

A Study of the Thermal C-C and C-H Bond Cleavage in the Aromatic Molecules: Acenaphthene and Acenaphthylene

Muthana Shanshal* and Hassan H. Abdullah**

Department of Chemistry, College of Science, University of Baghdad, Jadiriya, Baghdad, Iraq.

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Abstract

The thermal decomposition of the two aromatic hydrocarbons Acenaphthene and Acenaphthylene is studied applying the open shell semiempirical (Hartree-Fock) PM3 method. In this study all internal coordinates were varied, except the coordinate chosen to describe the reaction. All possible intermediates were considered on describing the reaction scheme. The preferred reaction path was assigned on the basis of comparing the activation energies of the different paths. The treatment shows that the *preferred* reaction paths lead to the formation of acetylene as a final product. This result is similar, but in the reverse direction, to former theoretical and experimental results reported in the literature, which showed that acetylene is a basic building unit within the natural formation reactions of Polycyclic Aromatic Hydrocarbon molecules.

Keywords: Acenaphthene; Acenaphthylene; Decomposition; PM3.

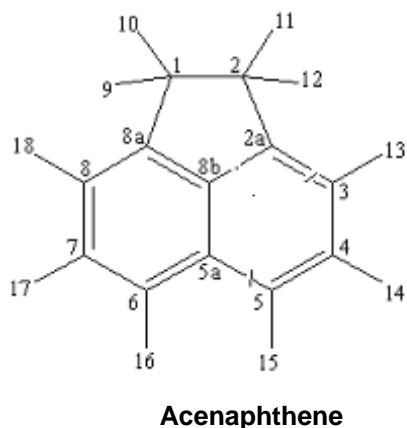
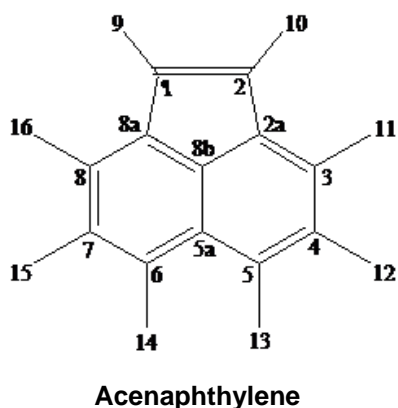
Introduction

Due to its importance for the chemical and petrochemical industry^[1] the thermal decomposition of polycyclic aromatic hydrocarbons (PAH) was subject of various theoretical and experimental studies^[1-8]. Ren et al.^[3] investigated the reactions as initiated by *insitu* H atoms, produced from the thermal decomposition of methanol at elevated temperatures. The isolated products were formed through recombination of the formed radicals with the H atoms. Theoretical, quantum mechanical studies were carried out for the decomposition reactions too^[4-7].

On the other hand, theoretical as well as experimental studies were done for the addition reactions of C₂H₂ to small aromatic hydrocarbons to yield higher PAH molecules and soot^[8-11]. In this paper we report a theoretical study for the thermal decomposition reactions of two aromatic hydrocarbons, Acenaphthene and Acenaphthylene.

* Corresponding author: e- mail: mshanshal2003@yahoo.com

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Method of treatment

The semiempirical PM3^[12] method, in the open shell and unrestricted form, was applied as it is programmed within the MOPAC program system^[13]. For the study of a bond breaking reaction, PM3 calculations were done for the molecule with various lengths of the bond. These bond lengths were kept constant while the other (3N-5) internal coordinates were varied. The energy values were plotted then against the "frozen" bond length values to yield the required reaction path. It was possible then to assign graphically the transition state and the products of the reaction (Figure 1). This type of calculation was repeated for all the succeeding reaction intermediates aiming towards the smallest acceptable reaction product. The acceptance of a reaction product is judged on the basis of the activation energy required for its generation. Accordingly, the described reaction paths in this work represent a summary of a big number of PM3 calculations (hundreds) done for the rupture of all the bonds in each "intermediate".

