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PAH growth initiation by hydrogen abstraction – A computational study

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are central subjects in combustion chemistry. PAHs represent a class of molecules with a structure build up of multiple benzene rings. They are formed by incomplete combustion processes and pose a danger to our environment, and also to living organisms due to their harmful properties, which increases with the growth of their structure. The aim of this work is to study the hydrogen abstraction reactions at previously determined initiation points of the highly carcinogenic 16 parent PAHs. The hydrogen abstractions are carried out with the help of hydrogen, hydroxyl and methyl radicals ($\cdot\text{H}$, $\cdot\text{OH}$, $\cdot\text{CH}_3$). The calculations have been carried out by applying the $\omega\text{B97XD/6-31+G(d,p)}$ level of theory. All in all, three reaction partners, 16 PAHs, 16 PAH radicals and 48 transition states have been computed and the corresponding zero-point energy (ΔE), enthalpy (ΔH), and Gibbs free energy (ΔG) values are determined. The results enables to identify which of the three applied radicals is more prone to start a reaction and initiate the further growth of PAHs in a given mechanism.

Rezümé

A policiklikus aromás szénhidrogének (PAH-ok) olyan sokoldalú vegyületek, amelyek számos különböző tudományterületen központi szerepet töltenek be, különös tekintettel az égéskémiára és az asztrokémiára. A PAH-ok szerkezetüket tekintve több összekapcsolódó aromás gyűrűből állnak. Tökéletlen égési folyamatok során keletkeznek és toxicitásuk - amely a szerkezet méretének növekedésével egyaránt nő - miatt az élő szervezetek szempontjából a jelenlétük nem kívánatos. A jelen kutatás célja az ún. „parent” PAH-ok lehetséges növekedési mechanizmusainak első lépésének a feltárása számítógépes kémiai módszerekkel. A vizsgált reakció mechanizmusok hidrogén absztrakcióval indulnak, s ezt a lépést hidrogén ($\cdot\text{H}$), hidroxil ($\cdot\text{HO}$), és metilgyökök ($\cdot\text{CH}_3$) segítségével modelleztük. A számolásokat az irodalomban hasonló rendszerek vizsgálatára korábban használt $\omega\text{B97XD/6-31+G(d,p)}$ elméleti szinten vittük véghez. Összeségében 3 reakciópartnert, 16 PAH-ot, 16 PAH gyököt és 48 átmeneti állapotot vizsgáltunk és reakciókhoz tartozó termodinamikai paraméterek (ΔE_0 , ΔH , ΔG) meghatározásra kerültek. Az eredmények lehetővé teszik, hogy jobban megérthessük a PAH-ok növekedését és feltárjuk az ezt befolyásoló tényezőket.

Introduction

Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (also known as PAHs) are chemical compounds with two or more fused benzene rings [1]. In the vast class of PAHs (several thousands), simple and complex ring systems can be formed as well, by including only carbon-carbon (C-C) and carbon and hydrogen (C-H) bonds (**Figure 1**).

