Radical−Molecule Reactions for Aromatic Growth: A Case Study for Cyclopentadienyl and Acenaphthylene

Dong Wang[†] and Angela Violi*

Department of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan 48104

avioli@umich.edu

Received May 22, 2006
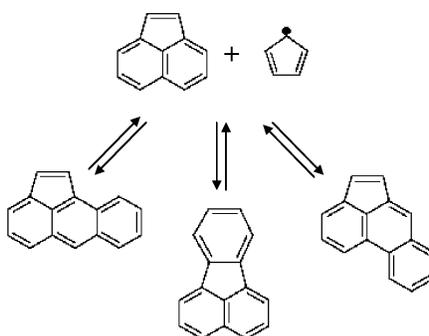
Polycyclic aromatic hydrocarbon growth from acenaphthylene and cyclopentadienyl was investigated by using the B3LYP/6-31G(d,p) and BH&HLYP/6-31G(d,p) levels of theory as well as transition state theory. The reaction pathways of cyclopentadienyl bearing hydrocarbons are different from those without these moieties and cannot be adequately accounted for by the existing acetylene addition and aryl−aryl addition mechanisms. The reaction mechanisms identified in this paper lead to the formation of fluoranthene, aceanthrylene, and acephenanthrylene. Rate constants of the radical−molecule addition and subsequent intramolecular addition steps predict that the 1,2 double bond in acenaphthylene is much more reactive than the 3,4 and 4,5 double bonds. Fluoranthene is the most abundant product produced at high temperatures and the yield of acephenanthrylene is bigger than that of aceanthrylene. The computational results are discussed in light of pyrolysis experiments on CPD−indene and CPD−acenaphthylene mixtures conducted by Prof. Mulholland's research group reported in a previous work.

Introduction

Polycyclic Aromatic Hydrocarbons (PAH) are important combustion-generated pollutants, both because of their role as potential soot precursors[1−2] and because of the inherent biological activity of particular PAH.[3−4]

The aromatic growth can proceed through different routes, and resonantly stabilized free radicals, such as propargyl and cyclopentadienyl, have been proposed as potential precursors.[5−12] In particular, the importance of cyclopentadienyl (CPDyl) moieties in PAH growth has been postulated because these radicals can attain relatively high concentrations in flames and at the same time they are reactive at multiple sites. Fuels containing cyclopentadienyl moieties have also shown high sooting tendencies.[13] In addition, relative to other aromatics,

* Address correspondence to this author.
[†] Present address: Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.
(1) Benish, T. G.; Lafleur, A. L.; Taghizadeh, K.; Howard, J. B. *Proc. Combust. Inst.* **1996**, *26*, 2319.
(2) Lafleur, A. L.; Howard, J. B.; Taghizadeh, K.; Plummer, E. F.; Scott, L. T.; Necula, A.; Swallow, K. C. *J. Phys. Chem.* **1996**, *100*, 17421.
(3) Durant, J. L.; Busby, W. F.; Lafleur, A. L.; Penman, B. W.; Crespi, C. L. *Mutat. Res.* **1996**, *371*, 123.
(4) Durant, J. L.; Lafleur, A. L.; Busby, W. F.; Donhoffner, L. L.; Penman, B. W.; Crespi, C. L. *Mutat. Res.* **1999**, *446*, 1.

(5) Melius, C. F.; Colvin, M. E.; Marinov, N. M.; Pitz, W. J.; Senkan, S. M. *Proc. Combust. Inst.* **1996**, *26*, 685.
(6) Castaldi, M. J.; Marinov, N. M.; Melius, C. F.; Huang, J.; Senkan, S. M.; Pitz, W. J.; Westbrook, C. K. *Proc. Combust. Inst.* **1996**, *26*, 693.
(7) Colket, M. B.; Seery, D. J. *Proc. Combust. Inst.* **1994**, *25*, 883.
(8) Pope, C. J.; Miller, J. A. *Proc. Combust. Inst.* **2000**, *28*, 1519.
(9) McEnally, C. S.; Pfefferle, L. D. *Proc. Combust. Inst.* **2000**, *28*, 2569.
(10) Lindstedt, P.; Maurice, L.; Meyer, M. *Faraday Discuss.* **2001**, *119*, 409.
(11) Frenklach, M.; Taki, S.; Durgaprasad, M. B.; Matula, R. A. *Combust. Flame* **1983**, *54*, 81.
(12) Frenklach, M. *Phys. Chem. Chem. Phys.* **2002**, *4* (11), 2028.

