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Dorra Khiri, Sonia Taamalli, Duy Quang Dao, Thanh-Binh Nguyen, Laurent Gasnot, et al.. Thermochemical and kinetic studies of hydrogen abstraction reaction from C₁₆H₁₀ isomers by H atoms. Computational and Theoretical Chemistry, 2021, pp.113257. 10.1016/j.comptc.2021.113257. hal-03204224

HAL Id: hal-03204224

<https://hal.science/hal-03204224>

Submitted on 9 May 2023

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Thermochemical and kinetic studies of hydrogen abstraction reaction from C₁₆H₁₀ isomers by H atoms

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Abstract

Ab initio calculations were used to derive thermochemical and kinetic properties of the hydrogen abstraction reaction from C₁₆H₁₀ isomers (pyrene, fluoranthene, aceanthrylene, and acephenanthrylene) by H atoms. The study of these reactions is very important to better understand the soot formation processes. The structural properties of all studied species were optimized using the B97D3/6-311++G(d,p) level of theory. The reaction energies and barrier heights were evaluated using several density functional theory methods (B97D3, B3LYP, and M06-2X) and compared to highly-correlated ab initio wave functions within the UCCSD(T)-F12 approach. It was shown that the UCCSD(T)-F12 computational protocol can be used with such large systems to provide more accurate results compared to DFT calculations. Reliable rate constants were obtained using the Transition State Theory **with Eckart's tunnelling correction** over the temperature range of **250-2500 K**. The influence of the structure and the position of the hydrogen abstraction C-H sites of C₁₆H₁₀ isomers on the energetics and the rate constant were discussed and compared with available literature data.

KEYWORDS: *Hydrogen abstraction, C₁₆H₁₀ isomers, PAHs, potential energy surface, UCCSD(T)-F12, kinetics.*

1. Introduction

One of the issues in understanding soot particle formation mechanisms is probably the nucleation process. Acceleration of new theories based on both experimental and theoretical observations has been observed over the past five years. One of the breaking points in this area is the possibility of stabilizing moderate-sized dimers in flame conditions. Recent numerical studies suggest moderate-sized dimers formation in flame conditions through covalent bonding formation [1–4]. Most recently, Frenklach and Mebel [2,3] explored a new mechanism of soot formation including collision between a polycyclic aromatic hydrocarbon (PAH) molecule and a PAH radical, the latter being produced after the H- abstraction reaction with H atoms. According to the authors, the obtained aromatic structure is stabilized by a covalently-bonded bridge. Moreover, our recent experimental investigations carried out in premixed [5] and diffusion flames [6,7] supported the idea that pyrene plays a central role in the nucleation process as theoretically suggested by Frenklach several years ago. All of these studies agree on activation of aromatic structures by H-abstraction reactions to fulfil the mission of the HACA mechanism (**Hydrogen-Abstraction-C₂H₂-Addition**) and also to initiate the sequence leading to PAH stabilomer. These new theories accentuate the role of propagating reactions involving H atoms and PAHs in early stage of the soot particle formation. It is therefore important to explore in-depth new numerical approaches involving the H-abstraction reactions with H atoms from different PAHs structures, especially from moderate size PAHs as pyrene.

Some kinetic data are available from theoretical investigations of the hydrogen abstraction reactions of PAH by H atom [8,9]. Violi *et al.* [8] calculated kinetic properties of hydrogen abstraction reactions by H atom from different PAHs (benzene, naphthalene, anthracene, phenanthrene, pyrene, acenaphthylene, acephenanthrylene, aceanthrylene, cyclopenta[cd]pyrene, dicyclopenta[cd,jk]pyrene and cyclopenta[fg]benzo[ghi]perylene)

using the BH&HLYP/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory. They considered two classes of PAH, the first one consisting of six membered ring and the second one five membered ring. The thermal rate constants were evaluated using the Reaction Class Transition State Theory/Linear Relationship (RC-TST/LER) approach. They showed that for both classes of PAHs, rate constants could be obtained based on the use of rate constants of their corresponding principal reactions that were corrected by the reaction symmetry factor. Recently, this type of reaction has been also studied by Hou and You [9]. The energetics of the H-abstraction reaction and the rate constants have been first investigated for benzene and naphthalene using several DFT methods among which the M06-2X/6-311G(d,p) level of theory showed the best performance compared to CCSD(T)/CBS calculations. The same methodology was then applied to a large set of PAH molecules using the M06-2X/6-311G(d,p)//B3LYP/6-31G(d,p) level of theory. They found that for the different studied PAHs, the barrier heights were very similar and just about 67 kJ mol⁻¹, confirming that the rate constants were not too impacted by the PAH molecule size, structure, and different reaction sites.

In this work, we provide a systematic high-level ab initio study of hydrogen abstraction reactions for four isomers of C₁₆H₁₀ (pyrene, fluoranthene, aceanthrylene, and acephenanthrylene) by H atom using highly correlated wave functions within the explicitly correlated UCCSD(T)-F12a method in comparison with the DFT approach. This work aims to demonstrate that the UCCSD(T)-F12 approach can be used not only for small species [10–12] but also for systems with specific structures and a large number of atoms such as PAHs.

To the best of our knowledge, there are no theoretical results on thermochemical properties and kinetic parameters of hydrogen abstraction reactions from fluoranthene by H atom in the literature while for the other isomers, the hydrogen abstraction reactions were investigated in

a few previous studies using the DFT approach either by H atom [8,9] and O atom [2], or by various radicals such as OH [13,14], methyl/ethyl [15], vinyl [16,17], and propargyl [18].