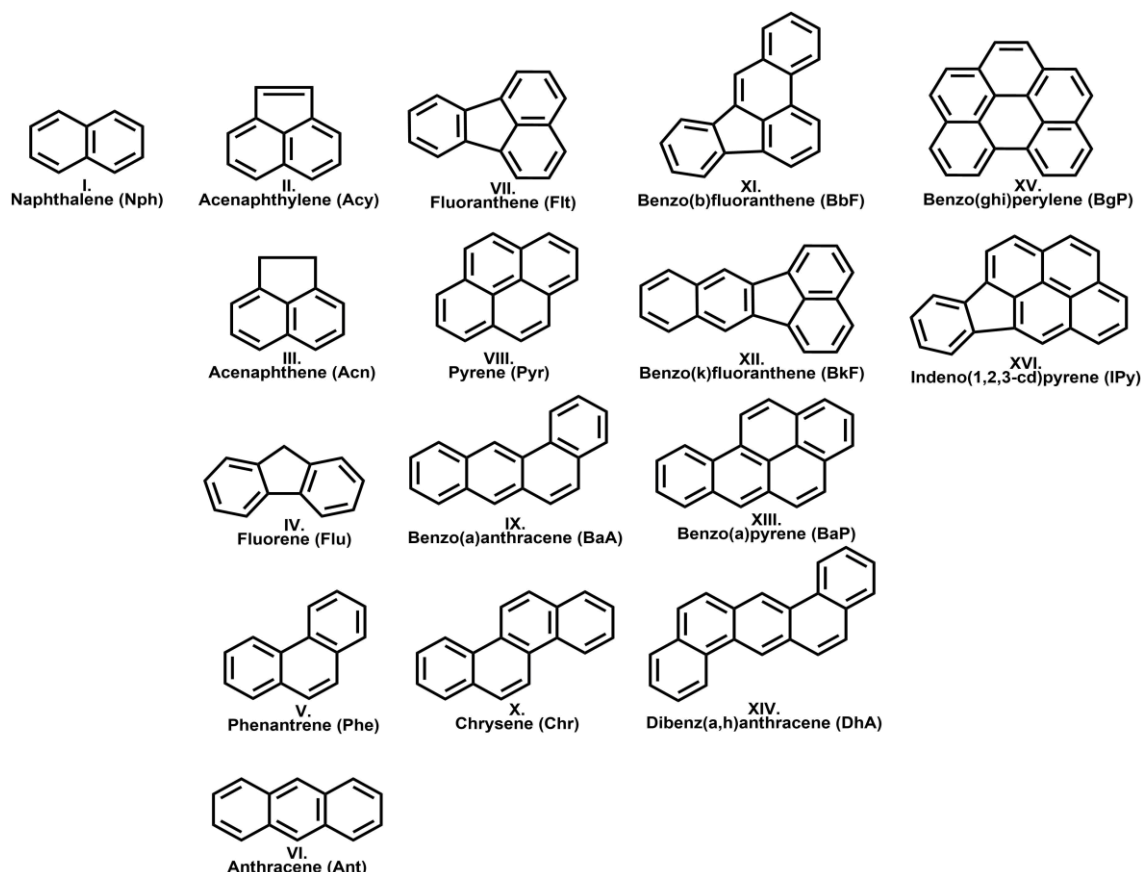


Figure 1 Chemical structures of 16 priority polycyclic aromatic hydrocarbons (PAHs) or „parent” PAHs.

PAHs are formed during the **incomplete combustion** of organic substances. The PAH emissions originate from both anthropogenic and natural activities (open burning of brushwood, straw, and moorland, forest fires) [2]–[7]. However, the sources of PAHs can be divided into stationary (*i.e.* heating and cooking, smoke, incineration, industrial emissions) and mobile emissions (*i.e.* transportation). Due to the diverse ring arrangements of PAHs, numerous physical, chemical, and biological characteristics can be attributed to them [8]. Their toxicity, mutagenicity and carcinogenicity were studied in numerous cases, based on which serious concerns are confirmed [8]–[10]. It is important to mention that PAHs are part of the Persistent

Organic Pollutant class, which means that they can persistently accumulate in the body fat of living organisms [11]. Since, PAHs have been detected in all four spheres of Earth (atmosphere [12], lithosphere [13], hydrosphere [14], biosphere [15], [16]), they are considered as mainly ubiquitous pollutants in the environment [17]. Attempts have been made to introduce legislation to reduce the emission of some PAH species [18]. However, due to their high concentrations (increasing global emission concentration [19]), these cannot be considered sufficient. The monitoring of PAHs has started more than 40 years ago, when a list about of the 16 priority (or „parent”) PAHs was published by the U.S. Environmental Protection Agency (EPA) in 1976 [17] (**Figure 1**). These molecules have been selected to represent all existing PAHs, taking into account their occurrence and their toxicological effects as well. For now it is selfexplanatory, that the list is incomplete, and PAHs with stronger detrimental effects should be added to them. However, the selected 16 molecules still can be considered as a suitable set of species for computational analysis of PAHs as they have a wide range of size and diverse molecular structures. The research of PAHs is highly significant because of their environmental and health effects. It is enough to mention their role in smog formation or their strongly proven detrimental biological effects. However, PAHs play a crucial role in material science and astrophysical studies as well, since they had been linked for being the source of previously unidentified infrared emission bands (UIR) (3.3, 6.2, 7.7, 8.6, 11.3, and 12.7 μm) detected in space [20], [21]. Moreover, $\approx 15\%$ of the interstellar carbon are attributed to PAHs [22], [23]. Their research for material scientists is also important, because PAHs play a very important role in the investigation of nanostructures, since they can be seen as key molecular building blocks leading to nanotubes and other species identified in combustion systems [24].

The PAH growth phenomena

The most important phenomena among PAHs is that they are able to grow. It means that during a combustion process PAHs can transform into larger molecules. The growth of PAHs is determined by a series of smaller reactions, which are together referred to as the growth mechanism. Until the formation of the sixth ring PAHs is called "small" PAHs, and which contain 10 or more rings are called "large" PAHs. If they are only built up from 6 membered rings, they belong to the alternant category, but if they contain 5 membered rings too, they can be classified as nonalternant ones. Polycyclic aromatic hydrocarbons don't stop growing until they have molecular characters. PAHs lose their molecular properties during **particle inception** through physical and/or chemical condensation and acquire the complex morphological and

chemical properties of condensed phases. As the first particles are formed, they continue to interact with the surrounding combustion environment. Molecules can be added to the system to increase their size and mass, H atoms or C atoms can be removed by dehydrogenation or by OH, respectively. Furthermore, the molecules can be **coagulated** with other structures or clusters (a coalescence event occurs when two clusters merge into one reducing free surface area, which occurs to minimize their free energy). The final stage of these processes is the formation of the so-called primary **soot particles**, with sizes ranging from 10 to 50 nm, and soot **aggregates** containing a large number of primary particles whose size can reach values as high as 1 μm .

The importance of hydrogen abstractions in PAH growth mechanisms

Numerous models were developed and validated with a large array of possible reactions for PAH growth. This is possible due to the diversity of molecules and radicals that are present in significant concentrations in hydrocarbon flames [25]. The PAH growth mechanisms can be classified into three major groups:

- acetylene additions (*e.g.* HACA and Diels-Alder)
- vinylacetylene additions (*e.g.* HAVA)
- radical reactions (*e.g.* MAC).

A well-known PAH growth reaction mechanism is abbreviated as HACA which stands for *hydrogen abstraction and acetylene (C_2H_2) addition* [26], [27]. As it can be seen from the name of the mechanism, it is based on two major steps. The first step represents the hydrogen abstraction to activate the molecule, and in the second step, acetylene addition takes place.