PAH with peripherally fused five-membered rings (CP-PAH) demonstrate a greater facility in undergoing certain kinds of reactions, such as isomerization involving intramolecular rearrangement.[14-15] This is due to the fact that the fusion of the cyclopenta ring alters the electronic properties of PAH, as demonstrated by differences in resonance energy[16] and measured differences[17] in ultraviolet—visible (UV) absorption, fluorescence.

Our group has recently reported Density Functional Theory (DFT) calculations to study possible reaction pathways during cyclopentadiene (CPD) pyrolysis.[18] An important result obtained is the identification of additional energetically favored pathways for the formation of naphthalene and benzene via C—C bond β-scission. In addition to major products which were found to be benzene, indene, and naphthalene, $C_{10}H_{10}$ compounds such as methylindene, dihydrofulvalene, and dihydronaphthalene were also observed in the experiment. The existence of these compounds further confirms the radical—molecule pathways involving intramolecular addition, C—H bond β-scission, and C—C bond β-scission identified based on quantum mechanical computations.

The importance of radical—molecule reactions for the growth of PAH and high molecular mass compounds has also been investigated by Violi et al.,[19-21] who proposed a sequence of radical—molecule reactions between aromatic compounds with 6 π-electron and compounds containing conjugated double bonds (e.g., acenaphthylene) to explain the formation of PAH and higher molecular mass compounds in flames. Through a two-step radical—molecule addition reaction followed by rearrangement of the carbon framework, this mechanism leads to the formation of high molecular mass compounds. The distinguishing features of the model lie in the chemical specificity of the routes considered, where the aromatic radical attacks the double bond of five-membered ring PAH. This involves specific compounds that form resonantly stabilized radical intermediates, relieving part of the large strain in the five-membered rings by formation of linear aggregates.

To study the importance of CPDyl moieties in PAH growth, Mulholland and co-workers[22-24] have conducted a detailed experimental analysis of PAH growth from cyclopentadiene (CPD) and indene (C_9H_8) both individually and as a mixture in a laminar flow reactor. Some of the products can be formed by reactions analogous to those in the radical—radical mechanism proposed by Melius and co-workers[5] that describes the conversion of two CPDyl radicals to naphthalene, but other experimentally observed species are instead more likely produced through a radical—molecule pathway in which a norborenyl-

(13) McEnally, C. S.; Pfefferle, L. D. *Combust. Sci. Technol.* **1998**, *131*, 323.
(14) Scott, L. T.; Roelofs, N. H. *J. Am. Chem. Soc.* **1987**, *109*, 5461.
(15) Howard, J. B.; Longwell, J. P.; Marr, J. A.; Pope, C. J.; Busby, W. F., Jr.; Lafleur, A. L.; Taghizadeh, K. *Combust. Flame* **1995**, *101*, 262.
(16) DasGupta, A.; DasGupta, N. K. *Can. J. Chem.* **1976**, *54*, 3227.
(17) Jenneskens, L. W.; Sarobe, M.; Zwikker, J. W. *Pure Appl. Chem.* **1996**, *68*, 219.
(18) Wang, D.; Violi, A.; Kim, D.-H.; Mulholland, J. A. *J. Phys. Chem. A* **2006**, *110* (14), 47195.
(19) D'Anna, A.; Violi, A. *Proc. Combust. Inst.* **1998**, *27*, 425.
(20) Violi, A.; Sarofim, A. F.; Truong, T. N. *Combust. Flame* **2001**, *126*, 1506.
(21) Violi, A.; Sarofim, A. F.; Truong, T. N. *Combust. Sci. Technol.* **2002**, *174* (11-12), 205.
(22) Mulholland, J. A.; Lu, M.; Kim, D.-H. *Proc. Combust. Inst.* **2000**, *28*, 2593.
(23) Lu, M.; Mulholland, J. A. *Chemosphere* **2001**, *42*, 189.
(24) Lu, M.; Mulholland, J. A. *Chemosphere* **2004**, *55* (4), 605.

