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Theoretical study of H-abstraction reactions by H-atoms from selected oxygenated polycyclic aromatic hydrocarbons (OPAHs)

Juan Carlos LIZARDO-HUERTA, Sonia TAAMALLI, Kanika SOOD, Laurent GASNOT, Florent LOUIS, Abderrahman EL BAKALI, Luc-Sy TRAN

Univ. Lille, CNRS, UMR 8522, Physico-Chimie des Processus de Combustion et de l'Atmosphère – PC2A, F-59000 Lille, France (juancarlos.lizardohuerta@univ-lille.fr)

Context

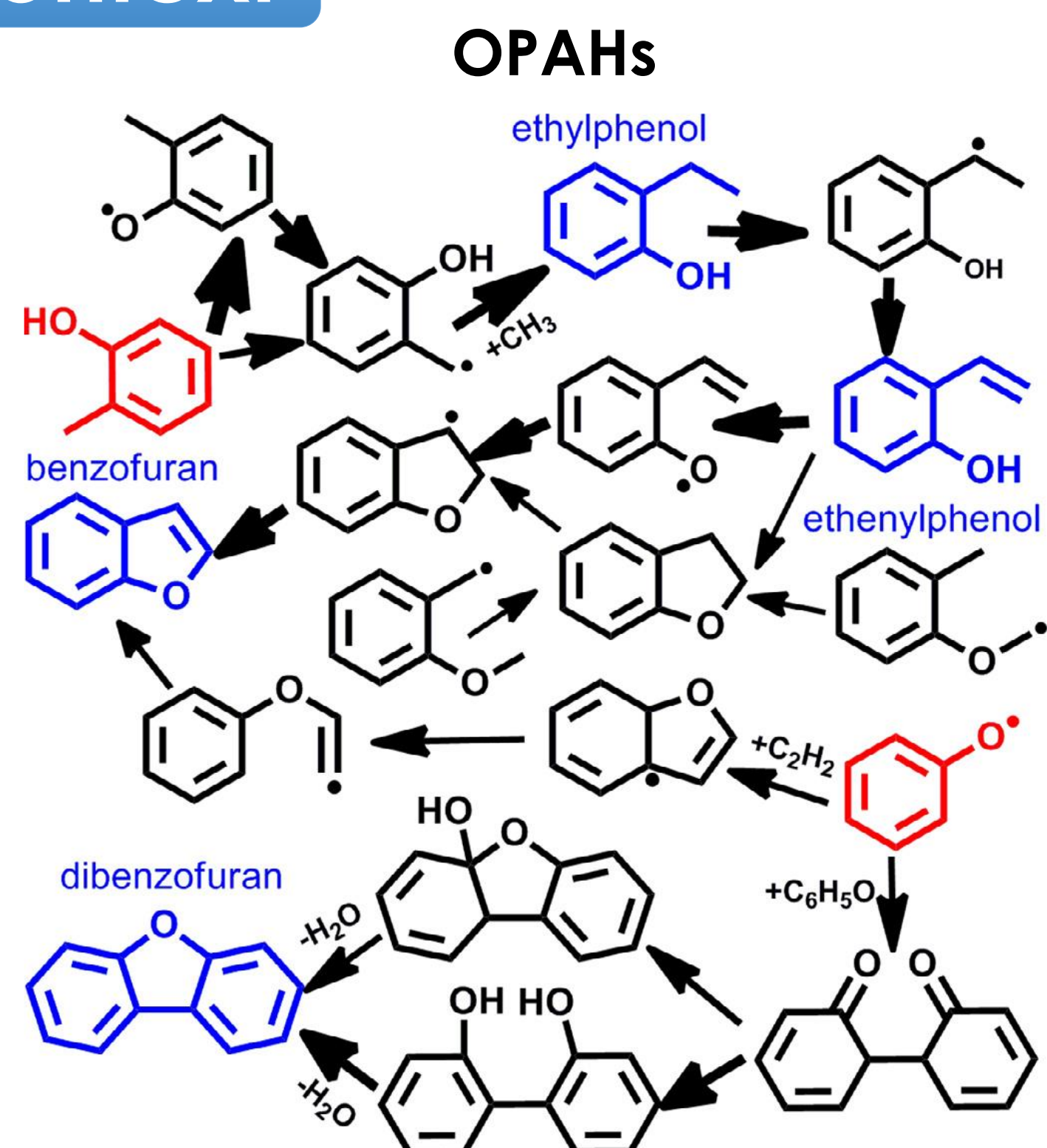
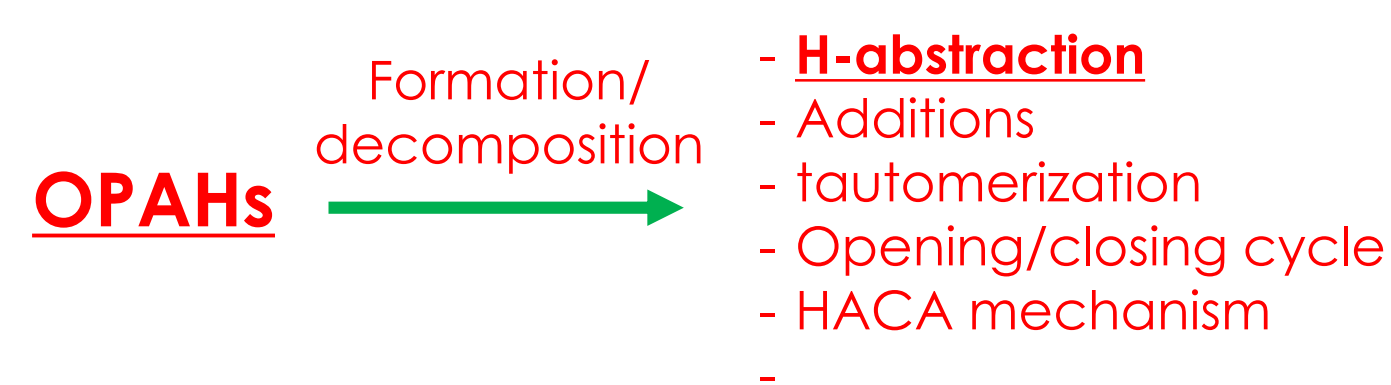