Another growth mechanism that involves acetylene addition is introduced by Otto Diels and Kurt Alder, and it is known as the *Diels-Alder reaction mechanism*. It is a very important reaction that leads to the formation of the carbon-carbon bond in a six-membered ring with high stereochemical control [28]. The traditional method of the formation of a cyclic compound via the Diels-Alder process is a reaction between butadiene and an olefin. However, a study carried out by Morokuma resulted in the conclusion that this mechanism can be applied also for larger molecules [29]. For example, a benzo(a)pyrene can be formed with the Diels-Alder mechanism from chrysene or benzo(a)anthracene in two steps [30]. The first step is acetylene addition which leads to the Diels-Alder adduct, and the second step is hydrogen abstraction. It is worth mentioning it has been proved that the PAH growth by Diels-Alder reaction is way slower than by HACA [17].

The famous *methyl addition cyclization* (MAC) mechanism uses methyl radicals ($\cdot\text{CH}_3$) in PAH formations [31], [32]. Methyl radicals are the simplest alkyl radicals in the flames of aliphatic or aromatic fuels, with a relatively high occurrence [33]. This reaction mechanism contains the addition of two or three methyl radicals to the previously formed radicals obtained by hydrogen abstractions, and is suitable for the formation of additional rings in aromatic structure, throughout hydrogen loss [17], [31], [32], [34].

A significant alternative of HACA is the so called *ethynyl addition mechanism* (EAM [35]) and the *hydrogen abstraction and ethynyl radical addition mechanisms* (HAERA) which involve ethynyl radical ($\cdot\text{C}_2\text{H}$) instead of acetylene (C_2H_2). The occurrence of this mechanism can have a high probability because $\cdot\text{C}_2\text{H}$ is formed in carbon rich environment, from the decomposition of acetylene [36]. These mechanisms also begin with hydrogen abstraction in order to form a PAH radical and followed by the addition of the ethynyl radical.

The HAVA (*hydrogen abstraction vinyl radical addition*) and the PAC (phenyl addition cyclization) mechanisms are also important [37]. Both of them begin with hydrogen abstractions to create the PAH radical, which can react easily with the vinyl or phenyl radical, in the case of HAVA and PAC respectively.

All in all, hydrogen abstractions are essential in a number of PAH growth mechanisms in order to form a radical from the reactant molecular structure.

Aim of study

PAHs represent a severe concern due to their detrimental effects on the environment and human health. These molecules can grow to larger and more toxic compounds via different reaction mechanisms which mostly begin with a radical formation. Since PAHs are united benzene rings with hydrogens on their edges, the PAH radical formation is most easily achieved by the removal of one of these hydrogens. The following study aims to analyze computationally the formation of the 16 priority PAH radicals via hydrogen abstraction by involving three different radicals: hydrogen atom ($\cdot\text{H}$), hydroxyl radical ($\cdot\text{OH}$), and methyl radical ($\cdot\text{CH}_3$) (**Figure 2**).

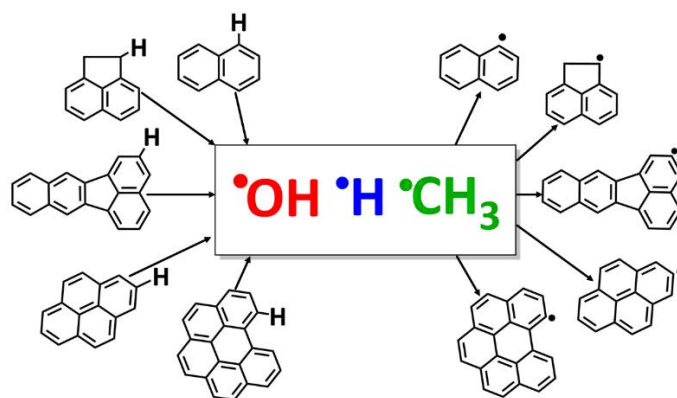


Figure 2 Schematic representation of the main focus of this work with some of the PAHs and the radicals involved ($\cdot\text{OH}$, $\cdot\text{H}$, $\cdot\text{CH}_3$).

In all 16 cases, the hydrogens were abstracted from those points where the C-H bonds are the weakest. These reaction initiation points were determined previously by Reizer and Fiser. By the study of these special hydrogen abstractions, a deeper understanding of PAH growth will be achieved as the first step of the processes will be analyzed.

Methods

Computational chemistry tools were used to study and describe hydrogen abstraction reactions. The 3D model of the studied compounds were created in GaussView 6.0 [38]. Then, the structures were optimized and frequency calculations were performed by using the ω B97XD/6-311++G(d,p) level of theory as it was proved to be efficient in the study of PAHs [30], [40]. The calculations have been carried out by using the Gaussian 09 [39] program package. The corresponding zero-point energy (E_0), enthalpy (H), and Gibbs free energy (G) of the structures were collected, and the thermodynamic quantities which describe the reactions were computed. All in all, 16 PAHs, 16 PAH radicals, and 48 transition states were calculated. By starting the GaussView 6.0, a blank window, and the user interface can be seen (**Figure 3**). In the blank window, the molecule of interest can be built by using the user interface.

