



TS	Reaction	k = A T ⁿ exp(-E _a /RT)		
		A	n	E _a
TS ₄₋₁	C ₆ H ₅ CHO + C ₆ H ₅ CO → A1CHO-A1CO-o	1.69×10 ³	2.61	11180
TS ₄₋₂	A1CHO-A1CO-o → A1CHO-CO-A1 + H	2.19×10 ¹²	0.45	33410
TS ₄₋₃	A1CO-CO-A1 → ATQuinonyl	2.31×10 ¹⁰	0.39	10050
TS ₄₋₄	ATQuinonyl → Anthraquinone + H	1.07×10 ¹¹	0.80	27440
TS ₄₋₅	A1CHO-A1CO-o → C ₆ H ₆ CHO-CO-C ₆ H ₄	1.49×10 ⁹	0.81	48480
TS ₄₋₆	C ₆ H ₆ CHO-CO-C ₆ H ₄ → C ₆ H ₆ -COH-CO-A1	4.03×10 ¹³	-0.80	2760
TS ₄₋₇	C ₆ H ₆ -COH-CO-A1 → C ₆ H ₆ -CO-CO-A1 + H	2.59×10 ¹¹	0.84	23460
TS ₄₋₈	C ₆ H ₆ -CO-CO-A1 → ATQ + H ₂	4.92×10 ⁹	1.15	83030
TS ₄₋₉	A1CHO-A1CO-o → ATQuinonyl-OH	1.99×10 ⁷	1.10	60270
TS ₄₋₁₀	ATQuinonyl-OH → ATQ-OH + H	1.39×10 ¹⁰	1.00	25580
TS ₄₋₁₁	ATQ-OH → anthraquinone + H ₂	1.40×10 ¹⁰	0.83	82360

Figure S1. Top panel: Potential energy surface (PES) for addition (combination) of the benzoyl radical to benzaldehyde going to the formation of 9,10-anthraquinone at the CBS-Q/CAM-B3LYP/6-311+G(2d,p) level of theory, including ZPE. Energies are in kcal/mol at 0K relative to the reactants. Notes: The H-abstraction reactions were not calculated in this work, so the connected line should not to indicate barriers; their rate constants were taken from benzaldehyde [2] as described in the main paper. **Bottom panel:** The corresponding rate constants (k) for a temperatures range of 500 to 2000 K computed at CBS-Q/CAM-B3LYP/6-311+G(2d,p) level of theory. Units are in cm, mol, s and cal.

References

1. Lizardo-Huerta JC, Taamalli S, Sood K, Gasnot L, Louis F, et al. 2022. Thermochemical and kinetic studies of H-abstraction reaction of benzofurans and benzodioxins by H-atoms. *Computational and Theoretical Chemistry* 1209:113589
2. Bounaceur R, Da Costa I, Fournet R, Billaud F, Battin-Leclerc F. 2005. Experimental and modeling study of the oxidation of toluene. *International Journal of Chemical Kinetics* 37:25–49
3. Chu T, Smith MC, Yang J, Liu M, Green WH. 2020. Theoretical study on the HACA chemistry of naphthalenyl radicals and acetylene: The formation of C₁₂H₈, C₁₄H₈, and C₁₄H₁₀ species. *International Journal of Chemical Kinetics* 52:752–68
4. Therrien RJ, Ergut A, Leventis YA, Richter H, Howard JB, et al. 2010. Investigation of critical equivalence ratio and chemical speciation in flames of ethylbenzene–ethanol blends. *Combustion and Flame* 157:296–312