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Chemical kinetics of representative quinones

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

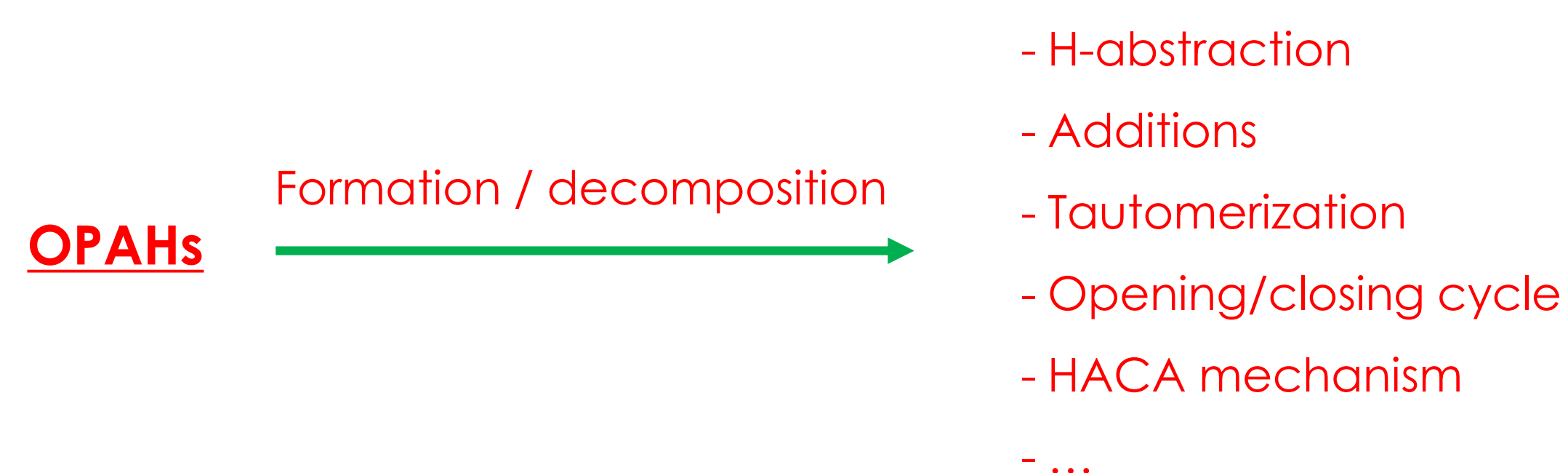
Univ. Lille, CNRS, UMR 8522, Physico-Chimie des Processus de Combustion et de l'Atmosphère – PC2A, F-59000 Lille, France

Context

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

Incomplete combustion process: Formation PAHs / OPAHs
 → Impact on the environment and human health
 → Fundamental still not understood

- From literature [1-2], OPAHs with larger ring sizes and involving chemical structures that include not only furans, but also fluorenones, aromatic ketones or quinones.



Methodology

Quantum chemical calculations: Gaussian 16

- Optimisation + frequencies: CAM-B3LYP/6-311+G(2d,p)
- CBS limit energy: modified CBS-QB3 composite method (denoted CBS-Q')

Thermokinetic data: ThermRot [3]

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

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

- The partition function of internal rotations were computed using a modified 1-DHR approach by using the ThermRot software [3]

- 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:

