



Reaction kinetics of the consumption mechanism of Oxygenated polycyclic Aromatic Hydrocarbons (OPAHs)

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Research motivation

Context

- ~80 % of global energy production come from the combustion of fossil fuels.
- Inclusion of more sustainable alternative fuels in combustion engines.

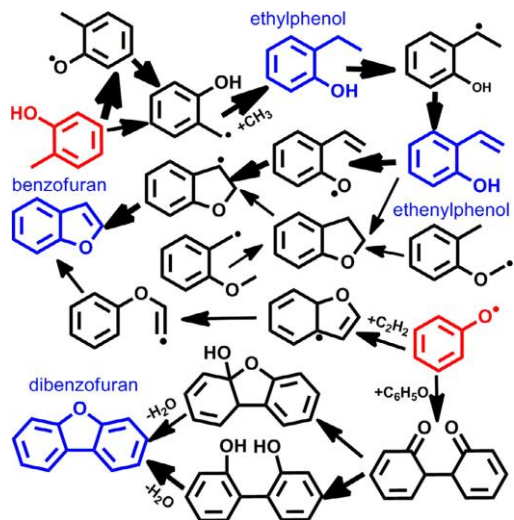


Figure 1: Reaction network for the formation of some OPAHs [1].

Incomplete combustion process: Formation PAHs/OPAHs

→ Impact on the environment and human health

→ Fundamental still not understood

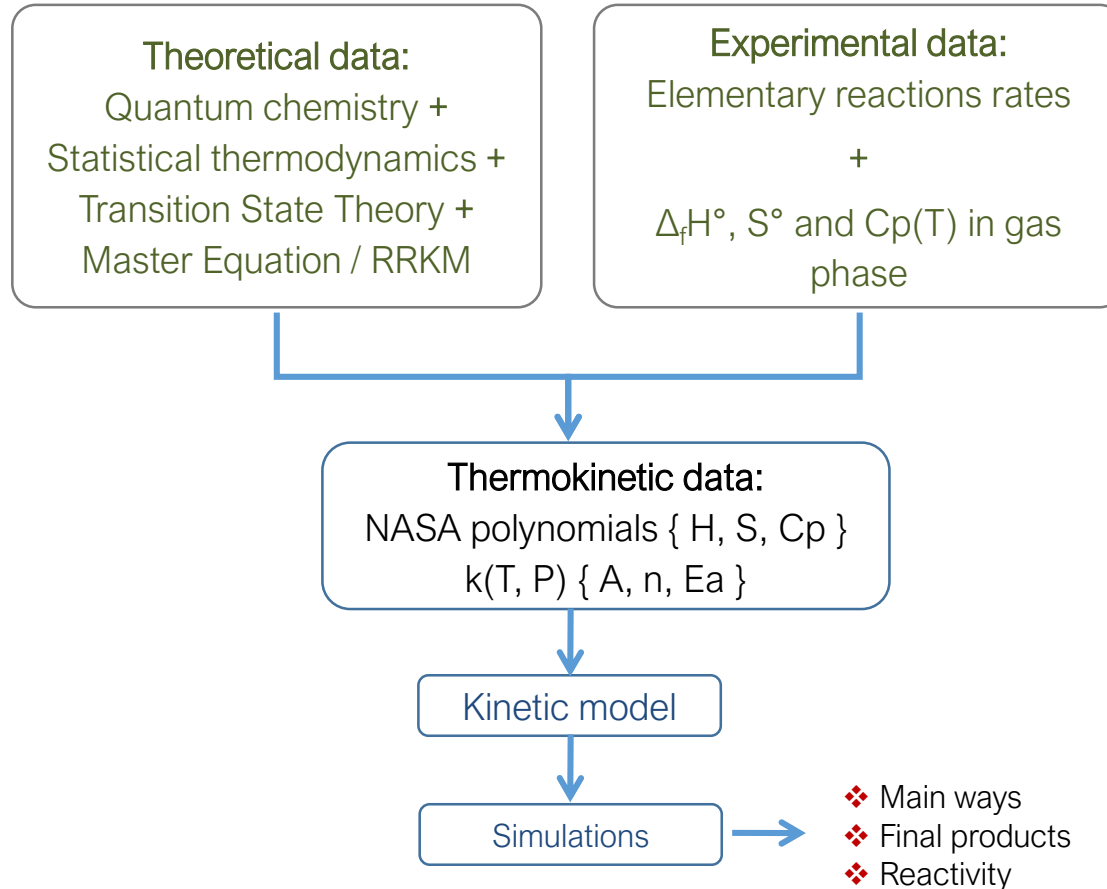
Aim: Investigation of the chemistry consumption of OPAHs