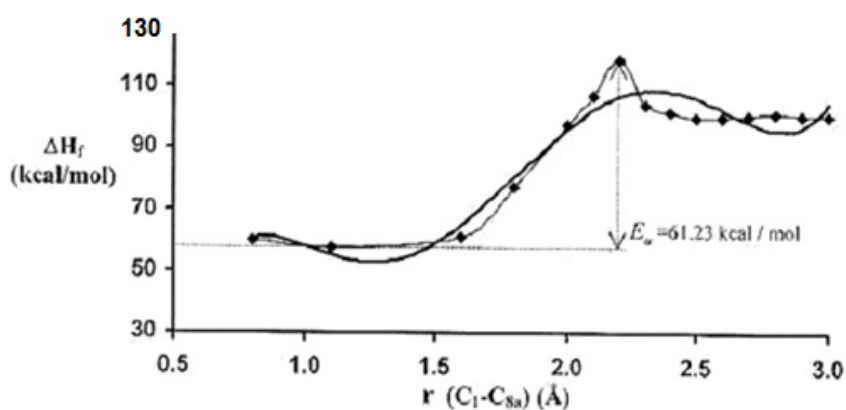


Figure 1: PM3 calculated reaction path (dotted line) of the C₁C_{8a} bond rupture reaction of C₂-acenaphthyl radical

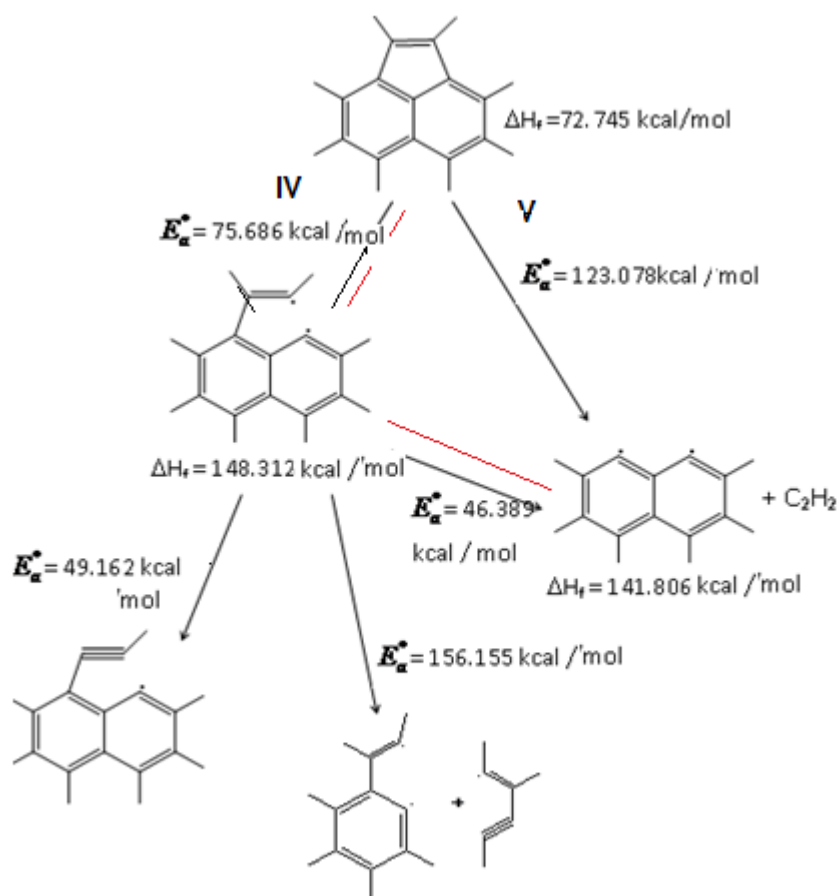
As seen in figure 1 the reaction energy is calculated as the difference; $\Delta H_{\text{react}} = \Delta H_{\text{f, product}} - \Delta H_{\text{f, reactant}}$ and considering the change in entropy being negligible within the reaction, $\Delta S_{\text{react.}} \approx 0.0$, $\Delta H_{\text{react}} \rightarrow \Delta E_{\text{react}}$.

Results and discussion

For the choice of the initial reaction step, it was necessary to evaluate the activation and reaction energies (E_a^*) for the rupture of the different C-C and C-H bonds as calculated according to the working scheme followed in this paper. The choice of E_a^* for the discussion of the reaction mechanism is acceptable here for two reasons; a- all cleavage reactions are endothermic and thus follow the Hammond postulate i.e. their transition states should be product like in structure; and b- they follow the Evans-Polanyi principle, i.e. their activation energies exhibit similar ordering in magnitudes as the final products.

