

Chemical kinetics of representative quinones

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This research focuses on the study of the reaction kinetics of Oxygenated Polycyclic Aromatic Hydrocarbons (OPAHs). OPAHs are formed during incomplete combustion processes of hydrocarbons, biofuels and biomass. Nowadays, OPAHs are becoming more important because more and more alternative fuels are being used to mitigate the effect of fossil fuels on global warming. This is due to the fact that the composition of some biofuels includes aromatic rings with oxygen atoms and that their decomposition processes lead almost directly to the formation of OPAHs. Recent studies show a significantly higher toxicity for OPAHs than for conventional PAHs [1]. This is because, like PAHs, OPAHs can be also considered as soot precursors, but with the particularity that they would lead to smaller soot particles which would not be trapped by particulate filters, consequently affecting human health by damaging the cardiovascular system, weakening the immune system and impairing the function of lungs [2].

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, such as benzofuran and dibenzofuran. However, according to the literature [3-4], authors have observed OPAHs with larger ring sizes (from 2 to 5 cycles) and involving chemical structures that include not only furans, but also fluorenones, aromatic ketones or quinones.

Thus, the aim of our project is to propose sub-mechanisms where the reaction pathways of representative OPAHs are included, by using theoretical methods. The presentation will cover a first part where we have studied the reaction pathways of quinones (**Figure 1**).

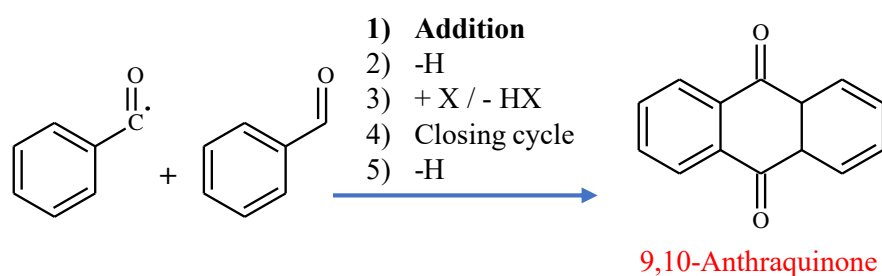


Figure 1: Proposed formation pathway for 9,10-Antraquinone

References

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- [2] H. I. Abdel-Shafy and M. S. M. Mansour, *Egypt J Pet*, **25** 107-123 (2016).
- [3] R. Nyström, I. Sadiksis, T.M. Ahmed, R. Westerholm, J.H. Koegler, A. Blomberg, T. Sandström, C. Boman, *Fuel*, **186** 261-269 (2016).
- [4] X. Li, Y. Zheng, C. Guan, C.S. Cheung, Z. Huang, *Environ Sci Pollut Res*, **25** 34131-34138 (2018).

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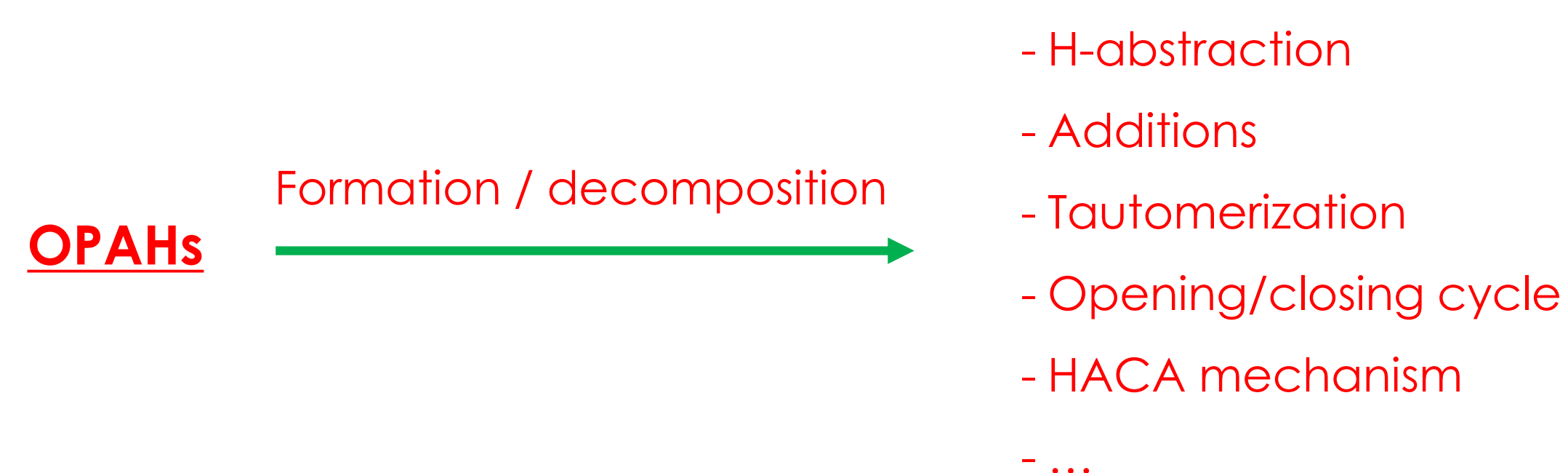
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Context