2. Computational details

2.1 Electronic structure calculations

The DFT method was used to investigate the hydrogen abstraction reaction from C₁₆H₁₀ isomers (pyrene, fluoranthene, aceanthrylene, and acephenanthrylene) by H atoms. This DFT approach has been recommended [19–25] for electronic structure calculations of hydrocarbon systems with an accuracy of less than 8 kJ mol⁻¹ for transition states barriers [26–29]. The geometry optimizations of reactants, products, and transition states (TS) were carried out using the pure dispersion corrected functional B97D3 [30,31] in conjunction with the 6-311++G(d,p) basis set [32]. The vibrational frequencies and the zero-point energies (ZPE) corrected by a suitable scaling factor of 0.988 to compensate the effects of anharmonicity were calculated at the same level of theory. The scaling factor was determined in our previous work by Nguyen *et al.* [33] based on the comparison between the computed harmonic frequencies with the experimental ones of fluoranthene, pyrene, benzene, and naphthalene. In order to verify the correct connection of the transition state to corresponding molecular complexes, the intrinsic reaction coordinate calculations (IRC) [34,35] have been carried out for all studied reactions. The stability of the wave function [36,37] has been checked for all studied species. Two other functionals were also employed for C₁₆H₁₀ isomers: B3LYP [38,39] and M06-2X [40,41]. The structures and frequencies obtained using B3LYP and M06-2X are similar to B97D3 results. However, the M06-2X underestimates activation Gibbs free energies in some cases as proved recently by Jasiński [42]. The B97D3 was chosen in this work based on our previous results [33], which showed that using hybrids functional, RHF-UHF instability was detected for some studied species.

More accurate single-point energy calculations have been considered to find the most reliable computational method. Benchmark calculations were also presented using three different DFT methods (B97D3, M06-2X, and B3LYP) with the 6-311++G(d,p) basis set and compared to available literature data. All previous calculations were performed on the ground state potential energy surface (PES) using the GAUSSIAN16 (A.03) program [43]. Additional single-point energy calculations have been performed with the MOLPRO2015 software [44] using highly-correlated wave functions within the explicitly correlated UCCSD(T)-F12a method [10,45] and the correlation consistent polarized double and triple zeta [46,47] (cc-pVDZ and cc-pVTZ) basis sets (they will be abbreviated as VDZ and VTZ throughout the manuscript). Such approach has been shown [10–12] to yield as accurate results as CCSD(T) calculations with cc-pVTZ and cc-pVQZ basis sets. It offers a particularly good compromise between accuracy and computational cost. The mono-configurational character of the ground states of all presented species (reactants, TS and products) is verified using the T1 diagnostics values, which are very small and less than 0.02 in the studied reactions. Hence, the usual single reference method (UCCSD(T)-F12) can be considered and the multi-reference methods are not necessary for such species. The collected values using UCCSD-(T)-F12a and UCCSD(T)-F12b methods show very similar results. For example, for site 1 of H abstraction reaction from pyrene $E_0 = 64.46$ and $65.02 \text{ kJ mol}^{-1}$, $\Delta_r H^\circ_{298\text{K}} = 37.70$ and $38.16 \text{ kJ mol}^{-1}$, and $\Delta_r G^\circ_{298\text{K}} = 27.76$ and $28.22 \text{ kJ mol}^{-1}$ using UCCSD-(T)-F12a/VTZ and UCCSD(T)-F12b/VTZ, respectively. For clarity, only those corresponding to UCCSD(T)-F12a will be presented here.

The thermodynamic properties including standard reaction enthalpies $\Delta_r H^\circ(T)$ and Gibbs free energies $\Delta_r G^\circ(T)$ are calculated over a wide temperature range (250–2500 K). The enthalpy at different temperatures is calculated including the scaled ZPE and the thermal contribution to enthalpy at temperature T [$ddH(T)$] obtained using the THERMO script [48].

2.2 Rate constant calculations

The canonical transition state theory (TST) [49–51] and GPOP (Gaussian post processor) code [52] were used to determine the kinetic parameters as described by the following expression:

$$k(T) = \chi \sigma \frac{k_B T}{h} \frac{Q_{TS}(T)}{Q_R(T)} \exp\left(-\frac{E_0}{k_B T}\right)$$

where χ is the tunneling factor, σ is the reaction path symmetry number expressed as $\sigma = \frac{\sigma_{rot,R}}{\sigma_{rot,TS}}$ with $\sigma_{rot,R}$ and $\sigma_{rot,TS}$ are the total rotational symmetry numbers of the reactant and the transition state, respectively; k_B is the Boltzmann constant, T is the temperature ranging from 250 to 2500 K, h is the Planck constant, and $Q_{TS}(T)$ and $Q_R(T)$ are the total partition function of the transition state and the reactants, respectively. E_0 is the vibrationally adiabatic barrier obtained from the energy difference between the transition state and reactants including the scaled ZPE. **The quantum tunnelling effect was computed using the one-dimensional Eckart approximation [53].**

3. Results and discussion

We focus here on the abstraction of the hydrogen atoms from four isomers of polycyclic aromatic hydrocarbons $C_{16}H_{10}$ (pyrene, fluoranthene, aceanthrylene, and acephenanthrylene) by H atom, which leads to the formation of different radicals and H_2 . The influence of the structure on the kinetics of the hydrogen abstraction reactions will be investigated.