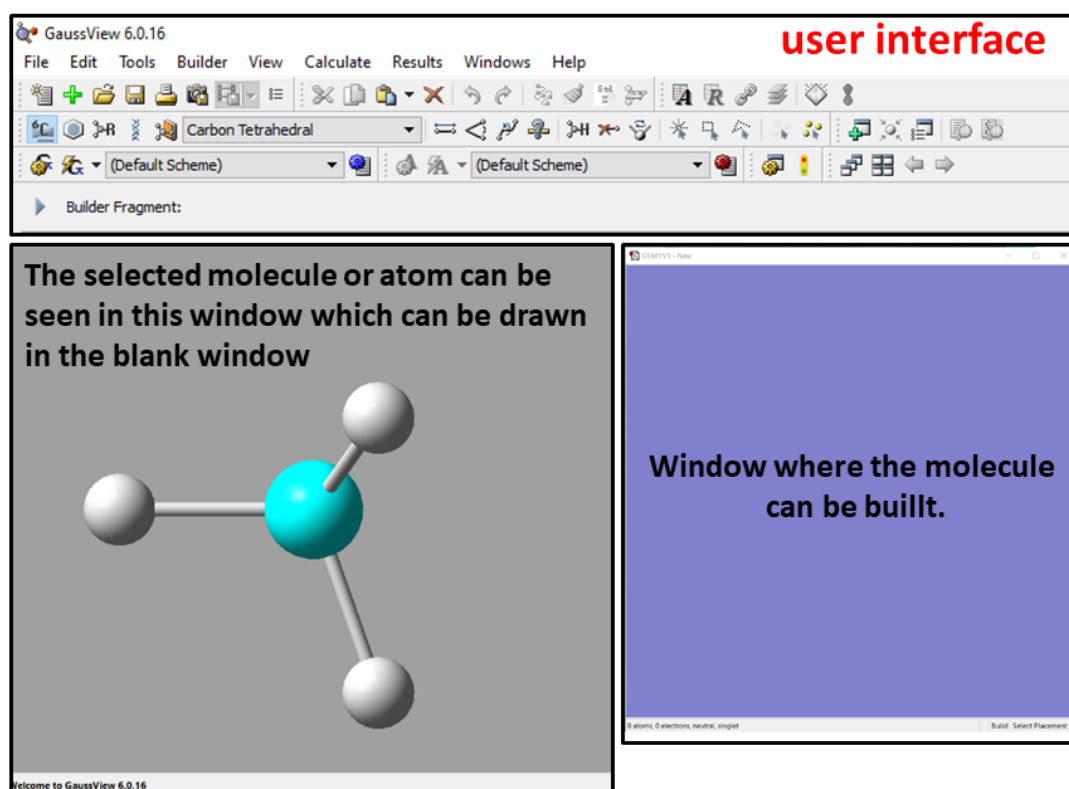


Figure 3 Opening windows of Gaussview 6.0

After the structure is created, it can be saved as a Gaussian input file. If this input file is opened in a text editor (*e.g.* TextPad) the following can be seen (**Figure 4**):

# wB97XD/6-31+G(d,p) Opt Freq				Method and basis set
Naphtalene.log				Title card
0	1	Charge and multiplicity		
C	2.43623	-0.70914	-0.00000	Coordinates of the atoms which build up the molecule
C	1.24586	-1.40389	-0.00000	
C	0.00000	-0.71726	0.00000	
C	-0.00000	0.71726	0.00000	
C	1.24586	1.40389	-0.00000	
C	2.43622	0.70915	0.00000	
H	-1.24418	-2.49105	0.00000	
H	3.38021	-1.24641	-0.00000	
H	1.24418	-2.49105	-0.00000	
C	-1.24586	-1.40389	0.00000	
C	-1.24586	1.40389	0.00000	
H	1.24418	2.49105	-0.00000	
H	3.38021	1.24642	0.00000	
C	-2.43623	0.70915	-0.00000	
C	-2.43622	-0.70915	-0.00000	
H	-1.24418	2.49105	0.00000	
H	-3.38022	1.24641	-0.00000	
H	-3.38021	-1.24641	-0.00000	

Figure 4 The structure of a Gaussian input file.

The input can be divided into three sections: route section, title section, and molecule specification (charge, multiplicity, atom types, and the corresponding coordinates). The route section contains the level of theory and the commands (*e.g.* Opt or Optimization). In the title section, a description or title can be added to the input file in question. The molecule specification include the charge and multiplicity of the molecule, and the corresponding atoms with their respective coordinates.

As soon as the input file is ready, the calculation can be carried out by using the Gaussian software. The calculation could take as long as a few seconds or several hours or even more. The software will generate an output file which can be opened by using a text editor or GaussView. If the calculation went well, the output file contains a final structure. However, it still has to be checked, and depending on whether a minima or a transition state is computed, different criteria have to be fulfilled. For example the molecule structure must have the correct number of negative frequencies, and their atoms must be arranged in a way which is expected. Furthermore, the output file reveals whether the calculation is done, because if it could not run properly then an error message shows up at the end of the output file. However, as it was mentioned before, even if the calculation seemingly terminated normally, to avoid false results, visual inspection of the structure in GaussView is necessary.

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WAR ES EIN GOTT DER DIESE ZEICHEN SCHRIEB?
- LUDWIG BOLTZMANN, QUOTING GOETHE, ABOUT MAXWELL'S EQUATIONS.
Job cpu time:      1 days  1 hours 42 minutes 40.1 seconds.
File lengths (MBytes):  RWF=   6330 Int=      0 D2E=      0 Chk=    28 Scr=
Normal termination of Gaussian 09 at Mon Nov  1 20:44:43 2021.