Figure 1: Reaction network for the formation of some OPAHs [1].

- OPAHs are formed during the incomplete combustion processes of hydrocarbons, biofuels and biomass.
- Recent studies show a significantly higher toxicity for OPAHs than for conventional polycyclic aromatic hydrocarbons (PAHs).
- Despite this concern, the fundamental principles of OPAHs chemistry are still not well understood, which explains why current combustion kinetic models do not incorporate an adequate mechanism of their formation and decomposition, and are rather oriented towards the formation of small OPAHs (2-3 cycles).



Methodology

Quantum chemical calculations: Gaussian 16, MOLPRO

- Optimisation + frequencies: CAM-B3LYP/6-311++G(d,p)
- CBS limit energy: CCSD(T)-F12a/cc-pV(D+T)Z

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

with $F = 1.3638$ (CCSD-F12 corr) and 1.6084 ((T) contribution) \rightarrow calculated in this work.

Thermokinetic data: ThermRot [3]

- The rate constants were determined from the Transition State Theory (TST):

$$k(T) = \kappa \sigma \frac{k_B T}{h} \frac{Q_{\text{TS}}(T)}{Q_{\text{R}}(T)} \exp\left(-\frac{E_0}{RT}\right)$$

- Rate coefficients were fitted over the temperatures (α , n , E_a) range 500 - 2000 K, with a three parameters Arrhenius expressions:

$$k(T) = AT^n \exp\left(-\frac{E_a}{RT}\right)$$

Symbols:

- Q_{R} ; Q_{TS} : global partition function of reactants and TSs;
- E_0 : barrier height at 0K;
- κ : transmission coefficient (Eckart 1-D);
- σ : reaction path degeneracy.

Aim

Calculate and evaluate the kinetic constants for the H-abstraction reactions from selected OPAHs