Table 1: PM3 calculated activation energies for the bond rupture reactions in acenaphthylene.

Bond(s)	E_a^* (kcal/mol)
C ₂ -H ₁₀	104.895
C ₃ -H ₁₁	97.507
C ₄ -H ₁₂	96.032
C ₅ -H ₁₃	91.372
C ₁ -C ₂	91.650
C ₂ -C _{2a}	75.686
C _{2a} -C _{8b}	150.983
C _{2a} -C ₃	105.074
C ₃ -C ₄	95.784
C ₄ -C ₅	99.617
C ₅ -C _{5a}	217.067
C ₂ -C _{2a} + C ₁ -C _{8a}	123.078
C _{2a} -C ₃ + C ₄ -C ₅	229.205
C _{2a} -C ₃ + C ₅ -C _{5a}	228.172



Scheme 2

The two schemes, combined together, show that, according to the E_a^* values, and in order for the reaction to proceed, the competition is expected to be among path I ($E_a^* = 91.37$ kcal/mol) and path IV ($E_a^* = 75.68$ kcal/mol). The initial step for path I is the rupture of a C-H bond, that for path IV is the rupture of an essential C-C single bond. The second step for path I is the rupture of a C-C bond ($E_a^* = 53.07$ kcal/mol).

Comparison of the reaction paths reveals that path IV includes the steps with the smallest activation energy values followed by the path I. In both cases the reaction proceeds towards the elimination of a C_2H_2 (acetylenic) fragment. The role of C_2H_2 as a template in these reactions is similar, but in the reverse direction, to that of the formation reactions of higher PAH's and soot as suggested by Frenklach et al. [7,8] and experimental studies [11].

Inspection of all 5 reaction paths shows that the formation of C_2H_2 fragment is preferred due to the smaller E_a^* values. Other formed cyclic aromatic compounds are either benzene or naphthalene derivatives. In the presence of H_2 , as was inspected by Ren's experiments [3] one should expect the following reaction products (Table 2).

Table 2. Expected aromatic products to be formed from the thermal degradation of acenaphthylene in the presence of H₂.