- OPAHs $\xrightarrow{\text{decomposition}}$
- H-abstraction
 - Additions
 - tautomerization
 - Opening/closing cycle
 - HACA mechanism
- Higher OPAHs

Previous Work – Formation of OPAHs

Reference	Year	Fuel/Biofuel	Reactor (analysis technique)	Detection of OPAHs
Nowakowska et al.	2014	Anisole	JSR 673-1173K, 800 Torr, $\tau=2s$ (GC-FID/MS)	benzofuran, dibenzofuran
Nyström et al.	2016	Rapeseed methyl ester biodiesel	Older off-road engine (HPLC/GC/MS)	9,10-anthraquinone, 4H-cyclopenta[def]phenanthren-4-one, 7H-benz[de]anthracen-7-one, benz[a]anthracene-7,12-dione
Li et al.	2018	Ultra-low sulfur diesel/waste cooking oil biodiesel	Steady engine (Solvent Extraction/GC/MS)	9,10-anthraquinone, 9-fluorenone, benzanthrone, benz[a]anthracene-7,12-dione, 1,4-naphthoquinone, 1-naphthaldehyde
Liu et al.	2019	Benzene/Phenol/C ₂ H ₂ /N ₂ Benzene/C ₂ H ₂ /N ₂ at 1400K	JSR (MS)	Naphtho[2,1-b]furan, 3-phenylfuran, 2-vinylbenzofuran, 9,10-anthraquinone, benz[a]anthracene-7,12-dione, Benzanthrone
Suzuki et al.	2020	Ethylene/O ₂ /N ₂	Flow Reactor 1050-1350K $\tau=0.40-1.5s$, $\phi=3-12$	benzofuran, dibenzofuran, 9-fluorenone, benzanthrone

Methodology



Computational Approach

- Quantum Chemical calculations: **Gaussian 16, MOLPRO**

- Opt + freq: CAM-B3LYP / 6-311++g(d,p)
- CBS limit energy: CCSD(T)-F12a/cc-pV(D+T)Z

$$E_{\text{cbs}} = \{(E_{\text{large}} - E_{\text{small}})F + E_{\text{small}}\} [2]$$

with $F = 1.363802$ (CCSD-F12 corr) and 1.6084 ((T) contribution) → [calculated in this work.](#)

- Thermokinetic data : **ThermRot** [3] - TST

- 1D tunnelling corrections (asymmetric Eckart)
- 1D-HR approach for hindered rotors from relaxed scans

[2] Schwenke, D.W., J. Chem. Phys. 2004, 122, 014107.

[3] Lizardo-Huerta, J.-C., Sirjean, B., Bounaceur, R., Fournet, R., Phys. Chem. Chem. Phys. 2016, 18, 12231–12251.