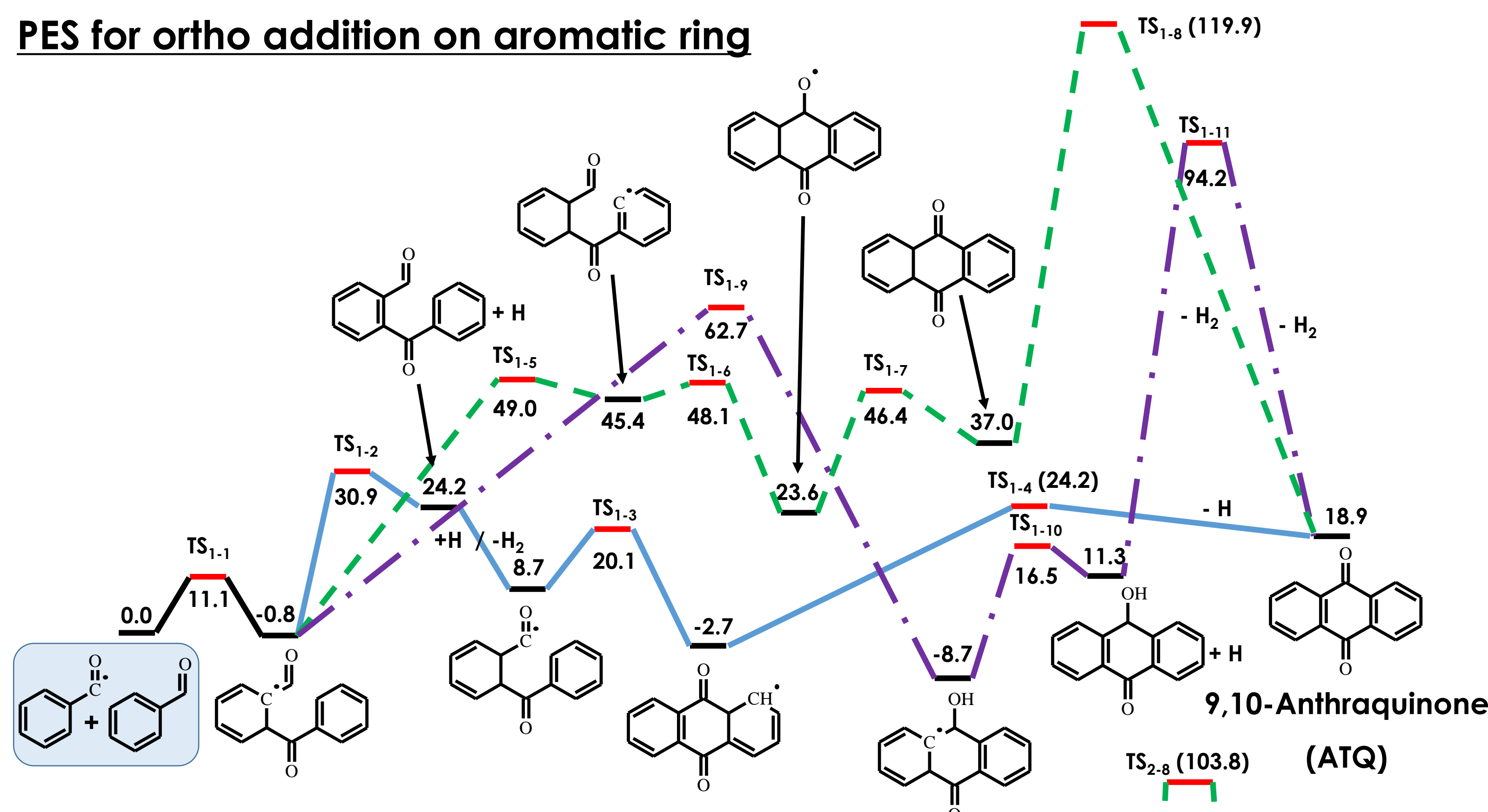
- Q_R , Q_{TS} : global partition function of reactants and TSs;
- E_0 : barrier height at 0K;
- κ : transmission coefficient (Eckart 1-D);
- σ : reaction path degeneracy.

Aim

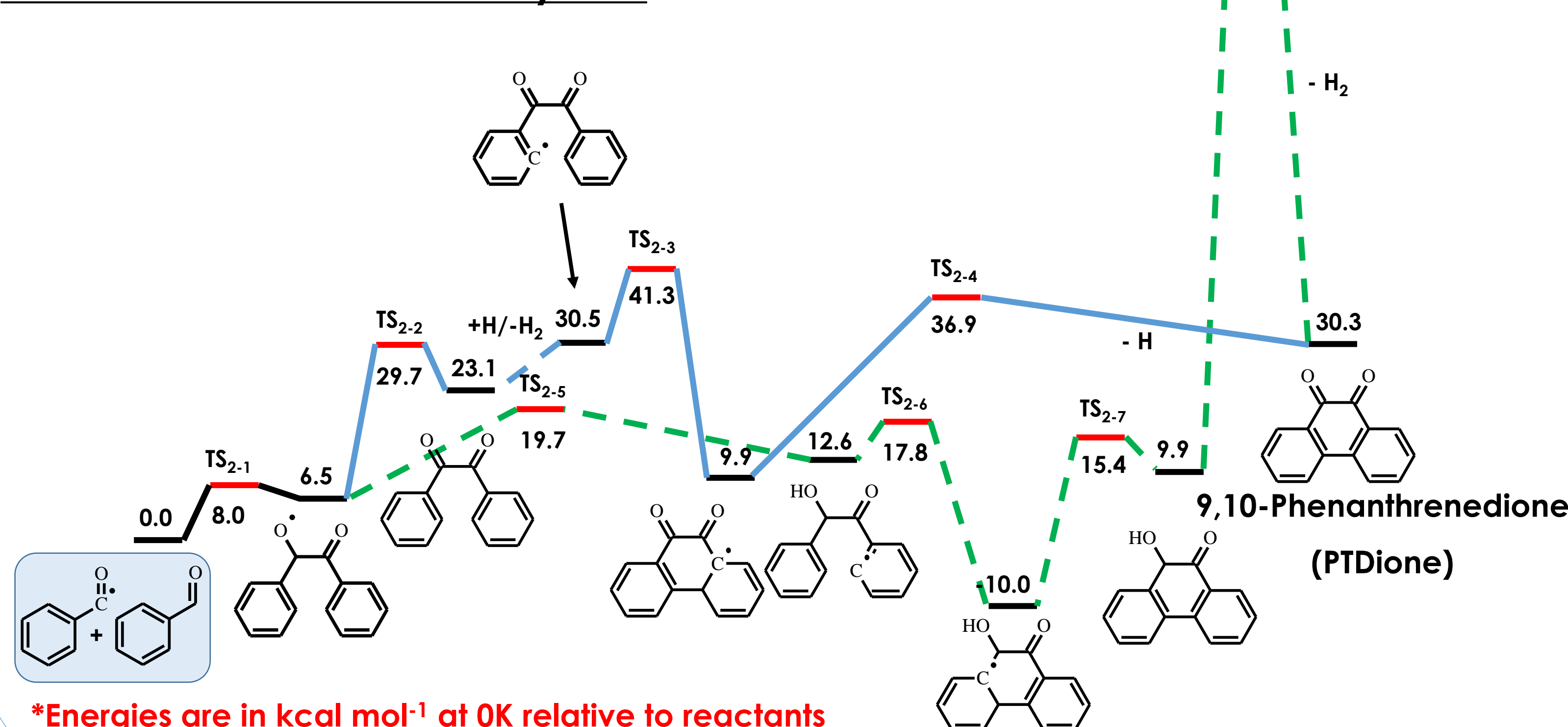
Calculate and evaluate the kinetic constants for the formation of quinones