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Figure 5 Screenshot from a Gaussian output file.

If the structure is correct, the thermodynamic parameters (*e.g.* zero-point energy) can be collected from the output file (**Figure 5** and **Figure 6**).

Zero-point correction=	0.148922 (Hartree/Particle)		
Thermal correction to Energy=	0.155712		
Thermal correction to Enthalpy=	0.156656		
Thermal correction to Gibbs Free Energy=	0.117714		
Sum of electronic and zero-point Energies=	-385.628510	←	E_0
Sum of electronic and thermal Energies=	-385.621720	←	E_T
Sum of electronic and thermal Enthalpies=	-385.620776	←	H
Sum of electronic and thermal Free Energies=	-385.659718	←	G
	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	97.711	28.640	Entropy 81.961

Figure 6 Thermochemistry in a Gaussian output file.

These steps have been followed and thereafter, the collected thermodynamic properties are sorted in Excel and used in further evaluation, in which the activation energy of each studied reaction is determined.

Results and Discussion

General considerations

Hydrogen abstractions from the 16 priority PAHs with three different radicals ($\cdot\text{H}$, $\cdot\text{OH}$, and $\cdot\text{CH}_3$) are studied and the thermodynamics of these reactions have been analyzed (**Figure 7**).

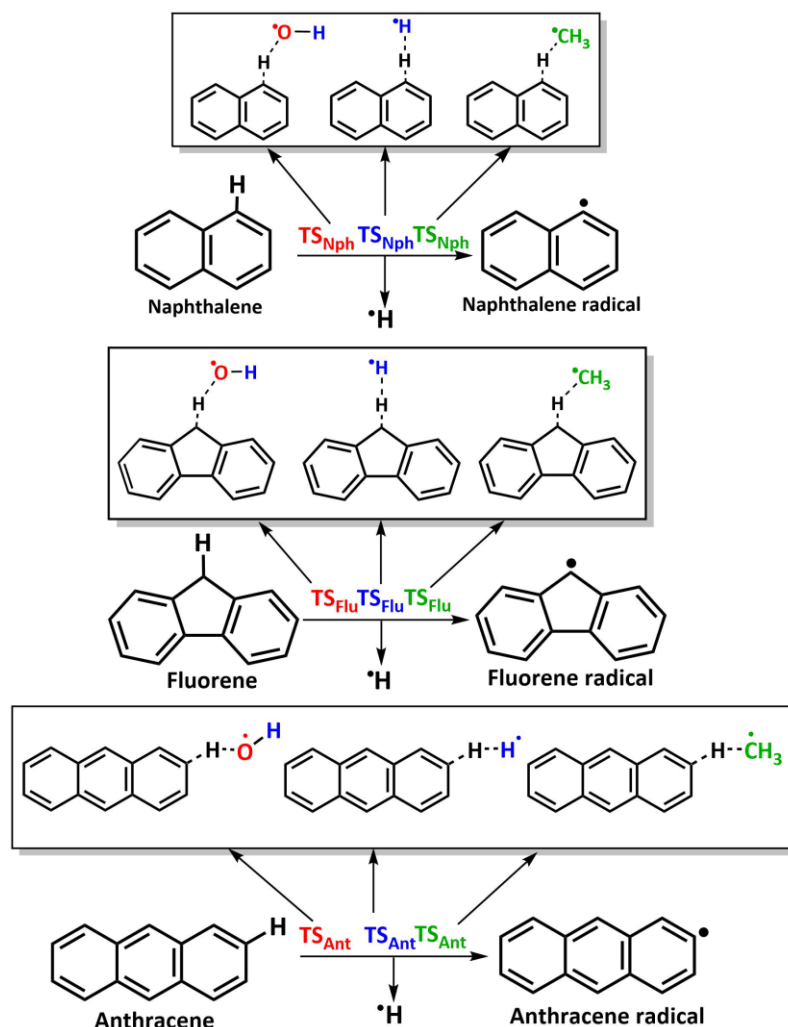


Figure 7 Schematic representation of hydrogen abstractions from naphthalene, fluorene and anthracene by involving hydrogen ($\cdot\text{H}$), hydroxyl ($\cdot\text{OH}$), and methyl radicals ($\cdot\text{CH}_3$), respectively.

All in all, 86 structures, including the reactants, products, radicals, and transition state structures have been computed. All structures were computed at the $\omega\text{B97XD}/6\text{-}311\text{++G(d,p)}$ level of theory. The activation energy (zero-point corrected, $\Delta E^\ddagger_0$), enthalpy and Gibbs free energy of the studied hydrogen abstraction reactions have been computed. The activation energy has to

be achieved by the reactant in order to reach the product side (**Hiba! A hivatkozási forrás nem található.**).