3.1 Structural properties

The structural parameters and vibrational frequencies of all studied $C_{16}H_{10}$ isomers were well investigated in our previous works [33,54] using several DFT approaches. The different structures and abstraction sites of studied isomers are summarized in Fig. 1.

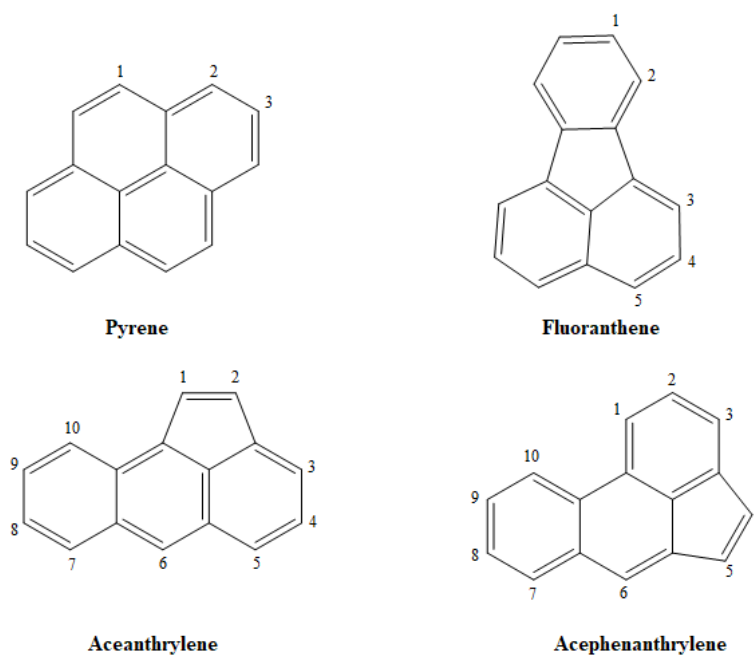


Fig. 1. Numbered hydrogen abstraction sites considered for the studied $C_{16}H_{10}$ isomers.

Abstraction sites of the different investigated isomers (10 abstraction sites for each isomer) can be classified into two groups based on the number of rings. The first group corresponds to the six-membered rings (all studied sites of pyrene and fluoranthene, sites 3 to 10 of aceanthrylene, and 1, 2, 3, 6 to 10 of acephenanthrylene). The second one corresponds to the five-membered rings (sites 1 and 2 of aceanthrylene and 4 and 5 of acephenanthrylene). For more details, the symmetry number of studied isomers, the number of unique sites and the ratio of different unique sites are reported in Table 1.

Table 1. The symmetry number, the number of unique sites, and the ratio of different unique sites of studied isomers

Isomer	Symmetry number	Number of unique sites	Ratio different unique sites
Pyrene	4	3 (1,2,3)	1:2:3=4:4:2
Fluoranthene	2	5 (1,2,3,4,5)	1:2:3:4:5=2:2:2:2:2
Aceanthrylene	1	10 (1...10)	1
Acephenanthrylene	1	10 (1...10)	1

The Cartesian coordinates of all reactants, products, transition states and molecular complexes relative to the H-abstraction reaction of H atom from C₁₆H₁₀ isomers optimized at UB97D3/6-311++G(d,p) level of theory are given in Table S1-S5 (Supplementary material) [55]. The corresponding vibrational frequencies are depicted in Table S6-S9 (Supplementary material) [55]. The spin contamination of wave function is examined and expectation values of $\langle S^2 \rangle$ are depicted in Table S10 (Supplementary material) [55] with scaled ZPE, S°_{298K} , and rotational constants.

For all studied transition states, the ratio ($L = \delta r(\text{H-C}) / \delta r(\text{H-H})$) between the elongation values of the C-H bond and the H-H bond is determined to identify the principal changes in the structural properties of the transition state. Table 2 presents the elongation values of the $r(\text{H-H})$ bond length, the $r(\text{H-C})$ bond length, the bond angle $\theta(\text{HCC})$, and the ratio L for the H-abstraction reaction of H atom from Pyrene. The corresponding values of other isomers are given in Table S11 (Supplementary material) [55].

The pre-reactive molecular complexes (MCR1 and MCR2 (=MCR3)) show similarities in their structures such as the presence of Van der Waals interactions between the H atom and the H atom of the Pyrene ($r(\text{H-H})$ ranging from about 5.004 to 5.061 Å). The $r(\text{H-C})$ bond length of these structures is similar to the corresponding one obtained in the Pyrene structure (1.089 Å). Three transition states were also identified. They share similar structural properties, the C-H breaking bond of pyrene is stretched up to about 1.4 Å. The forming H-H bond in TS1, TS2, and TS3 are longer (0.909, 0.905, and 0.908 Å) than the isolated product

H₂ molecule (0.746 Å). These transition states were also characterized by a nearly linear bond angle ($\theta(\text{HCC}) = 179$ degrees) between the three atoms involved in the reaction. The post-reactive molecular complexes (MCP1, MCP2, and MCP3) present as TS structures a linear bond angle ($\theta(\text{HCC}) = 180$ degrees). The H-H bond formed in those molecular complexes (0.751 Å) is very close to the one obtained in the isolated product, H₂ molecule (0.746 Å). The H-C bond lengths in MCP1, MCP2, and MCP3 (2.476, 2.468, and 2.477, respectively) are elongated with respect to the corresponding H-C bond in Pyrene (1.089 Å).