TABLE 1. Bond Properties Calculated at the B3LYP and BH&HLYP Levels[a]

compd	bond	bond length (Å)	bond order	site	D_0 (kcal/mol)	ΔE_B kcal/mol
	C1—C2	1.36	1.83	C1	114.59	13.10
					(113.77)	(16.49)
	C3—C4	1.43	1.18	C3	110.12	9.92
					(109.72)	(13.76)
	C4—C5	1.38	1.72	C4	110.11	9.78
					(109.47)	(13.40)
				C5	110.76	10.34
					(110.16)	(13.98)
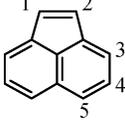
[a] D_0 is the ground-state C—H bond dissociation energy and ΔE_B is the barrier height of the hydrogen abstraction reaction by H. Numbers in parentheses are calculated at the BH&HLYP level.

type (bridged) radical intermediate is formed. This second reaction channel represents a route of PAH formation not previously proposed and was observed at all temperatures while most important at temperatures below 750 °C. For the CPD—acenaphthylene system, the main pyrolysis products are fluoranthene, acephenanthrylene, and aceanthrylene.[25] Trace amounts of $C_{17}H_{12}$ isomers were also detected. Among the $C_{16}H_{12}$ isomers, the yield of fluoranthene was 1 order of magnitude greater than the yields of acephenanthrylene and aceanthrylene. The authors suggested alternative routes and concluded that the reaction pathways of CPDyl bearing hydrocarbons are different from those without these moieties and cannot be adequately accounted for by the existing acetylene addition and aryl—aryl addition mechanisms.[23,25]

Drawing on these conclusions and in order to assess the mechanisms and rates for the radical—molecule interactions between PAH with CPD moieties, the acenaphthalene and CPDyl system is chosen for this study and possible reaction mechanisms are analyzed by using DTF calculations.

The objectives of this paper are as follows: (1) develop chemical mechanisms of PAH formation and growth based on experimental observations and; (2) determine molecular factors that control PAH product distributions based on computational study. In particular, which π bonds of acenaphtylene are resonance-stabilized CPDyl radicals most likely to add on and what are the subsequent pathways of condensation to form fused PAH products.

Computational Method

Recently, Mebel and co-workers[26] compared the reaction energies and barrier heights computed by Gaussian-3-type[27] (G3), which is expected to be accurate within 1-2 kcal/mol, and density functional methods for various types of processes involved in the PAH growth mechanism. They found considerable discrepancies in B3LYP and G3 computed barriers and reaction enthalpies for the acetylene cycloaddition reactions and the hydrogen abstraction reactions by H/OH radicals. For the acetylene addition, hydrogen loss, and disproportionation reactions the agreement is reasonably good.

(25) Lu M.; Mulholland, J. A. Private communication (2006).
(26) Kislov, V. V.; Islamova, N. I.; Kolker, A. M.; Lin, S. H.; Mebel, A. M. *J. Chem. Theory Comput.* **2005**, *1* (5), 908.
(27) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

FIGURE 1. Intramolecular pathway (Path A) for the addition of cyclopentadienyl to the C1 site of acenaphtylene leading to the formation of fluoranthene (P1) and its methyl-substituted compound (P2).

FIGURE 2. Potential energy surface for Pathway A.

The highly accurate relative energies of intermediates and transition states of chemical reactions are especially important when they are used for quantitative prediction of reaction rate constants.

However, because of the large computational demands of G3 methods, large systems of technological interest are most often treated by using much less expensive density functional methods.

The energy barriers predicted by the B3LYP method are usually accurate within 4−5 kcal/mol. These types of uncertainties correspond to uncertainties of about an order of magnitude in the predicted rates for temperature about 1000 K. This level of uncertainty is acceptable for deciding whether a particular reaction can be significant in a certain situation. However, if the reaction is important, the rate estimate can be refined by making experimental measurements at convenient temperatures, and then using the theoretical "preexponential factor" to improve the temperature extrapolation. As demonstrated by others, the less computationally demanding DFT+TST calculations also appear to be accurate enough to allow significantly improved extrapolations.[28]

In this paper, geometries and frequencies of the reactants, transition states, and products in the acenaphthylene−CPD system were calculated by using the hybrid density functional B3LYP method (i.e., Becke's three-parameter nonlocal exchange functional[29] with the nonlocal correlation function of Lee, Yang, and Parr[30−31]), with the 6-31G(d,p) basis set. To establish the relative

FIGURE 3. Intramolecular addition pathways leading to the formation of aceanthrylene (P3), acephenanthrylene (P6) and their methyl-substituted compounds.