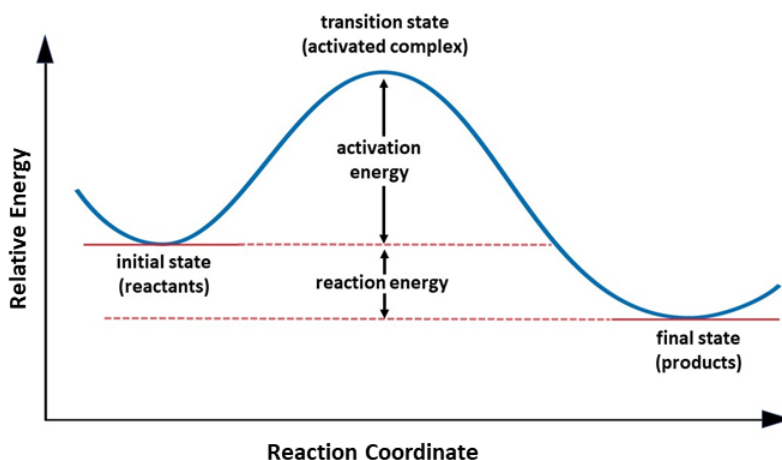


Figure 8 Schematic representation of the energetics of a simple reaction.

It is the energy gap between the energy of the transition states and the reactants, so the activation energy can be calculated by the subtraction of the transition states' energy from the reactants' energy. The activation enthalpy and Gibbs free energy can be computed using the values of the corresponding thermodynamic functions.

The reaction energy, enthalpy and Gibbs free energy is the change of the corresponding parameter in a given system during the reaction. These determines whether the product is preferred over the reactant or the otherway around and whether the system in which the reaction take place absorbs (endotherm reaction), or emits heat (exotherm reaction). The reaction energy value itself is the energy difference between the products and the reactants, so it can be calculated by the subtraction of the products' energy from the reactants' energy. The corresponding reaction enthalpy and Gibbs free energy values can be computed similarly.

Comparison of reaction initiation by different radicals

The most favorable radical formation is associated with $\cdot\text{H}$ induced hydrogen abstraction from acenaphthene, as this has the lowest activation energy ($\Delta E^\ddagger_0 = 19.00$ kJ/mol) among all of the studied reactions including those obtained by $\cdot\text{OH}$ and $\cdot\text{CH}_3$ radicals (**Table 1**). The maximum activation energy value analyzing all obtained results belongs to chrysene with 245.6 kJ/mol (**Table 1**).

Table 1 Activation energy (zero-point corrected, $\Delta E^\ddagger_0$), enthalpy ($\Delta H^\ddagger$) and Gibbs free energy ($\Delta G^\ddagger$) values of the studied hydrogen abstraction reactions in kJ/mol calculated at $\omega\text{B97XD/6-31+G(d,p)}$ level of theory.

	$\cdot\text{H}$ abstraction by $\cdot\text{H}$			$\cdot\text{H}$ abstraction by $\cdot\text{OH}$			$\cdot\text{H}$ abstraction by $\cdot\text{CH}_3$		
	$\Delta E^\ddagger_0$	$\Delta H^\ddagger$	$\Delta G^\ddagger$	$\Delta E^\ddagger_0$	$\Delta H^\ddagger$	$\Delta G^\ddagger$	$\Delta E^\ddagger_0$	$\Delta H^\ddagger$	$\Delta G^\ddagger$
	kJ/mol			kJ/mol			kJ/mol		
Nph	56.87	53.62	80.57	62.62	60.67	95.51	77.60	75.36	113.99
Acy	56.06	52.76	79.91	64.42	62.62	96.98	78.24	78.23	117.13
Acn	19.00	14.84	44.15	145.99	143.05	178.88	44.31	40.93	84.68
Flu	20.43	16.47	44.96	48.86	46.80	80.01	41.30	38.33	80.22
Phe	57.88	54.13	81.79	63.87	61.37	98.58	212.9	209.5	252.57
Ant	56.30	53.07	80.04	65.25	63.21	98.20	78.30	75.88	116.78
Flt	55.82	52.56	79.60	64.11	62.31	96.77	78.00	75.44	117.03
Pyr	56.71	53.47	80.42	62.29	60.47	95.33	224.45	221.51	264.00
BaA	212.87	208.59	236.29	63.86	61.21	99.25	244.9	241.4	284.12
Chr	58.30	54.48	82.33	65.92	63.10	101.9	245.6	241.9	285.86
BbF	57.92	54.25	81.91	63.37	60.92	98.24	80.09	77.17	119.78
BkF	55.74	52.51	79.51	64.27	62.43	97.09	77.51	75.19	115.86
BaP	57.48	53.77	81.31	64.40	61.81	99.65	80.21	77.34	119.62
Ipy	57.31	53.90	81.39	65.90	63.94	98.81	79.22	77.04	116.78
BgP	58.08	54.45	79.83	64.12	61.55	97.69	79.79	74.53	123.59
DhA	58.01	54.29	81.83	62.36	60.17	96.66	277.2	273.4	317.10

The activation energy values of the hydrogen abstraction reactions carried out by a hydrogen atom are in the range of 19.00 kJ/mol to 212.87 kJ/mol. However, the highest activation energy value with $\cdot\text{H}$ promoted hydrogen abstraction ($\Delta E^\ddagger_0 = 212.87$ kJ/mol) is associated with benzo(a)anthracene (BaA, **Figure 9**, **Table 1**). It can be observed that the activation energy of fluorene is 20.43 kJ/mol, which is really close to the one of acenaphthene ($\Delta E^\ddagger_0 = 19.00$ kJ/mol). This can be explained by the fact that the hydrogen abstractions took place in both cases from the aliphatic part of these molecules. It can also be seen that the activation energy values with the exception of BaA, and the two PAH with aliphatic moiety (Acn, Flu) are in a very narrow range between 55.74 kJ/mol (BkF) and 58.30 (Chr) (**Figure 9**, **Table 1**).