The same structural properties of pre-reactive molecular complexes, post-reactive molecular complexes, and transition states are also observed for the H-abstraction reaction of H atom from fluoranthene, aceanthrylene, and acephenanthrylene as shown in Table S11 (Supplementary material) [55].

Table 2. Elongation values of the r(H-H) bond length, the r(H-C) bond length, the bond angle $\theta(\text{HCC})$ and the ratio L for the H-abstraction reaction of H atom from pyrene. Distances are given in angstroms and bond angles in degrees.

H + pyrene	r(H-H) Å	r(H-C) Å	$\theta(\text{HCC})$ °	L
MCR1	5.061	1.089	138.9	
TS1	0.909	1.408	179.2	1.96
MCP1	0.751	2.476	179.8	
MCR2	5.004	1.089	149.2	
TS2	0.905	1.417	179.4	2.07
MCP2	0.752	2.468	179.5	
MCR3	5.004	1.089	149.2	
TS3	0.908	1.400	180.0	1.93
MCP3	0.751	2.477	180.0	

The ratio L is quite similar for the transition states of all abstraction sites corresponding to the six-membered rings (L ranging from about 1.78 to 2.07), however, for the transition states of other abstraction sites corresponding to five-membered rings the L values are about 3. All L values show that the transition states are product-like because $L > 1$.

In order to find out the difference between the transition state structures of the two studied groups of abstraction sites, we present in Fig. 2 the geometry of two different transition states of hydrogen abstraction from aceanthrylene isomer corresponding to TS1-Acean (site 1: five-membered rings) and TS3-Acean (site 3: six-membered rings). As shown in Figure 2, the C-H-H angle and the H-H bond of TS1-Acean are similar to those of the TS3-Acean while there is a slight difference of 0.09 Å between the C-H bond of TS1-Acean and TS3-Acean. Comparable results were observed for all studied transition states.

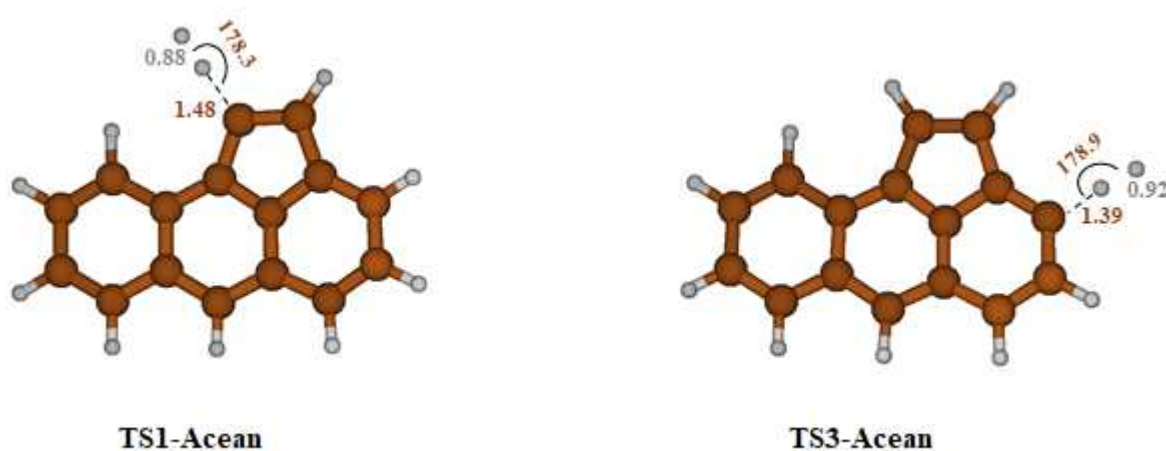


Fig. 2. Transition states of hydrogen abstraction from aceanthrylene isomer corresponding to TS1-Acean (site 1: five-membered rings) and TS3-Acean (site 3: six-membered rings). Distances are given in Å and bond angles in degrees.

3.2 Energy barriers and reaction energies

In order to verify whether the UCCSD(T)-F12 method is suitable to energetic calculations of large systems such as PAHs, we start with a comparison between the results of the DFT

calculations and available literature data for pyrene isomer. Three DFT methods including (B97D3, B3LYP, and M06-2X) in combining with the 6-311++G(d,p) basis set are used and compared with highly-correlated wave functions within the explicitly correlated UCCSD(T)-F12a/(VDZ and VTZ) methods for the hydrogen abstraction reaction from pyrene by H atom. Table 3 gives the calculated barrier height (E_0), the standard reaction energy ($\Delta_r H^\circ_{298\text{K}}$) and standard Gibbs free reaction energies ($\Delta_r G^\circ_{298\text{K}}$) at different levels of theory for the abstraction reactions of pyrene isomer compared to available literature data [8,9]. If we consider the UCCSD(T)-F12a/VTZ//B97D3/6-311++G(d,p) level of theory as the reference value, it can be seen that both B97D3 and B3LYP methods underestimate the barrier height by about 36 and 19 kJ mol^{-1} , respectively, while the M06-2X method overestimates the barrier height by about 3 kJ mol^{-1} . The different M062X/6-311++G(d,p) single-point energy calculations based on different B97D3, B3LYP, and M062X geometries provide similar results for E_0 values within $\pm 2 \text{ kJ mol}^{-1}$ and confirm that the DFT M06-2X has the best performance among the different studied DFT methods. These trends were also revealed by Hou and You [9]. The same conclusions can be withdrawn when using the UCCSD(T)-F12a level of theory with different geometries (B97D3, B3LYP, and M062X). These results confirm that the barrier height does not depend on geometry calculations.