TABLE 2. Arrhenius Parameters for the Addition Reactions of Pathways A, B1, B2, C1, and C2[a]

reactions	forward			reverse		
	A	n	E_a (kcal/mol)	A	n	E_a (kcal/mol)
R = A1	3.43	2.84	10.7	6.23×10^{12}	0.43	21.7
R = B1_1	1.52	2.80	16.0	2.32×10^{12}	0.36	13.0
R = B1_2	1.55	2.79	19.4	3.40×10^{12}	0.28	9.85
R = C1_1	1.39	2.79	19.6	2.96×10^{12}	0.28	9.78
R = C1_2	2.05	2.81	14.1	3.12×10^{12}	0.41	15.5
A1 = A2	2.05×10^{11}	0.12	32.1	2.68×10^{11}	-0.08	7.14
B1_1 = B2	5.00×10^{10}	0.34	52.2	1.13×10^{12}	0.38	3.00
B1_2 = B2	6.93×10^{10}	0.28	45.7	1.09×10^{12}	0.39	3.02
C1_1 = C2	2.21×10^{11}	0.11	30.2	1.81×10^{12}	0.38	10.1
C1_2 = C2	1.53×10^{11}	0.16	37.6	1.75×10^{12}	0.33	6.30

[a] The unit of the rate constant $k(T) = A(T^n) \exp(-E_a/RT)$ is s^{-1} for monomolecular reactions and $cm^3 \ mol^{-1} \ s^{-1}$ for bimolecular reactions.

FIGURE 4. Rate constants ($k_0 = 1 \ cm^3 \ mol^{-1} \ s^{-1}$) for the first addition step R → A1 (circle), R → B1_1 (square), R → B1_2 (diamond), and R → C1_2 (triangle up).

FIGURE 5. Optimized structure of the bridged structure B2 computed at the B3LYP/6-31G(d,p) level of theory.

reactivity of the double bonds in acenaphthylene, the BH&HLYP method, which predicts rather accurate barrier heights, was applied to the hydrogen abstraction reactions from different carbon sites of acenaphthylene. Closed-shell restricted wavefunctions were used for the singlet states and open-shell unrestricted wavefunctions were used for the doublet states.

Transition Structures (TS) were identified by the existence of only one imaginary frequency in the normal mode coordinate analysis, an evaluation of the TS geometry, and the reaction coordinate's vibrational motion. The frequency calculations also allow the zero-point energy (ZPE) corrections to be obtained. In case of transition structures, the movement of atoms in the imaginary frequency mode can be displayed to see if the atoms are moving in the right direction toward the reactant and product.

Intrinsic Reaction Coordinate (IRC) calculations were carried out to guarantee that the transition states found indeed connect the reactant and product of the reaction step. All computations were done by using the Gaussian 03 program.[32]

Unimolecular reactions of the chemically activated and stabilized adduct resulting from addition or combination reactions were analyzed by first constructing potential energy diagrams for the reaction system. The enthalpies and entropies were then treated with conventional transition-state theory to calculate Arrhenius preexponential factors and energies of activation that result in high-pressure-limit rate constants (k^∞) as functions of temperature. Nonlinear Arrhenius effects resulting from changes in the thermochemical properties of the respective transition state relative to those of its adduct with temperature were incorporated by using a two-parameter Arrhenius preexponential factor (A, n) in AT^n. Rate constants of the radical−molecule addition and following intramolecular addition steps in each pathway were calculated from the transition state theory (TST), using TheRate code (THEoretical RATEs)[33] at the CSEO online resource (http://www.cseo.net). The transmission coefficients which account for the quantum mechanical tunneling effect were calculated by using the Eckart method.[34]

The thermal rate coefficient is expressed as

$$k(T) = \kappa(T)\sigma \frac{k_B T}{h} \frac{Q^{\neq}(T)}{\Phi^R(T)} e^{-\Delta V^{\neq}/k_B T}$$

where κ is the transmission coefficient accounting for the quantum mechanical tunneling effects, σ is the reaction symmetry number,

(28) Susnow, R. G.; Dean, A. M.; Green, W. H. *Chem. Phys. Lett.* **1999**, *312*, 262.