Structural properties

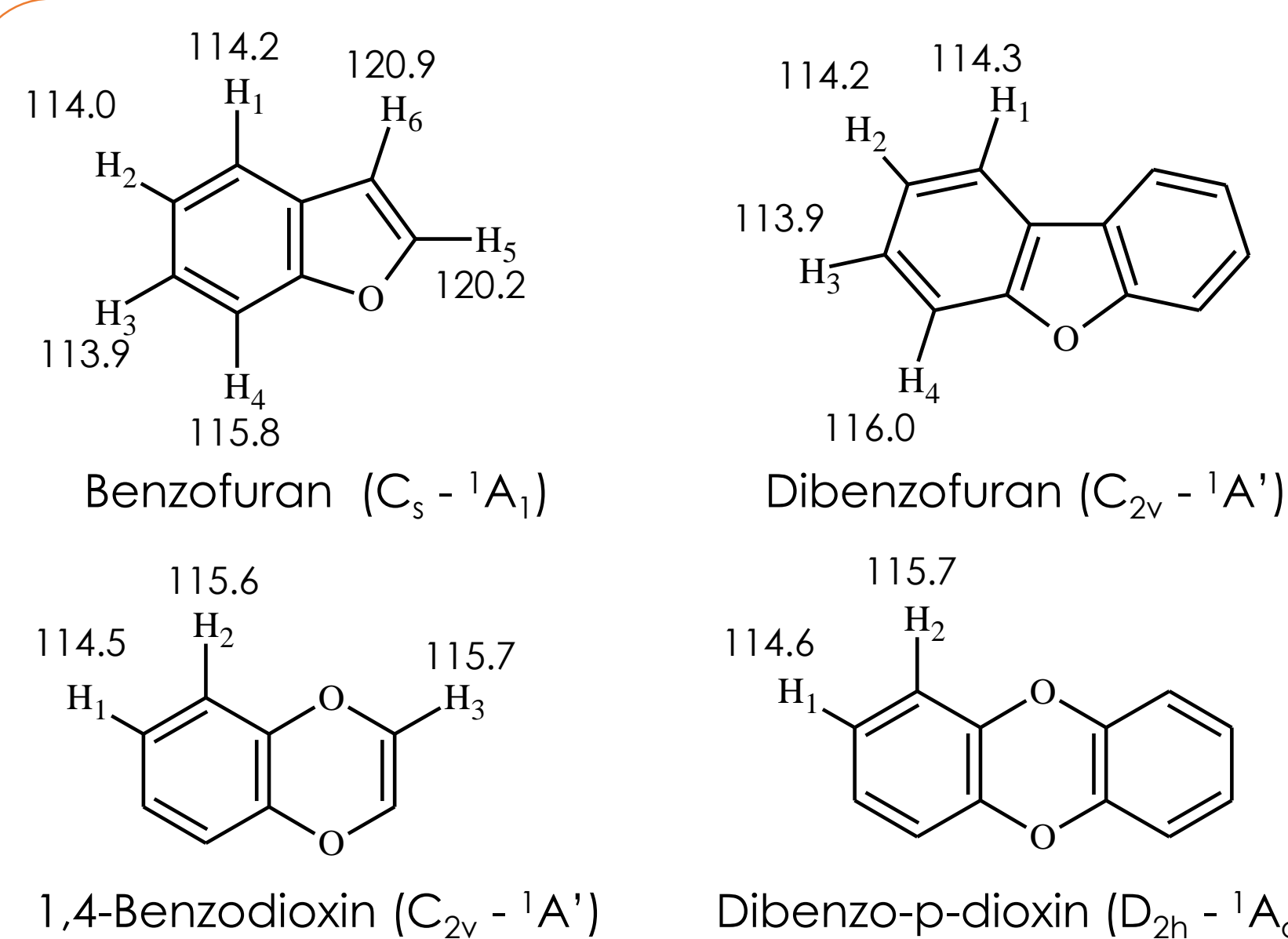


Figure 2: BDE at 298 K (in kcal mol⁻¹) calculated at CCSD(T)-F12/CBS//CAM-B3LYP/6-311++G(d,p) level of theory of OPAHs studied.