Table 3. Calculated barrier height (E_0), reaction energy ($\Delta_r H^\circ_{298K}$) and standard Gibbs free reaction energies ($\Delta_r G^\circ_{298K}$) at different studied level of theories of the abstraction reactions of pyrene isomer compared to available literature data (in kJ mol^{-1})

	Methods	R1			R2			R3		
		E_0	$\Delta_r H^\circ_{298K}$	$\Delta_r G^\circ_{298K}$	E_0	$\Delta_r H^\circ_{298K}$	$\Delta_r G^\circ_{298K}$	E_0	$\Delta_r H^\circ_{298K}$	$\Delta_r G^\circ_{298K}$
This work	B97D3/6-311++G(d,p)//B97D3/6-311++G(d,p)	28.41	13.89	6.47	29.54	18.30	8.44	27.89	14.91	6.73
	B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p)	45.56	23.23	15.89	48.14	27.56	17.83	45.58	25.35	17.30
	M06-2X/6-311++G(d,p)//M06-2X/6-311++G(d,p)	67.54	34.69	27.43	69.21	38.66	29.05	67.26	35.85	27.87
	M06-2X/6-311++G(d,p)//B97D3/6-311++G(d,p)	69.01	34.26	26.84	70.32	38.25	28.40	68.12	35.51	27.33
	M06-2X/6-311++G(d,p)//B3LYP/6-311++G(d,p)	69.11	34.49	27.15	70.82	38.43	28.71	69.12	35.71	27.65
	UCCSD(T)-F12a/VDZ//B97D3/6-311++G(d,p)	66.19	39.60	29.65	67.40	41.07	31.22	65.48	38.63	30.45
	UCCSD(T)-F12a/VDZ//B3LYP/6-311++G(d,p)	67.45	39.85	30.05	68.95	41.38	31.65	67.47	38.97	30.92
	UCCSD(T)-F12a/VDZ//M06-2X/6-311++G(d,p)	65.48	40.02	30.37	66.87	41.62	32.01	62.69	39.18	31.20
	UCCSD(T)-F12a/VTZ//B97D3/6-311++G(d,p)	64.46	37.70	27.76	65.73	39.27	29.41	63.70	36.63	28.44
	Average value ^a	64.63	37.87	28.54						
Frenklach and Mebel [3]	G3(CC,MP2)//B3LYP/6-311G**	67.36								
Violi <i>et al.</i> [8]	BH&HLYP/6-31G(d,p)//B3LYP/6-31G(d,p) ^b	64.98								
Hou and You [9]	M06-2X/6-311G(d,p)//B3LYP/6-311G(d,p) ^b	69.43								

^a Average value calculated at the UCCSD(T)-F12a/VTZ//B97D3/6-311++G(d,p) level of theory from different abstraction reactions. ^b Average value.

The performance of the UCCSD(T)-F12a/VTZ method has been examined in comparison with DFT calculations and available literature data [3,8,9] considering the average value from different abstraction reactions. An excellent agreement is observed between the UCCSD(T)-F12a/VTZ level of theory (64.63 kJ mol⁻¹) and the one used by Violi *et al.* [8] at the BH&HLYP/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory (64.98 kJ mol⁻¹) while a fair agreement is noticed with the E_0 value (69.43 kJ mol⁻¹) calculated by Hou and You [9] at the M062X/6-311G(d,p)//B3LYP/6-311G(d,p) level of theory (difference of about 5 kJ mol⁻¹) and with the E_0 value (67.36 kJ mol⁻¹) obtained by Frenklach and Mebel [3] using the G3(CC,MP2)//B3LYP/6-311G(d,p) level of theory (difference of about 3 kJ mol⁻¹).

The results confirm that the UCCSD(T)-F12a/VTZ level of theory performs well in the energetic calculations. This level of theory will therefore be used for the study of hydrogen abstraction reactions of other isomers (fluoranthene, aceanthrylene, and acephenanthrylene). The corresponding UCCSD(T)-F12a/VTZ barrier height (E_0), the standard reaction energy at 298 K ($\Delta_r H^\circ_{298K}$) and the standard Gibbs free reaction energies ($\Delta_r G^\circ_{298K}$) are summarized in Table 4. It is showed that the E_0 values corresponding to the first group (six-membered rings) are 65 kJ mol⁻¹ on average for all studied isomers and about 12 kJ mol⁻¹ lower than that of the corresponding values of the second group (five-membered rings) (about 77 kJ mol⁻¹). This result shows the sensibility of the energy barrier to the structure of the C₁₆H₁₀ isomers. The calculated UCCSD(T)-F12a/VTZ barrier heights of H-abstraction reactions from aceanthrylene and acephenanthrylene corresponding to the six-membered rings and five-membered rings groups ((64.40 and 64.65 kJ mol⁻¹) and (76.37 and 77.03 kJ mol⁻¹), respectively) compare well with the corresponding values obtained by Violi *et al.* [8] at the BH&HLYP/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory ((62.84 and 64.14 kJ mol⁻¹), and (74.64 and 74.02 kJ mol⁻¹), respectively).