(29) Becke, A. D. *J. Chem. Phys.* **1992**, *96*, 2155. Becke, A. D. *J. Chem. Phys.* **1992**, *97*, 9173. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(30) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(31) Hebre, W.; Radom, L.; Schleyer, P. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2004.

(33) Ducan, W. T.; Bell, R. L.; Truong, T. N. *J. Comput. Chem.* **1998**, *19*, 1039.

(34) Truong, T. N.; Truhlar, D. G. *J. Chem. Phys.* **1990**, *93*, 1761.

FIGURE 6. Potential energy surfaces for Pathways B1, B2, C1, and C2.

$Q^{\neq}$ and Φ^R are the total partition functions (per unit volume) of the transition state and reactant, respectively, $\Delta V^{\neq}$ is the classical barrier height, T is the temperature, and k_B and h are the Boltzmann and Planck constants, respectively.

Results and Discussion

Acenaphthylene belongs to the class of polycyclic hydrocarbons which besides typical aromatic behavior can undergo reactions that are more typical of unsaturated rather than aromatic systems. Specifically, these compounds are characterized by the pronounced reactivity and aliphatic character of some of their bonds,[35] e.g., 9,10 position in anthracene, 9,10 double bond in phenanthrene,[36] and 1,2 double bond in acenaphthylene, and they react with electrophilic reagents by addition rather than by substitution.[37]

Acenaphthylene is representative of fully conjugated PAH with external five-membered rings. Its 1,2 double bond is to a large extent isolated from other π-electron systems, and is unique for its aliphatic character. The other two aromatic bonds (3,4 and 4,5—see insert in Table 1) can also function as diene in some [4 + 2] cycloadditions.[38−40] Recent studies have also shown that the π bonds of the aromatic ring can react as dienophile.[41,42] The length of the three double bonds in the acenaphthylene molecule is in the sequence C1−C2 (1.36 Å) < C4−C5 (1.38 Å) < C3−C4 (1.43 Å), and the bond order is reversed, C1−C2 (1.83) > C4−C5 (1.72) > C3−C4 (1.18) (see Table 1). The bond order was predicted by using the AIM feature in Gaussian based on the theory of atoms in molecules developed by Bader and co-workers,[43] which defines chemical properties on the basis of the topology of the electron density.

The fusion of the cyclopenta ring alters not only the electronic property of the 1,2 double bond but also the 3,4 and 4,5 aromatic bonds properties, which are either elongated toward a single bond or compressed toward a typical double bond. It can be anticipated, from the bond properties, that the addition of CPDyl to the 4,5 bond will be easier than that to the 3,4 bond.

Table 1 also reports the C−H bond dissociation energies and the barrier heights (ΔE_B) for the hydrogen abstraction reactions by H from different carbon sites computed at both the B3LYP/6-31G(d,p) and BH&HLYP levels of theory. The energy required for the C1−H bond cleavage is a few kilocalories per mole higher than those required for other aryl-H bonds, so is the barrier height of the hydrogen abstraction reactions.

Figure 1 shows the intramolecular pathway (Path A) for the addition of cyclopentadienyl to the C1 site of acenaphtylene. The two main products identified are fluoranthene (P1) and methylfluoranthene (P2).

The reaction pathway begins with the formation of intermediate A1, and the energy barrier for this step is 12 kcal/mol placing the product 9 kcal/mol below the reactants R (acenaphthylene + CPDyl). The intramolecular addition to the isolated π bond of acenaphtylene forms a bridged structure A2.

(35) Clar, E. *The Aromatic Sextet*; Wiley: London, UK, 1972.

(36) Garratt, P. J. *Aromaticity*; Wiley: New York, 1986.

(37) Badger, G. M. *Aromatic Character and Aromaticity*; Cambridge University Press: London, UK, 1969.

(38) Grimme, W.; Grommes, T.; Roth, W. R.; Breuckmann, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31* (7), 872.

(39) Miller, R. G.; Stiles, M. *J. Am. Chem. Soc.* **1963**, *85*, 1798.