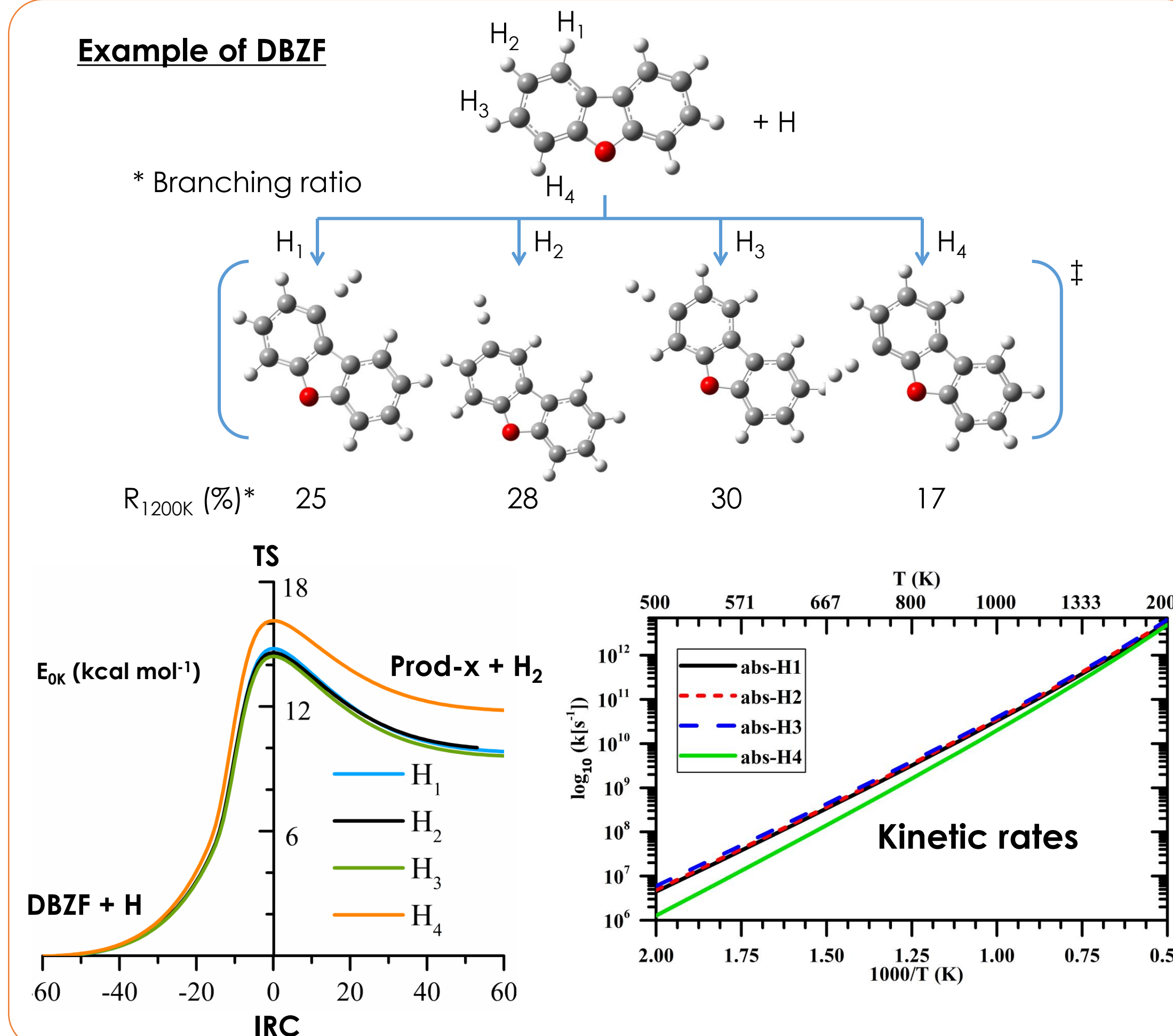
Looking for analogous abstraction sites (C-H BDEs):

- **Group 1** \rightarrow close to the benzene's C-H BDEs and without the influence of the O-atom ($H_1 - H_3$ in BZF and DBZF, and H_1 in BZD and DBZD);
- **group 2** \rightarrow C-H bonded to the carbon located in the β -position with respect to the oxygen atom (H_4 in BZF and DBZF, H_2 in BZD and DBZD);
- **group 3** \rightarrow C-H bonded to the carbon located in the dioxin ring (H_3 in BZD) and
- **group 4** \rightarrow C-H in the furan ring (H_5 and H_6 in BZF).