Table 4. Calculated UCCSD(T)-F12a/VTZ//B97D3/6-311++G(d,p) barrier height (E_0), the reaction energy ($\Delta_r H^\circ_{298\text{K}}$) and the standard Gibbs free reaction energies ($\Delta_r G^\circ_{298\text{K}}$) of the different abstraction reactions of studied C₁₆H₁₀ isomers (in kJ mol⁻¹)

Reaction	E_0	$\Delta_r H^\circ_{298\text{K}}$	$\Delta_r G^\circ_{298\text{K}}$
Fluoranthene			
R1	64.46	37.25	29.22
R2	64.13	37.40	29.33
R3	64.26	37.34	29.30
R4	62.94	35.73	27.61
R5	65.85	39.35	31.31
Average value	64.33	37.41	29.35
Aceanthrylene			
R1	75.60	51.62	45.15
R2	77.15	54.14	47.60
Average value	76.37 74.64^a	52.88	46.37
R3	63.46	35.65	29.33
R4	63.02	35.86	29.44
R5	65.50	39.11	32.75
R6	66.35	40.46	34.16
R7	64.20	37.15	30.67
R8	64.09	36.97	30.58
R9	63.51	36.09	29.74
R10	65.03	37.34	30.85
Average value	64.40 62.84^a	37.33	30.94
Acephenanthrylene			
R4	76.70	52.66	46.24
R5	77.35	53.83	47.42
Average value	77.03 74.02^a	53.25	46.83
R1	65.44	35.98	29.72
R2	62.82	35.95	29.56
R3	64.92	37.71	31.36
R6	64.44	37.29	30.80
R7	64.69	37.56	31.07
R8	64.88	37.91	31.44
R9	64.18	37.07	30.70
R10	65.83	34.97	28.63
Average value	64.65 64.14^a	36.81	30.41

^aVioli *et al.* [8] (BH&HLYP/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory).

For the H-abstraction reactions from fluoranthene by H atom, the barrier height (64.33 kJ mol⁻¹) is similar to those obtained for the first group (six-membered rings) of other isomers.

Furthermore, we can observe that the pre-reactive complexes of all the studied reactions are not stable. They lie only a fraction of kJ mol⁻¹ below the reactants (0.08 to 0.22 kJ mol⁻¹). It indicates that the presence of such pre-reactive complexes cannot impact the kinetics of different studied reactions. Then the reactants have to overcome the barrier to insure the formation of products. MCP1, MCP2 and MCP3 formed in the H + pyrene reaction are more stable than the corresponding products by approximately 4 kJ mol⁻¹ using the UCCSD(T)-F12a/VTZ//B97D3/6-311++G(d,p) level of theory and this is the case for all abstraction sites for different studied reactions.

The positive $\Delta_r H^\circ_{298K}$ values confirm that all abstraction reactions considered in this study are endothermic. These trends were expected from the calculated L values ($L > 1$, the transition states are product-like). All these results agree with Hammond's postulate [56] as discussed previously by Rayez *et al.* [57] in their ab initio studies of the reactions of chlorine atoms with fluoro- and chloro-substituted methanes. The reaction enthalpies of the second group are larger than that of the first one. The same conclusions are taken by Hou and You [9] and Cao *et al.* [17] in their studies on the kinetics of hydrogen abstraction reaction from PAH by H and vinyl radical, respectively. The standard reaction enthalpies and standard Gibbs free reaction energies at 1500 K are given in Table S12 (Supplementary material) [55].

The bond dissociation energies (BDEs) of C-H bonds at 298 K obtained using different DFT methods and compared to UCCSD(T)-F12a calculations for pyrene are resumed in Table5. Corresponding values of other studied C₁₆H₁₀ isomers at the UCCSD(T)-F12a/VTZ level of theory are given in Table S13 (Supplementary material) [55]. The obtained results demonstrate that for the abstraction sites corresponding to six-membered rings the BDEs are

close to those obtained for abstraction sites corresponding to five-membered rings. The average BDE for the first group (six-membered rings) is about 473.7 kJ mol⁻¹, which is lower by 15.8 kJ mol⁻¹ than the corresponding average value of the second group (five-membered rings). For pyrene, our calculated values for different abstraction sites 1, 2, and 3 using DFT methods are in good agreement with the corresponding values of Barckholtz *et al.* [55] obtained using the B3LYP/6-31G(d) level of theory which are lower by 9.7, 9.2, and 9.0 kJ mol⁻¹ than our corresponding values of UCCSD(T)-F12a/VTZ level of theory.

Table 5. Calculated bond dissociation energies (BDEs) of C-H bonds at 298 K for pyrene isomer (in kJ mol⁻¹)

		R1	R2	R3
This work	B97D3/6-311++G(d,p)//B97D3/6-311++G(d,p)	460.9	462.7	459.4
	B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p)	463.7	465.5	463.3
	M06-2X/6-311++G(d,p)//M06-2X/6-311++G(d,p)	466.5	468.1	465.2
	M06-2X/6-311++G(d,p)//B97D3/6-311++G(d,p)	466.3	467.8	465.0
	M06-2X/6-311++G(d,p)//B3LYP/6-311++G(d,p)	466.9	468.4	465.7
	UCCSD(T)-F12a/VDZ//B97D3/6-311++G(d,p)	471.6	473.1	470.7
	UCCSD(T)-F12a/VDZ//B3LYP/6-311++G(d,p)	472.3	473.8	471.4
	UCCSD(T)-F12a/VDZ//M06-2X/6-311++G(d,p)	471.8	473.4	471.0
	UCCSD(T)-F12a/VTZ//B97D3/6-311++G(d,p)	474.1	475.7	473.0
Barckholtz <i>et al.</i> [58]	B3LYP/6-31G(d)	464.4	466.5	464.0

3.3 Kinetic parameters

To derive the rate rule of each abstraction reaction from C₁₆H₁₀ isomers, the average value of the rate constants at each temperature is used. This method is mentioned in several theoretical studies on the kinetics of H-abstraction reaction of PAHs [17,59–61]. The fitted Arrhenius parameters (*A*, *n*, *E_a*) are given in Table 6.