- ~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:

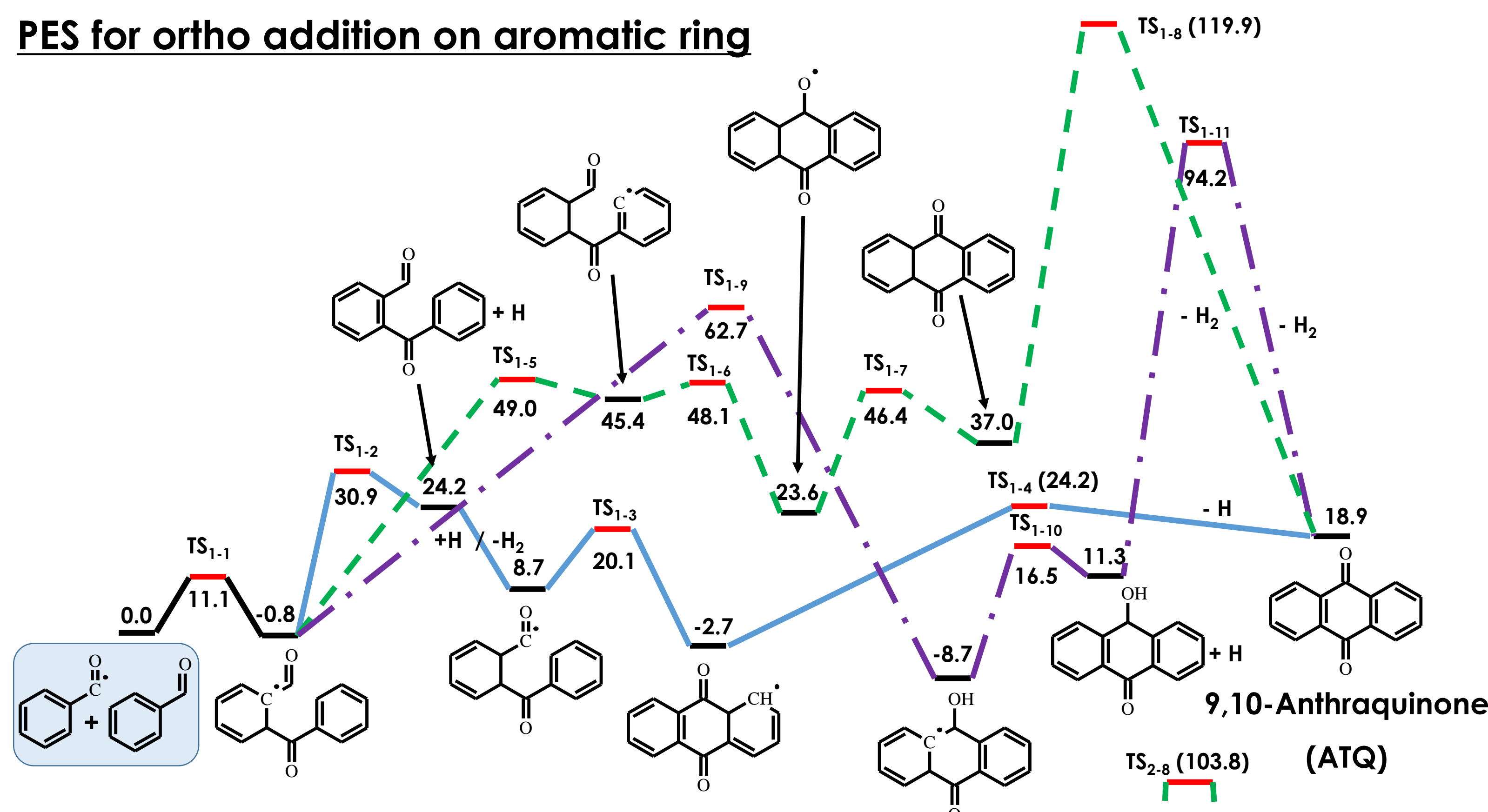
- Q_R , Q_{TS} : global partition function of reactants and TSs;
- E_0 : barrier height at 0K;
- κ : transmission coefficient (Eckart 1-D);
- σ : reaction path degeneracy.