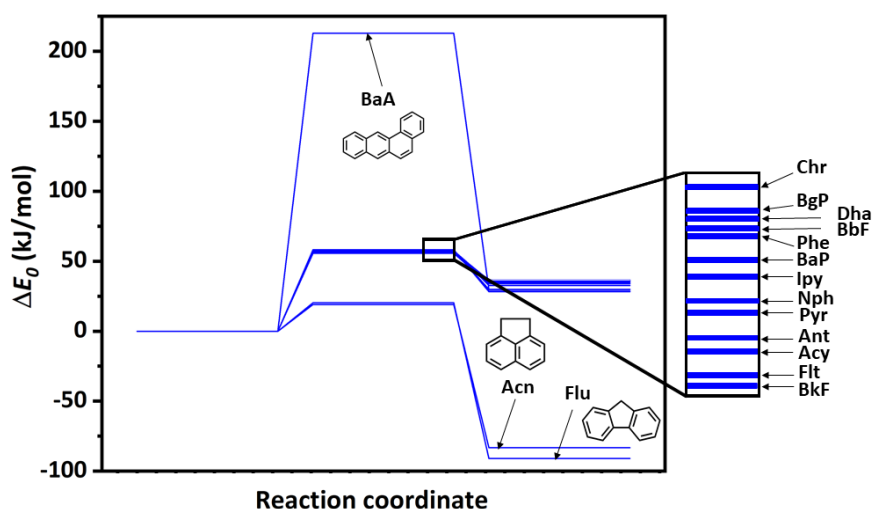


Figure 9 The potential energy curves (PECs) of the studied hydrogen abstractions with $\cdot\text{H}$ radical calculated at the $\omega\text{B97XD/6-31+G(d,p)}$ level of theory.

The activation energy values corresponding to the hydrogen abstractions with hydroxyl radical are similar to the processes involving $\cdot\text{H}$, but this radical formation route has a different very high energy case, when acenaphthene is the reaction partner and thus, this can be considered as the least favorable route in this set of processes (**Figure 10, Table 1**). The most favourable PAH radical formation occurs in the case of fluorene when $\cdot\text{OH}$ is considered as reaction partner, as it has the smallest activation energy ($\Delta E^\ddagger_0 = 48.86$ kJ/mol) among all. The activation energy values are in a range between 48.86 kJ/mol (Flu) and 145.90 kJ/mol (Acn). The selection of the abstractor in radical formation has a key role. This is highlighted in the case of acenaphthene, where the abstraction of the same hydrogen atom from the same molecule has an activation energy value as low as 19.00 kJ/mol and as high as 145.99 kJ/mol, if $\cdot\text{H}$ or $\cdot\text{OH}$ is used as abstractors, respectively (**Table 1, Figure 9, Figure 10**).

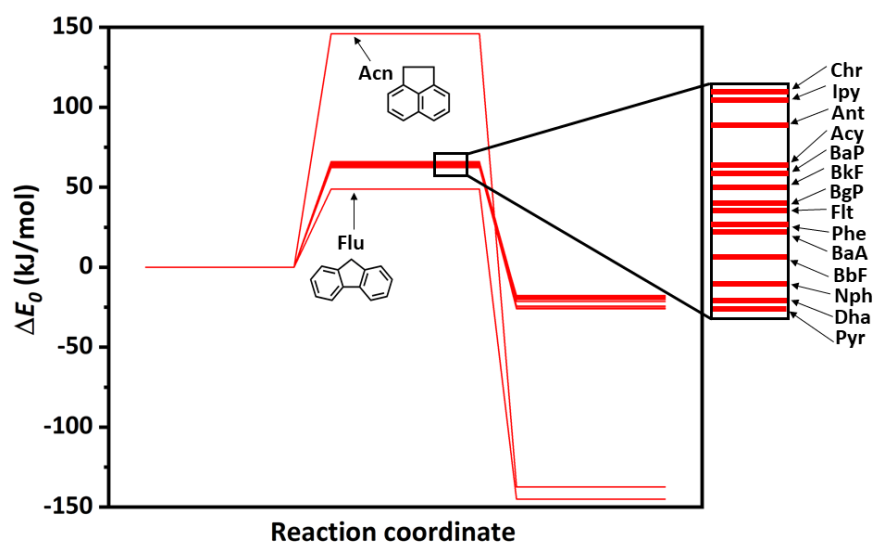


Figure 10 The potential energy curves (PECs) of the studied hydrogen abstractions with $\cdot\text{OH}$ radical calculated at the $\omega\text{B97XD/6-31+G(d,p)}$ level of theory.

The third hydrogen abstraction route which was investigated, is the hydrogen abstraction with methyl radical (**Figure 11**). In these reactions, there were some which had to be done multiple times, because the calculations failed and the orientation of the radical had to be finetuned, or the structures were not appropriate, nevertheless all of the transition states were located. Based on the relative energy values, three different groups can be identified.