H-abstractions – Structural properties

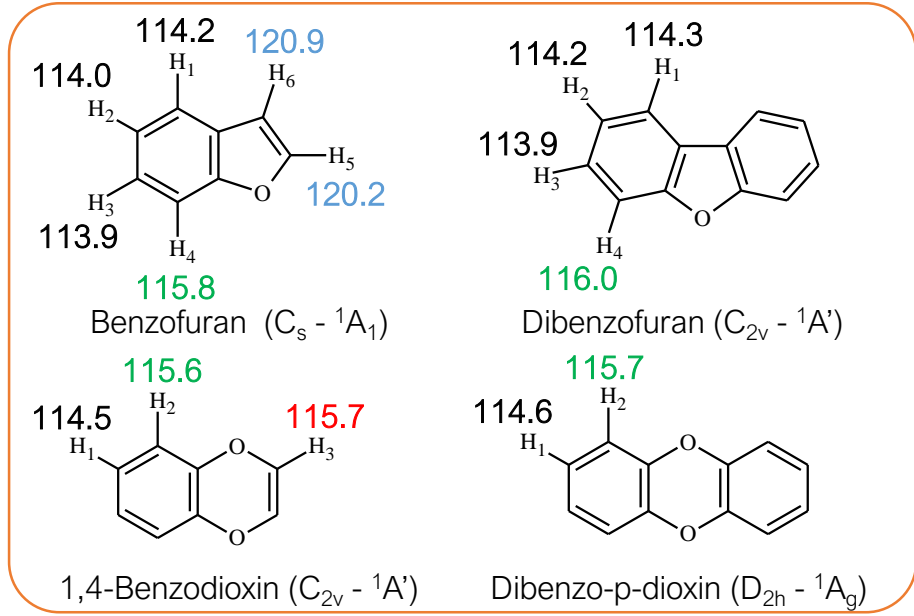


Figure 2: BDE at 298 K (in kcal mol⁻¹) calculated at CCSD(T)-F12/CBS//CAM-B3LYP/6-311++G(d,p) level of theory of OPAHs studied.

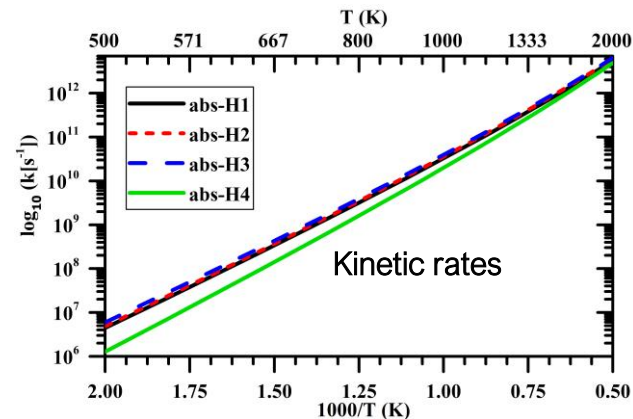
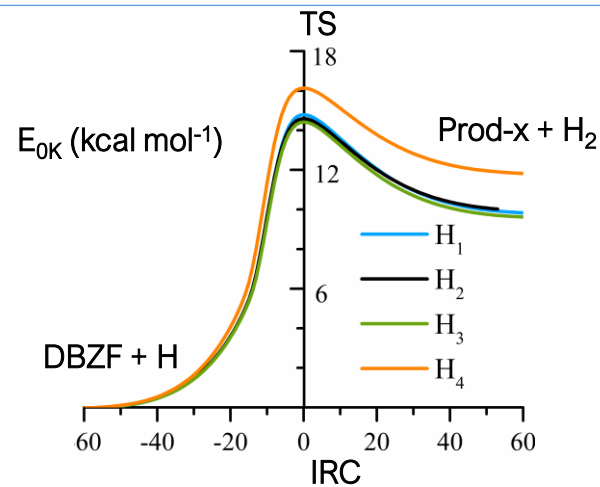
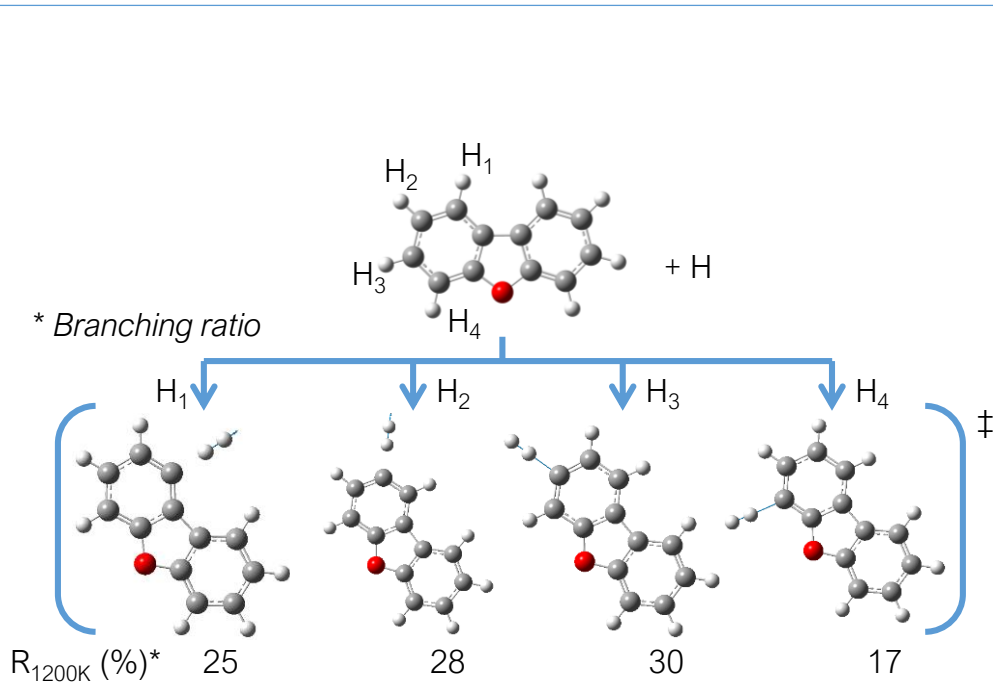
Table 1: Symmetry number, number of unique H-abstraction sites, and the reaction path degeneracy of studied OPAHs.