Results

PES for ortho addition on aromatic ring



PES for addition on carbonyl site



*Energies are in kcal mol⁻¹ at 0K relative to reactants

Units are in cal mol cm³ s

Kinetic parameters

TS	Reaction	k = A T ⁿ exp(-E _a /RT)		
		A	n	E _a
Addition on aromatic ring				
TS ₁₋₁	A1CHO + A1CO -- ortho-add --> A1CHO-A1CO-o	1.69×10 ³	2.61	11180
TS ₁₋₂	A1CHO-A1CO-o -- C-H b-scission --> A1CHO-CO-A1 + H	2.19×10 ¹²	0.45	33410
TS ₁₋₃	A1CO-CO-A1 -- Closing cycle --> 9,10-Anthraquinonyl	2.31×10 ¹⁰	0.39	10050
TS ₁₋₄	9,10-Anthraquinonyl -- C-H b-scission --> 9,10-Anthraquinone + H	1.07×10 ¹¹	0.80	27440
TS ₁₋₅	A1CHO-A1CO-o -- isom6 --> C6H6CHO-CO-C6H4	1.49×10 ⁹	0.81	48480
TS ₁₋₆	C6H6CHO-CO-C6H4 -- closing cycle --> C6H6-CO-CO-A1	4.03×10 ¹³	-0.80	2760
TS ₁₋₇	C6H6-CO-CO-A1 -- C-H b-scission --> C6H6-CO-CO-A1 + H	2.59×10 ¹¹	0.84	23460
TS ₁₋₈	C6H6-CO-CO-A1 -- H2 elimination --> ATQ + H2	4.92×10 ⁹	1.15	83030
TS ₁₋₉	A1CHO-A1CO-o -- isom7 --> Anthraquinonyl-OH	1.99×10 ⁷	1.10	60270
TS ₁₋₁₀	Anthraquinonyl-OH -- C-H b-scission --> Anthraquinone-OH+H	1.39×10 ¹⁰	1.00	25580
TS ₁₋₁₁	Anthraquinone-OH -- H2 elimination --> ATQ + H2	1.40×10 ¹⁰	0.83	82360
Addition on carbonyl site				
TS ₂₋₁	A1CHO + A1CO = A1CHO-COA1	4.26×10 ⁰	3.03	6890
TS ₂₋₂	A1CHO-COA1 = A1CO-COA1 + H	1.00×10 ¹⁰	1.06	23300
TS ₂₋₃	C6H4CO-COA1 = 9,10-Phenanthredionyl	8.07×10 ¹⁰	0.12	10380
TS ₂₋₄	9,10-Phenanthredionyl = 9,10-Phenanthredione + H	2.61×10 ¹¹	0.82	27620
TS ₂₋₅	A1CHO-COA1 = A1CHOH-CO-C6H4	3.78×10 ⁶	1.65	5740
TS ₂₋₆	A1CHOH-CO-C6H4 = Hphenanthreneonyl-OH	2.39×10 ¹²	-0.51	4910
TS ₂₋₇	Hphenanthreneonyl-OH = Hphenanthreneone-OH+H	1.18×10 ¹¹	0.74	26030
TS ₂₋₈	Hphenanthreneone-OH = PTDione + H2	5.61×10 ⁸	1.29	86980

Conclusion

- We have studied the chemistry of formation of representative quinones by recombination of the benzoyl radical and benzaldehyde, leading to the formation of anthraquinone and phenanthredione.
- The different pathway include: addition, isomerisation, H-abstraction, closing cycle and β-scission reactions.
- The pathways conducting to 9,10-anthraquinone is the most favourable.

Reference

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

Acknowledgments

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