on the heats of formation for the intermediates and the transition states in the dihydrofulvalene-to-naphthalene mechanism (R4) show that PM3 can be used as a screening tool for higher level theory. These preliminary computational results are in qualitative agreement with the experimental findings.

Acknowledgments

The support of the National Science Foundation (collaborative research grant CTS-0210089) is gratefully acknowledged.

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