Analogous abstraction sites (C-H BDEs):

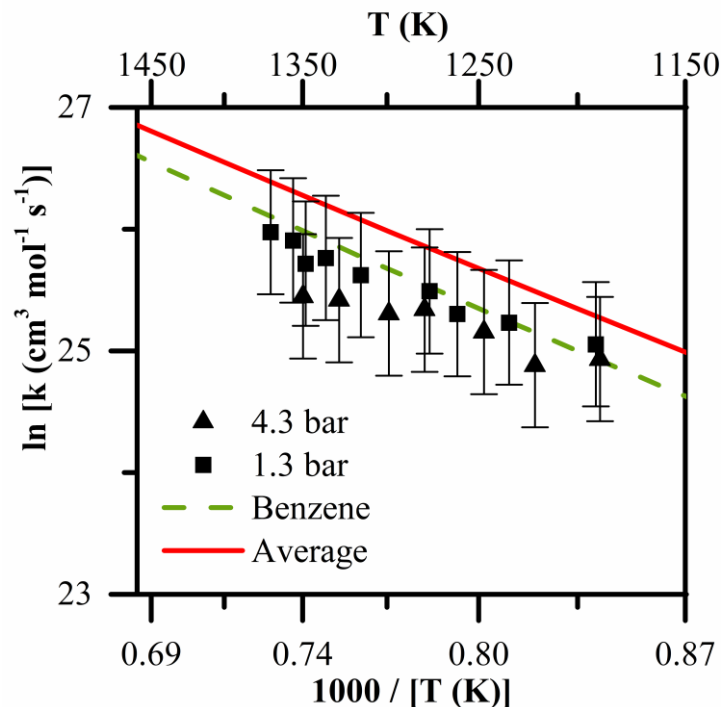
- **Group 1** → close to the benzene's C-H BDEs and without the influence of the O-atom;
- **group 2** → C-H bonded to the carbon located in the β-position with respect to the oxygen atom;
- **group 3** → C-H bonded to the carbon located in the dioxin ring, and
- **group 4** → C-H in the furan ring.