(40) Ciganek, E. *Tetruhedron Leu.* **1967**, 3321.

(41) Martin, J. C.; Muchowski, J. M. *J. Org. Chem.* **1984**, *49*, 1040

(42) Neidlein, R.; Tadesse, L. *Helv. Chim. Acta* **1988**, *71*, 249.

(43) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon: Oxford, UK, 1990.

The unpaired electron is on the bridged carbon atom, which destabilizes the system so that the intramolecular addition step is endothermic. The barrier height, which is 33 kcal/mol for A1 → A2 is accordingly higher than the initial addition step.

The endo bicyclic adduct undergoes H migration reaction, producing a more stable intermediate (A3). The subsequent bridge opening reaction produces an extra six-member ring and restores the resonance structure (A4). The following 1,3-H shift reaction substantially lowers the energy (A5), and the final loss of methyl group produces the fully conjugated system, fluoranthene (P1). Figure 2 shows the potential energy surface for Pathway A.

The reaction pathways for the addition of CPDyl to the other three carbon sites of acenaphthylene (C3, C4, and C5) are illustrated in Figure 3. The main products are aceanthrylene (P3) and acephenanthrylene (P6).

The energy required for the three additions is in the sequence C5 (16 kcal/mol) < C3 (18 kcal/mol) < C4 (21 kcal/mol). The reactions CPDyl + acenaphthylene → B1_1 (Path B1), B1_2 (Path B2), C1_1 (Path C1), and C1_2 (Path C2) are all endothermic by 4.8, 11.3, 11.6, and 0.4 kcal/mol, respectively. Figure 4 shows the computed rate constants for the first addition step to the four carbon sites of acenapthylene.

Intermediates B1_2 and C1_1 are two conformers in which the added five-member ring orients differently from the parent acenaphthylene. The further intramolecular rearrangements to either the C3 or the C5 site of acenaphthylene lead to the formation of bridged intermediates B2 or C2. The energy required for the addition to the C4−C5 bond is 31 kcal/mol for the reaction C1_1 → C2 (Path C1) and 38 kcal/mol for C1_2 → C2 (Path C2). These values are about 10−20 kcal/mol lower than those relative to the addition to the C3−C4 bond, 53 kcal/mol for B1_1 → B2 (Path B1), and 46 kcal/mol for B1_2 → B2 (Path B2), respectively. Table 2 reports the Arrhenius parameters relative to the first two steps of Pathways A, B1, B2, C1, and C2.

As mentioned before, the intermediates with the radical on the bridged atom (B2 and C2) are not stable, and they rearrange themselves through H migration to form resonance-stabilized structures B3_1, B3_2, C3_1, and C3_2 that are a few tens of kilocalories per mole lower in energy. As an example, Figure 5 reports the optimized structure of B2 at the B3LYP-6-31G-(d,p) level.

The subsequent bridge opening reaction produces an extra six-member ring and the final loss of methyl group leads to two fully conjugated systems: aceanthrylene (P3), and acephenanthrylene (P6). Figure 6 shows the potential energy surfaces for the four pathways identified: Path B1, Path B2, Path C1, and Path C2.

The forward and reverse energy barriers of each reaction step involved in the intramolecular addition pathway are reported in Table 3.

In summary, the addition of CPDyl to the C1−C2 bond of acenaphthylene leads to the formation of fluoranthene (P1); the addition to the C3−C4 bond produces aceanthrylene (P3); and the addition to the C4−C5 bond yields acephenanthrylene (P6). On the basis of our computations, fluoranthene is expected to have the largest yield among the three products, and acephenanthrylene is favored over aceanthrylene. The experimental results from Mulholland's group[23,25] showed that at 800 °C and above, the $C_{16}H_{10}$ isomers (P1, P3, and P6) from CPD and acenaphthylene reactions were present in significant amount.