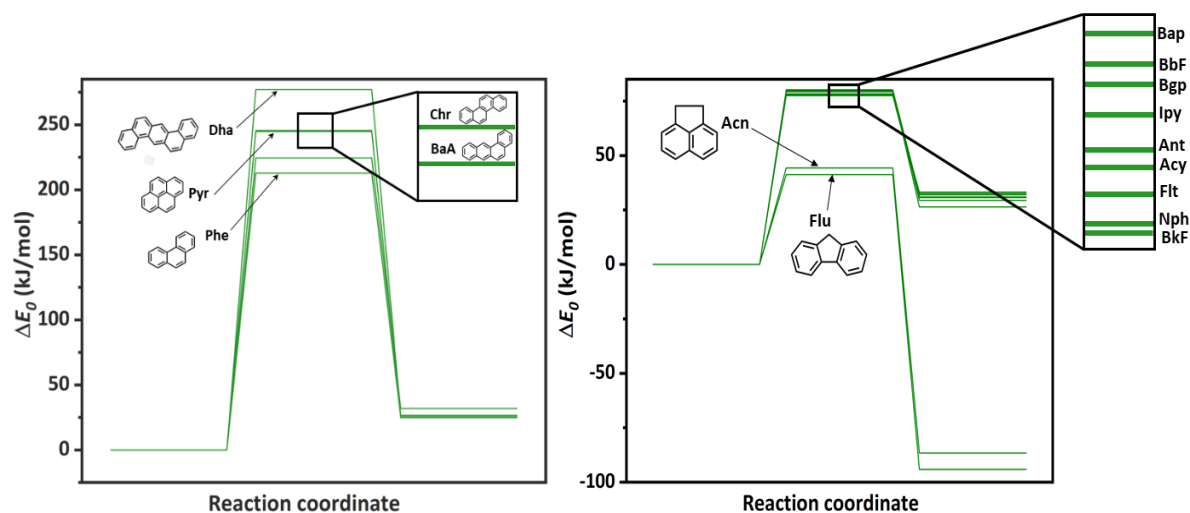


Figure 11 The potential energy curves (PECs) obtained in hydrogen abstractions with $\cdot\text{CH}_3$ radical.

There are five reactions within which the activation energy is higher than 200 kJ/mol, and thus, these are the least favorable cases. The order of these high activation energy radical formations are decreasing from the highest energy reaction which belongs to dibenz(a,h)anthracene, all

along to phenantrene, throughout chrysene, benzo(a)anthracene, and pyrene. Moreover there are reactions with activation energy values between 77-81 kJ/mol. The activation energy of the radical formation reaction here can be listed from the highest benzo(a)pyrene, to the lowest benzo(k)fluoranthene, and in between there is the case of benzo(b)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, anthracene, acenaphthylene, and naphthalene. Lastly, there is a group within which the activation energy values are below 45 kJ/mol, but only two molecules (acenaphthene and fluorene) are belong to this. Fluorene radical formation has the lowest energy gap in between the reactants and transition state, and thus, this molecules is the most prone to the attack of methyl radicals within „parent” PAHs. By comparing the three studied radical reaction partners, it can be seen, that the hydrogen atom is the most favourable for PAH radical formation and thus, growth initiation, in all cases except one, benzo(a)anthracene. In this case, $\cdot\text{OH}$ is a better reaction partner, as it has the lowest activation energy, thus, PAH radical formation most likely to occur in the presence of hydroxyl radical during the growth starting from BaA. All in all, the highest activation energy values are associated with the reactions which involves methyl radicals, but the other two groups have also larger activation energy values. However, most $\Delta E_0^\ddagger$ values are in the range of 60-80 kJ/mol, if the three studied radicals are considered as reaction partners.

Conclusion

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds with two or more fused benzene rings, containing only carbon and hydrogen atoms. PAHs have detrimental biological effects, and their toxicity, mutagenicity, and carcinogenicity is proven. In 1976, the U.S. Environmental Protection Agency (EPA) published a list within which 16 PAHs have been mentioned as priority species or „parent” PAHs. From that time the monitoring of these compounds is getting more and more intense. In our everyday life, we are nonstop exposed to polycyclic aromatic hydrocarbons. Therefore, it is important to monitor the presence of PAHs and understand the processes leading to their formation and growth.

Most of the reaction mechanisms which are associated with PAH formation and growth include a hydrogen abstraction to activate the aromatic ring, and after that further steps (*e.g.* acetylene addition) could take place. Therefore, hydrogen abstraction has an important role in PAH growth and formation. Thus, to achieve a deeper understanding of PAHs formation and growth, it is inevitable to study this reaction. In this work 48 reactions are investigated for the formation of selected radicals from the 16 „parent” PAHs. All in all, PAH growth initiations have been successfully studied by using computational tools and the corresponding transition states have been located. The calculations indicate that hydrogen abstractions carried out by a hydrogen atom are more favourable for all of the „parent” PAHs, except for benzo(a)anthracene, where hydroxyl radical is more potent reaction partner. The smallest activation energy is belong to the reaction of acenaphthene with hydrogen atom ($\Delta E^\ddagger_0 = 19.00$ kJ/mol), while the second most favourable reaction is associated with the fluorene - $\cdot\text{H}$ process ($\Delta E^\ddagger_0 = 20.43$ kJ/mol). PAH growth initiation by methyl radical is not so favorable, because the corresponding activation energies are much higher compared to the ones obtained with the other two radical reaction partners ($\cdot\text{OH}$ and $\cdot\text{H}$). Further analysis of the structures and the reactions can be carried out. The results contribute to the deeper understanding of PAH formation and growth.

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