Aim

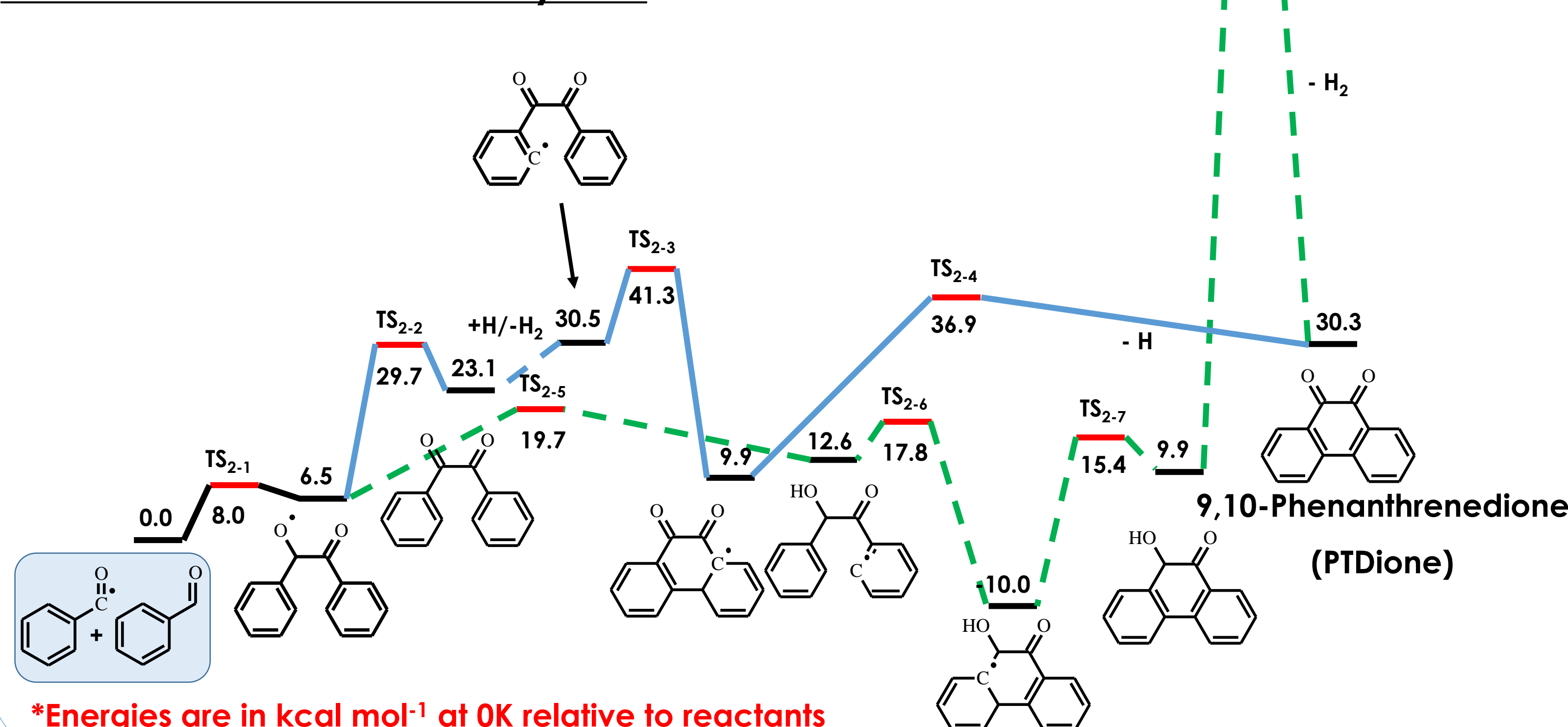
Calculate and evaluate the kinetic constants for the formation of quinones

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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Acknowledgments

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