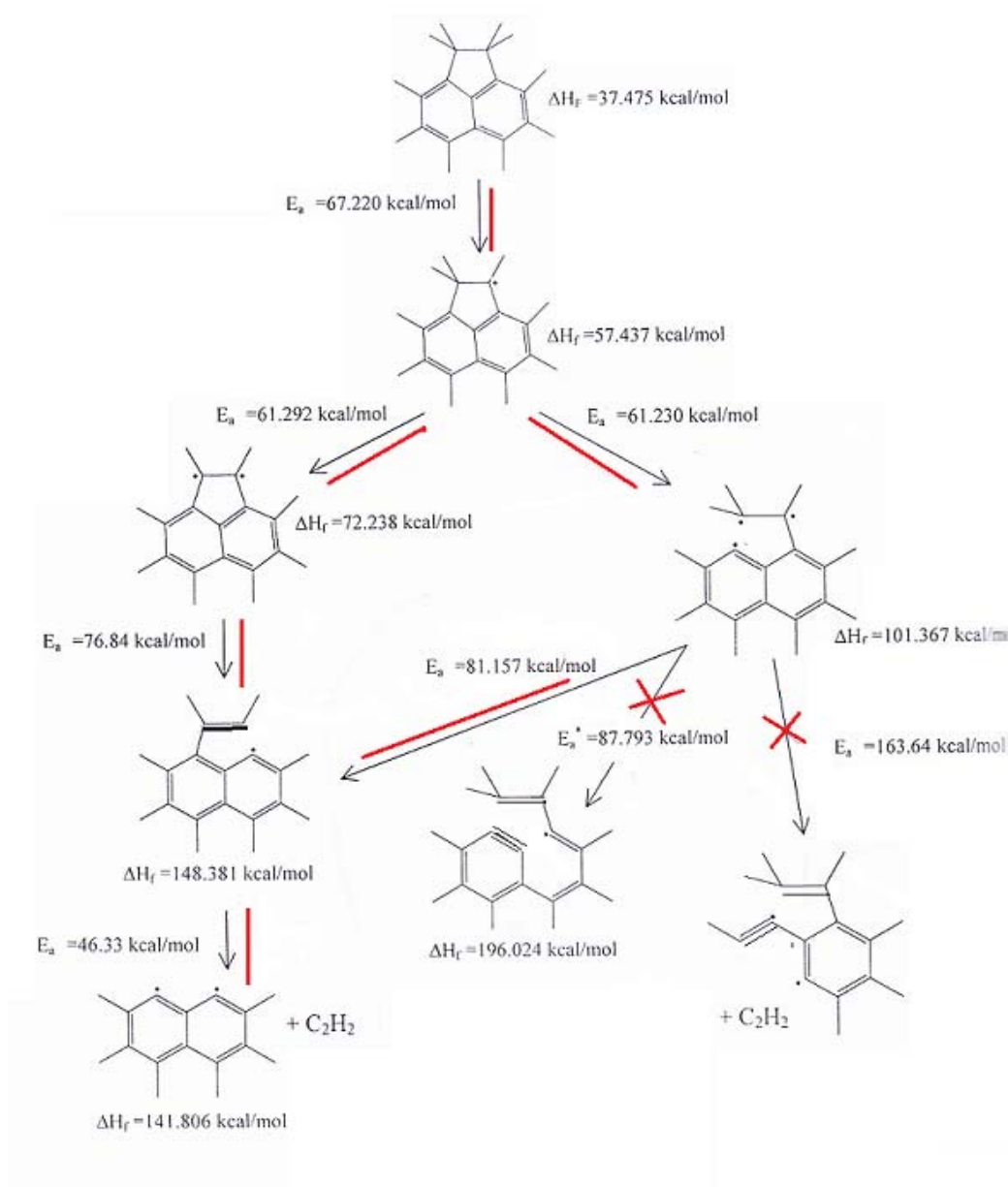
No.	Compound	ΔH_f (kcal / mol)
1	Acenaphthylene	72.745
2	Naphthalene	39.089
3	1-vinyl-naphthalene	54.722
4	1-methylene-7-vinyl-1H-indene	79.506
5	1-methylene-1H-indene	63.755
6	1,2-divinyl-benzene	54.819
7	1-vinyl-benzene	39.089
8	Butadiene	30.989
9	1-buta-1,3-dienyl-3-vinyl-benzene	70.124
10	Benzene	23.386

Thermal decomposition of Acenaphthene molecule.

In a similar treatment, the activation energies of the thermal bond breaking reactions were calculated for the different bonds in acenaphthene molecule. Table 3 shows the calculated E_a^* values for the different C-H and C-C bonds of the molecule. Apparent from the values of table 3 are the relatively low values of activation energies for the cleavage of the bonds C₁-C₂ (51.14kcal/mol) and C₂-H₁₁ (67.32kcal/mol). The calculated E_a^* values for the other bonds are exceedingly higher, 92.49kcal/mol (C₅-H₁₅) at least. Accordingly, the discussion of the decomposition reaction path has to be limited to those paths that start with the cleavage of either of these two bonds; i.e. path I for the C₂-H₁₁ and path II for the C₁-C₂ bond. Scheme 3 shows the reaction starting with the cleavage of the C₂-H₁₁ bond.

Table 3: PM3 calculated activation energies for the bond rupture reactions in acenaphthene.

