Chemical kinetics of representative quinones

Juan Carlos Lizardo Huerta, Sonia Taamalli, Kanika Sood, Laurent Gasnot, Florent Louis, Abderrahman El Bakali, Luc-Sy Tran

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.

OPAHs —Formation / decomposition→

- H-abstraction
- Additions
- Tautomerization
- Opening/closing cycle
- HACA mechanism
- …

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 (***a, 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.

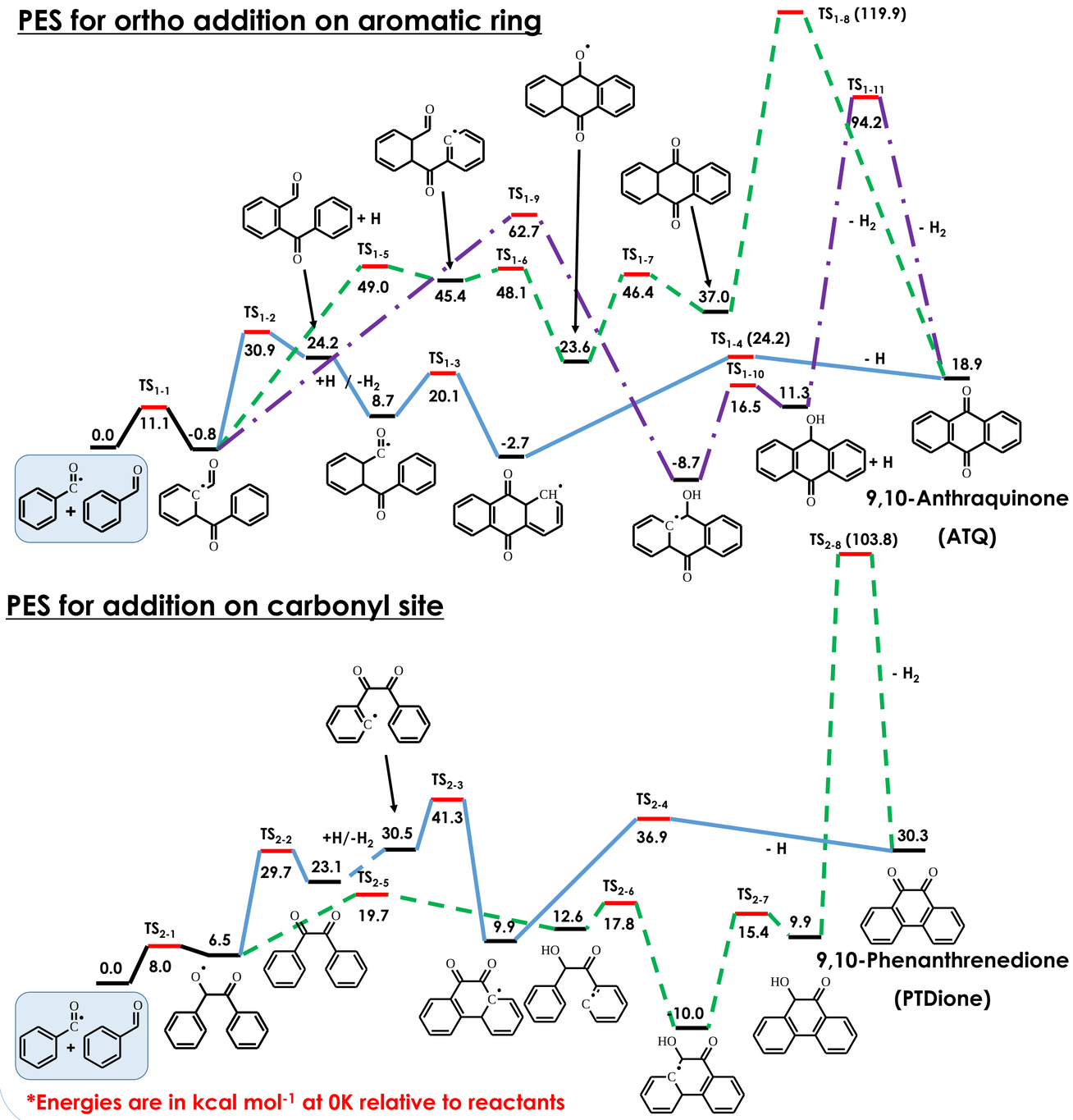
Aim

Calculate and evaluate the kinetic constants for the formation of quinones

Results

Recombinaison of benzoyl radical and benzaldehyde

PES for ortho addition on aromatic ring



PES for addition on carbonyl site

*Energies are in kcal mol^{-1} at 0K relative to reactants

Kinetic parameters

TS	Reaction	k = A Tⁿ exp(-Ea/RT)		
		A	n	Ea
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 -- Clossing 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-COH-CO-A1	4.03×10^{13}	-0.80	2760
TS_{1-7}	C6H6-COH-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-Phenanthrenedionyl	8.07×10^{10}	0.12	10380
TS_{2-4}	9,10-Phenanthrenedionyl = 9,10-Phenanthrenedione + 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

Units are in cal mol cm^3 s

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 phenanthrenedione.
- 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

[1] H. I. Abdel-Shafy and M. S. M. Mansour, Egypt J Pet, 25 107-123 (2016).

[2] R. Nyström, I. Sadiktsis, T.M. Ahmed, R. Westerholm, J.H. Koegler, A. Blomberg, T. Sandström, C. Boman, Fuel, 186 261-269 (2016).

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

Acknowledgments

- This work was supported by the I-SITE ULNE through the "Biofuel-Soot" project (R-JEUNES-19-010-TRAN).
- High performance computing resources were provided by the Centre de Resources Informatiques (CRI) of the University of Lille and IDRIS under the allocation 2020-101578 made by GENCI.
- We appreciated the support from the French ANR agency Contract No. ANR-11-LABX-0005 "Chemical and Physical Properties of the Atmosphere" (CAPPA).
- The authors thank the Région Hauts-de-France, and the Ministère de l'Enseignement Supérieur et de la Recherche (CPER Climibio), and the European Fund for Regional Economic Development for their support.