TABLE 3. Energy Barriers for All the Steps Present in Pathways A, B1, B2, C1, and C2

reactions	forward (kcal/mol)	reverse (kcal/mol)
R = A1	12.13	21.24
A1 = A2	32.59	11.76
A2 = A3	43.77	57.38
A3 = A4	40.27	40.73
A4 = A5	26.71	59.49
A5 = P1	21.28	10.33
A5 = P2	28.63	4.94
R = B1_1	17.53	12.7
B1_1 = B2	52.74	2.98
B2 = B3_1	30.69	77.44
B3_1 = B4_1	46.63	21.63
B4_1 = B5_1	14.82	76.46
B5_1 = P3	27.26	8.32
B5_1 = P4	37.64	3.93
R = B1_2	20.92	9.63
B1_2 = B2	46.26	2.96
B2 = B3_2	32.32	73.01
B3_2 = B4_2	44.5	23.47
B4_2 = B5_2	15.23	79.88
B5_2 = P3	27.92	8.06
B5_2 = P5	36.77	3.57
R = C1_1	21.17	9.58
C1_1 = C2	30.62	9.88
C2 = C3_1	37.46	55.65
C3_1 = C4_1	35.63	31.94
C4_1 = C5_1	20.71	68.95
C5_1 = P6	23.46	9.6
C5_1 = P7	32.03	4.29
R = C1_2	15.61	15.21
C1_2 = C2	38.09	6.16
C2 = C3_2	35.26	65.11
C3_2 = C4_2	39.98	27.42
C4_2 = C5_2	21.27	64.27
C5_2 = P6	21.56	10.15
C5_2 = P8	34.11	4.99

Among the $C_{16}H_{10}$ isomers experimentally identified, the yield of fluoranthene from both acenaphthylene−CPD mixture and CPD alone was 1 order of magnitude greater than the yields of acephenanthrylene and aceanthrylene, which is in agreement with our prediction that the C1 site is the most preferential reaction site. In the reaction pathways proposed, the formation of methyl substituents (P2, P4, P5, P7, and P8) of fluoranthene, aceanthrylene, and acephenanthrylene has been included and the trace amount of $C_{17}H_{12}$ isomers experimentally detected provides further validation for our computational results.

The DFT and TST calculations also indicate that formation of acephenanthrylene is favored over aceanthrylene both energetically and kinetically. The pyrolysis experiments showed that below 875 °C the production of acephenanthrylene was larger than that of aceanthrylene while above 875 °C aceanthrylene took over. To fully understand these observations we need to take into account the well-documented thermal interconversions of aceanthrylene, acephenanthrylene, and fluoranthene,[14,44] which showed that acephenanthrylene is slightly less stable than aceanthrylene under the rearrangement conditions (at 1100 °C).

Conclusions

In this paper, a detailed study of radical−molecule reaction pathways for the acenaphthylene−CPDyl system is performed by using density functional theory and transition state theory.

(44) Sarobe, M.; Jenneskens, L. W.; Wesseling, J.; Snoeijer, J. D.; Zwikker, J. W.; Wiersum, U. E. *Liebigs Ann. Recl.* **1997**, 1207.

The presence of resonance-stabilized CPDyl radicals prolongs the chain of aromatic growth and results in PAH formation by rearrangement rather than ring fragmentation.

The intramolecular addition pathways are identified for the acenaphthylene—CPDyl system, which lead to the production of fluoranthene, aceanthrylene, and acephenanthrylene respectively with one CPDyl moiety retained. The reactivity with respect to the addition of CPDyl is compared within the three double bonds in acenaphthylene.

PAH products from the bridge route retain the CPDyl moiety while having one carbon less than the sum of reactants, as a result of the breaking of the bridged structure and loss of CH_3 radicals.

As expected the 1,2 double bond in the five-member ring is the most preferential site for addition due to its aliphatic character, while the 4,5 bond is relatively more reactive than the 3,4 bond. Accordingly, the yields of products resulting from the addition to the three bonds are expected to be in the order fluoranthene > acephenanthrylene > aceanthrylene, which is consistent with the pyrolysis experiments reported by Mulholland's research group. The C—H bond β-scission and C—C bond β-scission pathways established for the CPDyl—CPD adduct in our previous work are not feasible for the CPDyl—acenaphthylene adduct.

Supporting Information Available: Cartesian coordinates of the intermediates and transition structures optimized at the B3LYP/6-31G(d,p) level, and total and zero-point energies for the reaction pathways of acenaphthylene and cyclopentadienyl radical addition. This material is available free of charge via the Internet at http://pubs.acs.org.

JO061036Y