Table 6. Fitted Arrhenius parameters (A, n, E_a) for the obtained rate rule using the UCCSD(T)-F12a/VTZ//B97D3/6-311++G(d,p) level of theory

Reactions		A	n	E_a
Six-membered rings				
Pyr + H = Pyr● + H ₂	This work	4.29×10^8	2.07	58.21
	^a Violi <i>et al.</i> [8]	9.45×10^7	1.77	54.63
	^b Hou and You [9]	9.08×10^8	1.67	67.81
Flthn + H = Flthn● + H ₂	This work	2.24×10^8	2.08	57.53
Acean + H = Acean● + H ₂	This work	1.36×10^7	2.04	58.16
	^a Violi <i>et al.</i> [8]	2.37×10^7	1.77	54.63
Aceph + H = Aceph● + H ₂	This work	9.73×10^6	2.07	57.70
	^a Violi <i>et al.</i> [8]	2.37×10^7	1.77	54.63
Five-membered rings				
Acean + H = Acean● + H ₂	This work	4.30×10^7	1.98	71.54
	^a Violi <i>et al.</i> [8]	1.64×10^8	1.71	67.93
Aceph + H = Aceph● + H ₂	This work	4.30×10^7	1.98	72.10
	^a Violi <i>et al.</i> [8]	1.64×10^8	1.71	67.93

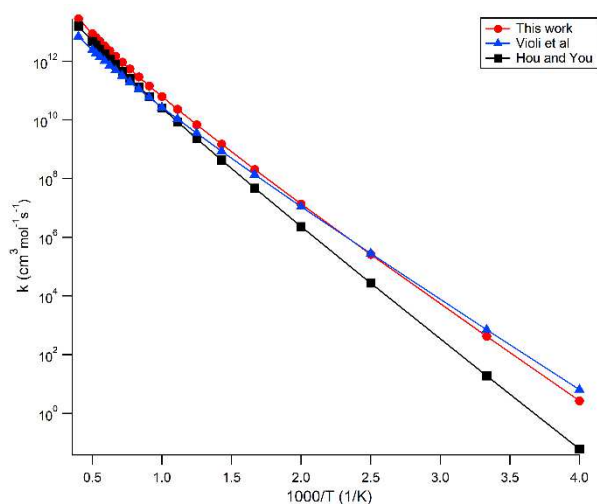
Note: A in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ and E_a in kJ mol^{-1} . ● correspond to radicals. ^a(BH&HLYP/6-31G(d,p)//B3LYP/6-31G(d,p)). ^b(M06-2X/6-311G(d,p)//B3LYP/6-311G(d,p)).

The one-dimensional Eckart approximation [53] was used to consider the quantum tunnelling effect in this work. It is rather accurate enough for the temperatures of interest for combustion chemistry. For the site 1 of H-abstraction reaction from pyrene, tunnelling effect is more predominant at lower temperatures ($\chi = 3.3, 1.1,$ and 1.0 at $250, 1000,$ and 2500 K, respectively). Thus, according to barrier height, the tunnelling effect does not have an important contribution at high temperature in combustion conditions. The tunnelling factor χ is quite the same for all studied reactions. This result confirmed that one-dimensional Eckart approximation was rather accurate enough.

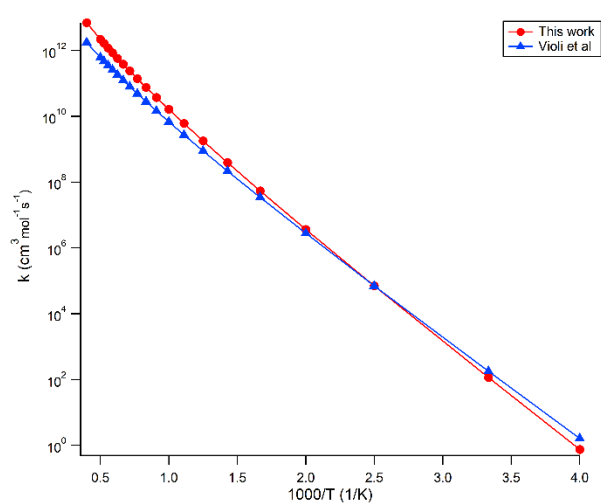
The calculated per site rate constant with the TST method and the corresponding rate rule are given in Table S14 (Supplementary material) [55] for all studied reactions. Our results are in good agreement with the values obtained by Violi *et al.* [8] at the BH&HLYP/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory. Our activation energy is larger by about 3.5 kJ mol^{-1} for both six and five-membered rings than the calculated value of Violi *et al.* [8]. For

pyrene, the activation energy using the UCCSD(T)-F12a/VTZ approach is about 10 kJ mol⁻¹ lower than the value calculated by Hou and You [9] at the M06-2X/6-311G(d,p)//B3LYP/6-311G(d,p) level of theory, which confirms that the M06-2X underestimates activation energies in some cases as mentioned recently by Jasiński [42].