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

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

Energy barriers and kinetic constants



Validation of calculated kinetic constants

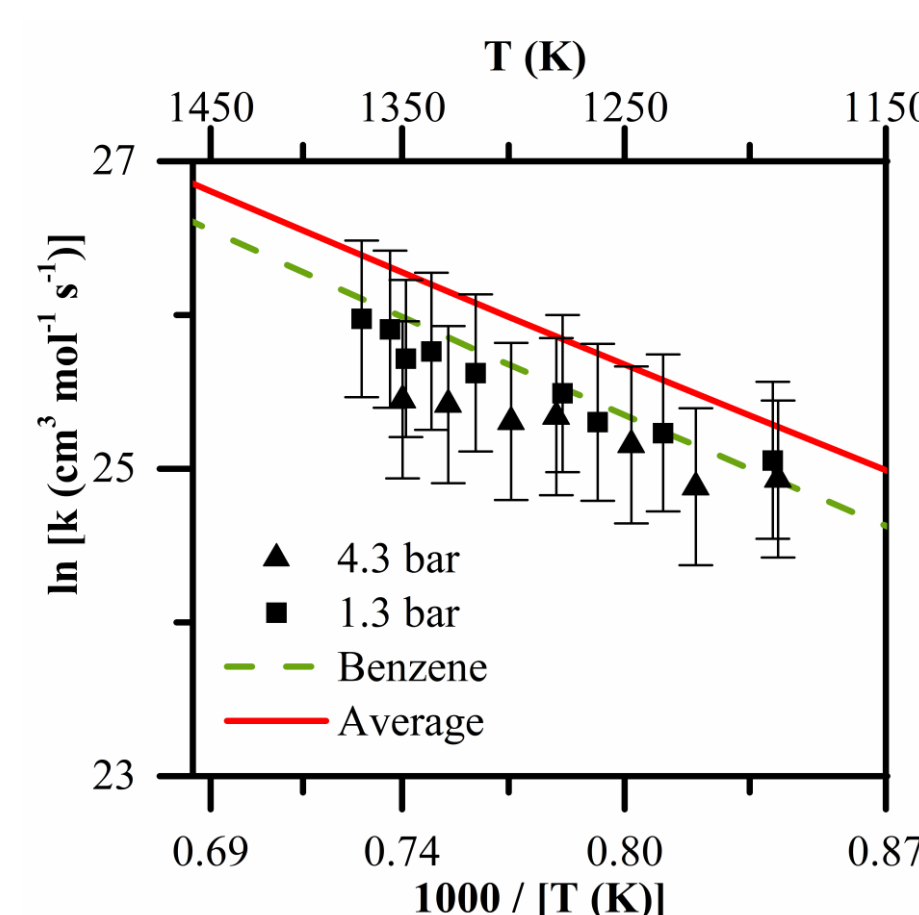


Figure 3: Experimental (symbols) [4] and calculated in this work (dash dotted) for benzene and compared to average rate constants (solid line) for H-abstraction of H-benzene type (group 1).

Kinetic parameters (per transferable H-atom)

H-type	$k = A T^n \exp(-E_a/RT)$			k_{1200K}	R_{1200K} (%)
	A	n	E_a		
Benzofuran (BZF)					
H_1 (g1)	9.36×10^6	2.16	14600	9.18×10^{10}	23
H_2 (g1)	8.74×10^6	2.17	14310	10.4×10^{10}	25
H_3 (g1)	8.06×10^6	2.18	14240	10.6×10^{10}	26
H_4 (g2)	1.64×10^7	2.11	15960	6.38×10^{10}	16
H_5 (g4)	4.71×10^7	2.05	20160	2.06×10^{10}	5
H_6 (g4)	8.83×10^7	1.96	20220	2.00×10^{10}	5
Dibenzofuran (DBZF)					
H_1 (g1)	8.52×10^6	2.16	14460	8.88×10^{10}	25
H_2 (g1)	9.25×10^6	2.16	14470	9.59×10^{10}	28
H_3 (g1)	7.58×10^6	2.19	14210	10.8×10^{10}	30
H_4 (g2)	1.72×10^7	2.10	16060	5.98×10^{10}	17
1,4-benzodioxin (BZD)					
H_1 (g1)	1.08×10^7	2.17	14770	10.6×10^{10}	50
H_2 (g2)	1.58×10^7	2.12	15680	7.42×10^{10}	35
H_3 (g3)	7.66×10^6	2.17	16930	3.04×10^{10}	15
Dibenzo-p-dioxin (DBZD)					
H_1 (g1)	1.33×10^7	2.17	14800	12.9×10^{10}	64
H_2 (g2)	1.61×10^7	2.11	15730	6.90×10^{10}	36
Average values (per abstracted H-atom)					
Group 1	8.03×10^6	2.19	14440	10.4×10^{10}	
Group 2	1.51×10^7	2.12	15820	6.69×10^{10}	
Group 3	7.66×10^6	2.17	16930	3.04×10^{10}	
Group 4	6.45×10^7	2.01	20190	2.10×10^{10}	

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.

Conclusion

- 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.

Reference

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Acknowledgments

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