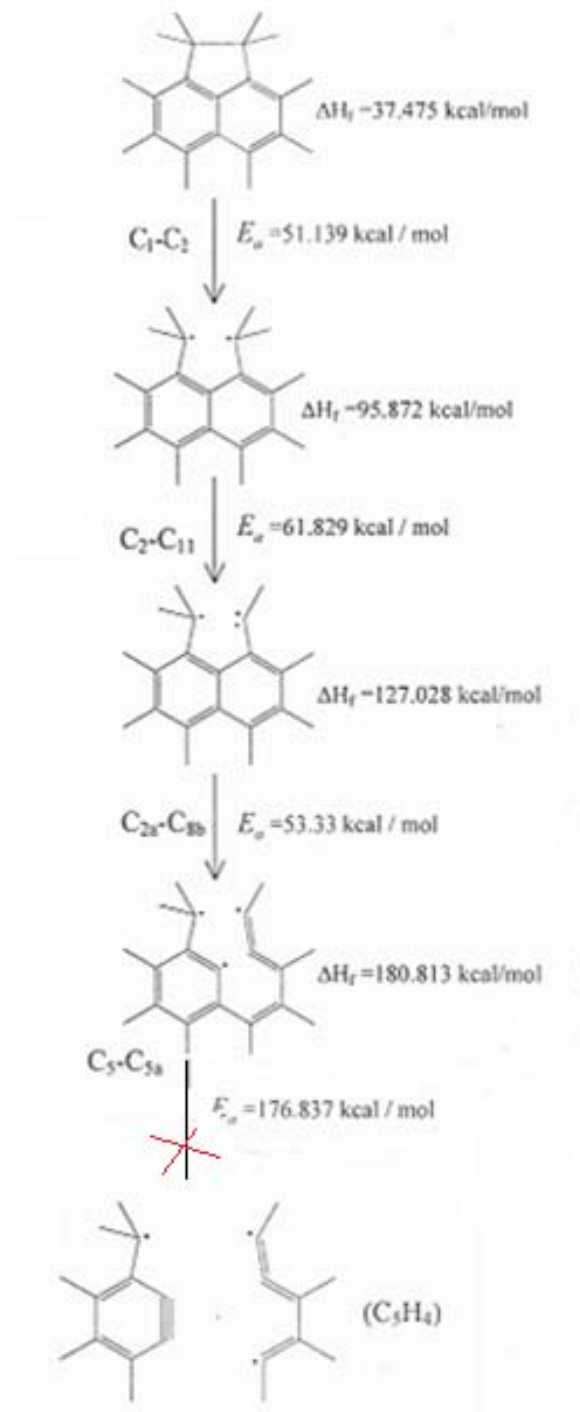
Bond(s)	E_a^* (kcal/mol)
C ₂ -H ₁₁	67.220
C ₃ -H ₁₃	96.442
C ₄ -H ₁₄	96.151
C ₅ -H ₁₅	92.486
C ₁ -C ₂	51.139
C ₂ -C _{2a}	210.908
C _{2a} -C _{8b}	157.000
C _{2a} -C ₃	128.682
C ₃ -C ₄	217.920
C ₄ -C ₅	102.602
C ₅ -C _{5a}	223.700
C ₂ -C _{2a} + C ₁ -C _{8a}	122.386
C ₃ -C ₄ + C ₅ -C _{5a}	143.365
C _{2a} -C ₃ + C ₄ -C ₅	154.820
C _{2a} -C ₃ + C ₅ -C _{5a}	236.185



Scheme 3

In this scheme one may follow the path with the least E_a^* values (recognized with the bold color). Obviously the route with the successive E_a^* values; 67.22kcal/mol, 61.29kcal/mol, 76.84kcal/mol and 46.33kcal/mol is of higher priority. It leads to the formation of C_2H_2 and naphthylbiradical. The other branch of the "reaction tree" includes higher activation energy values, such as 163.64kcal/mol, 87.79kcal/mol and 81.16kcal/mol, and is to be neglected.

Scheme 4 shows the 2nd probable reaction path starting with cleavage of the C_1 - C_2 bond ($E_a=51.14$ kcal/mol).



Scheme 4

It includes an E_a^* value of 176.84 kcal/mol which is higher than any value in path I. For this reason, this path should be eliminated from the discussion of the mechanism of this decomposition reaction. Path I is left then as the only acceptable description of the reaction mechanism.

Conclusion

According to the PM3 (semiempirical H-F) treatment, the decomposition of the aromatic acenaphthene and acenaphthylene molecules proceeds towards the formation of an acetylenic fragment and an aromatic molecule. In this reaction, the acetylenic fragment constitutes the basic template, similar to the thermal formation of PAH's and soot in which acetylene forms the basic template too, as found in former works, both theoretically and experimentally.

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