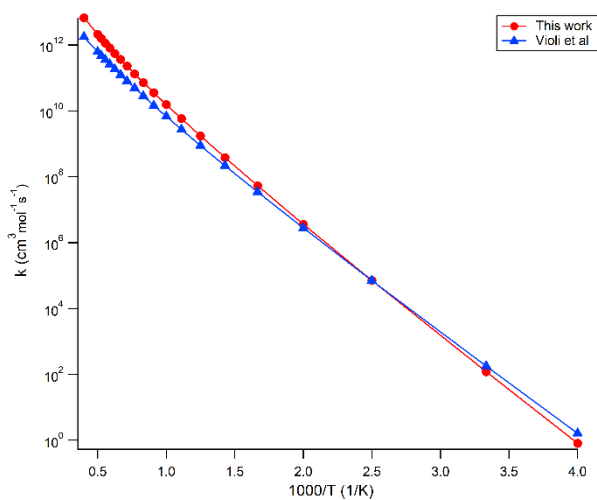
Fig. 3 presents the comparison of our calculated rate constant (rate rule) with available literature data [8,9] for pyrene, aceanthrylene, and acephenanthrylene for six-membered rings. It confirms the good agreement between our results and those of Violi *et al.* [8]. A similar conclusion can be withdrawn from the comparison of our results obtained for five-membered rings in the case of aceanthrylene and acephenanthrylene with available literature data [2]. Corresponding figure can be found also in Supplementary material (Fig. S1) [55].



a-Pyrene



b- Aceanthrylene



c- Acephenanthrylene

Note: This work (UCCSD(T)-F12a/VTZ). Violi *et al.* [8] (BH&HLYP/6-31G(d,p)//B3LYP/6-31G(d,p)). Hou and You [9] (M06-2X/6-311G(d,p)//B3LYP/6-311G(d,p)).

Fig. 3. Comparison of the calculated rate constant of pyrene, aceanthrylene and acephenanthrylene (six-membered rings) with available literature data.

4 Conclusion

We have considered the hydrogen abstraction reaction from $C_{16}H_{10}$ isomers (pyrene, fluoranthene, aceanthrylene, and acephenanthrylene) by H atoms. It has been studied using different DFT methods (B97D3, B3LYP, and M06-2X) and compared with additional calculations using the UCCSD(T)-F12/VTZ//B97D3/6-311++G(d,p) level of theory. The energy barriers were very sensitive to the structure of studied $C_{16}H_{10}$ isomers. The use of the UCCSD(T)-F12/VTZ allowed obtaining quantitative values for thermodynamic and kinetic calculations of hydrogen abstraction reaction from PAHs. As can be clearly seen from our results, this approach provided a particularly favourable compromise between accuracy and computational cost when it was used for the electronic structure and energetics calculations for large systems such as $C_{16}H_{10}$ isomers studied in this work. Our results are well compared with available literature data for pyrene, aceanthrylene and acephenanthrylene and they provided the first theoretical determination of thermochemical and kinetic properties of the hydrogen abstraction reaction from fluoranthene by H atom.

CRedit authorship contribution statement

Dorra Khiri: Investigation - writing - review & editing. Sonia Taamalli: Investigation. Duy Quang Dao: Investigation. Thanh-Binh Nguyen: Investigation. Laurent Gasnot: Funding acquisition. Florent Louis: Writing - review & editing. Ivan Černušák: review & editing. Abderrahman El Bakali: Conceptualization, Project administration.

Declaration of Competing Interest

The authors declare no competing financial interest.

Acknowledgments

This work was supported by the Hauts-de-France region and European Regional Development Fund. This research is funded by the CLIMIBIO project. We appreciated the support from the LABEX CaPPA (Chemical and Physical Properties of the Atmosphere), which is funded by the French National Research Agency (ANR) through the PIA (Programme d'Investissement d'Avenir) under contract ANR-11-LABX-0005-01 and also the Regional Council "Hauts de France" and the "European Funds for Regional Economic Development". The calculations presented in this paper were carried out at the Centre de Ressources Informatiques (CRI) of the University of Lille and the Centre Régional Informatique et d'Applications Numériques de Normandie (CRIANN). This work was granted access to the HPC resources of IDRIS under the allocation 2020-101578 made by GENCI. This work was supported in part by the Slovak Grant Agency VEGA (grant 1/0777/19) and by the high-performance computing facility of the Centre for Information Technology (<https://uniba.sk/en/HPC-Clara>) at Comenius University.

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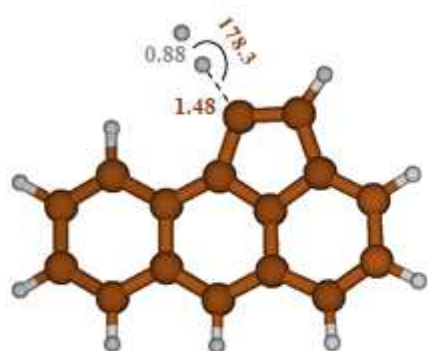
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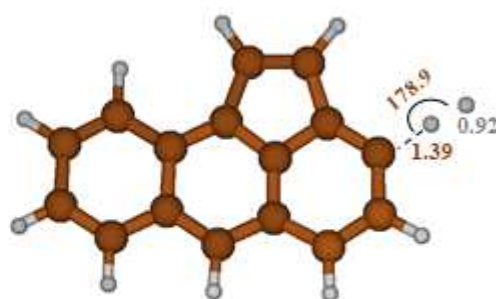
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Graphical Abstract



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TS3-Acean