OPAHs	Symmetry number	Number of unique sites	Reaction path degeneracy (σ)
Benzofuran	1	6 (1,2,3,4,5,6)	1
Dibenzofuran	2	4 (1,2,3,4)	2
1,4-Benzodioxin	2	3 (1,2,3)	2
Dibenzo-p-dioxin	4	2 (1,2)	4

H-abstractions - Dibenzofuran



Validations of calculated kinetic constants



In general the values obtained in this work are in good agreement for the evaluated range of temperature

Figure 3: Experimental (symbols) [4] and calculated in this work (dash dotted) for benzene and compared to average rate constants (solid line) for H-abstraction of H-benzene type (group 1).

[4] Giri, B.R., Bentz, T., Hippler, H., Olzmann, M., *Zeitschrift Für Physikalische Chemie* 2009, 223, 539–549.

Kinetic parameters (per transferable H-atom)

Table 2: Kinetic constants (k) for a temperature range of 500 to 2000 K and branching ratio at 1200 K computed at **CCSD(T)-F12/CBS** level of theory. Units are in cm, mol, s and cal.

H-type	k = A T ⁿ exp(-E _a /RT)			k _{1200K}	R _{1200K} (%)	H-type	k = A T ⁿ exp(-E _a /RT)			k _{1200K}	R _{1200K} (%)
	A	n	E _a				A	n	E _a		
Benzofuran (BZF)						1,4-benzodioxin (BZD)					
H ₁ (g1)	9.36×10 ⁶	2.16	14600	9.18×10 ¹⁰	23	H ₁ (g1)	1.08×10 ⁷	2.17	14770	10.6×10 ¹⁰	50
H ₂ (g1)	8.74×10 ⁶	2.17	14310	10.4×10 ¹⁰	25	H ₂ (g2)	1.58×10 ⁷	2.12	15680	7.42×10 ¹⁰	35
H ₃ (g1)	8.06×10 ⁶	2.18	14240	10.6×10 ¹⁰	26	H ₃ (g3)	7.66×10 ⁶	2.17	16930	3.04×10 ¹⁰	15
H ₄ (g2)	1.64×10 ⁷	2.11	15960	6.38×10 ¹⁰	16	Dibenzo-p-dioxin (DBZD)					
H ₅ (g4)	4.71×10 ⁷	2.05	20160	2.06×10 ¹⁰	5	H ₁ (g1)	1.33×10 ⁷	2.17	14800	12.9×10 ¹⁰	64
H ₆ (g4)	8.83×10 ⁷	1.96	20220	2.00×10 ¹⁰	5	H ₂ (g2)	1.61×10 ⁷	2.11	15730	6.90×10 ¹⁰	36
Dibenzofuran (DBZF)						Average values (per abstracted H-atom)					
H ₁ (g1)	8.52×10 ⁶	2.16	14460	8.88×10 ¹⁰	25	Group 1	8.03×10 ⁶	2.19	14440	10.4×10 ¹⁰	
H ₂ (g1)	9.25×10 ⁶	2.16	14470	9.59×10 ¹⁰	28	Group 2	1.51×10 ⁷	2.12	15820	6.69×10 ¹⁰	
H ₃ (g1)	7.58×10 ⁶	2.19	14210	10.8×10 ¹⁰	30	Group 3	7.66×10 ⁶	2.17	16930	3.04×10 ¹⁰	
H ₄ (g2)	1.72×10 ⁷	2.10	16060	5.98×10 ¹⁰	17	Group 4	6.45×10 ⁷	2.01	20190	2.10×10 ¹⁰	

Outlook

- OPAHs are formed during the incomplete combustion processes.
- OPAHs show a significantly higher toxicity than PAHs.
- Fundamentals of OPAHs chemistry are still not understood.
- We have studied the H-abstractions reaction of some OPAHs (two benzofurans and two benzodioxins) by H-atoms in a systematic way.
- With respect to the BDEs of the C-H bonds, we have classified the possible H-abstraction sites into four groups.
- We have calculated and evaluated the kinetic constants for the H-abstraction reactions for each of these H-atoms thereby deducing the average values for each type of the H-abstracted atom.

Acknowledgments

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