Rate Rule Modeling of PAHs Growth: from Gaseous to Solid Phase

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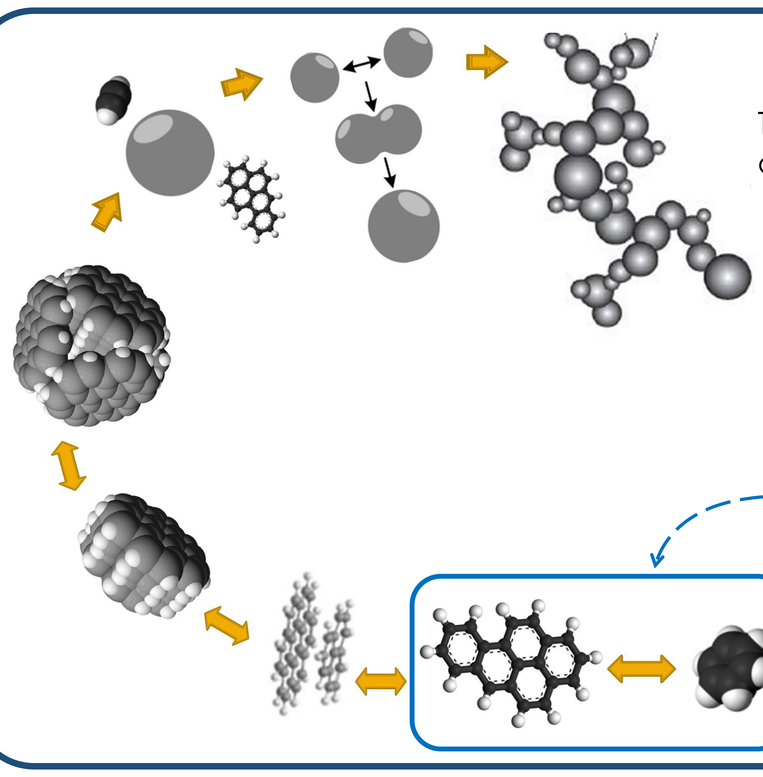
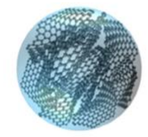
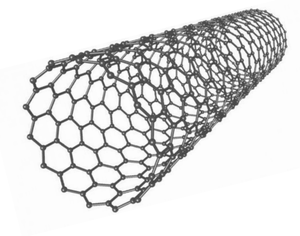


Motivation & Challenges

The **transition** to clean energy requires low-emission combustion technologies and advanced biofuels that help achieve **net-zero carbon emissions**.

PAHs play a *key role* in the pyrolysis and combustion of hydrocarbons and biomass, acting as **intermediates** in *soot formation*.





Once considered only harmful, carbonaceous nanoparticles are now valued for their potential in **material applications** [1] — e.g., *carbon black* for batteries, *carbon nanodots*, and *nanotubes* for electronics.

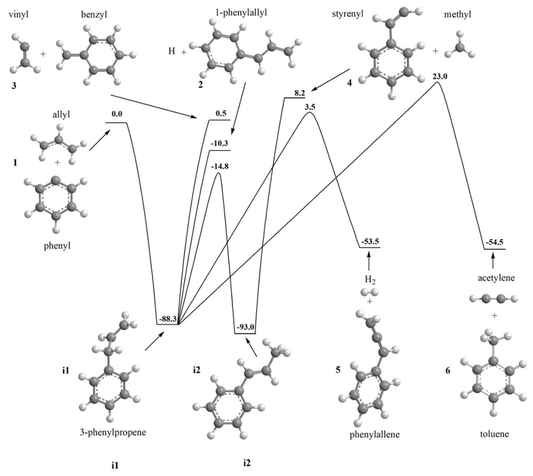
This work focuses on a critical intermediate step in soot formation — **the transition from small PAHs to larger, multi-ring PAHs** — where gas-phase molecules begin to form early-stage solid-like structures.

Quantum chemical calculations are too demanding for large PAHs. Developing **rate rules** enables to bridge small-to-large PAHs efficiently, supporting predictive modeling across gas-to-solid transitions.

Methods

Two complementary approaches are employed to determine the reaction rates involved in PAH growth:

1. **Master Equation-based Lumping (MEL):**
   Literature PESs [2] are analyzed using MEL [3] to extract kinetic parameters. By combining MEL with the Pseudo Steady-State Approximation (PSSA), we *lump* minor species and reduce model complexity while retaining accuracy in reactivity and product distribution.



2. **Ab Initio Kinetics with EStokTP:**
   We use EStokTP to compute rate constants from first principles. The method combines quantum calculations of stationary points, *transition state theory* for microcanonical rate constants, and a *master equation* solver to obtain temperature- and pressure-dependent rates automatically.

$$\frac{dn_i(E,t)}{dt} = z \sum_{E'=0}^{\infty} [P(E,E') \cdot n_i(E') - P(E',E) \cdot n_i(E)] \quad \textit{Collision Energy Transfer}$$

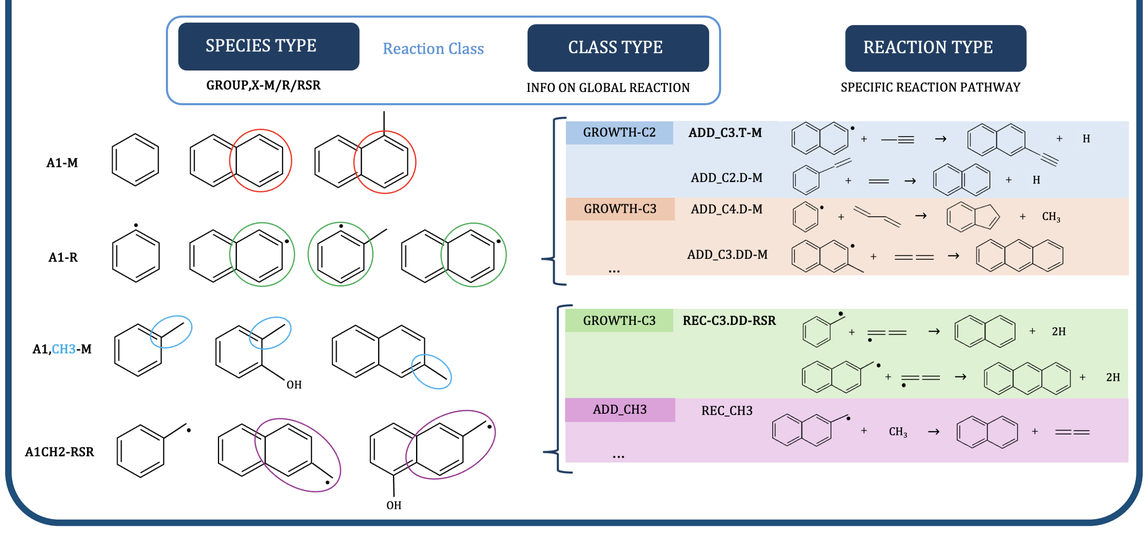
$$+ \sum_{j \neq i}^{\infty} [k_{ji}(E) \cdot n_j(E) - k_{ij}(E) \cdot n_{ij}(E)] \quad \textit{Intercorversion between Wells}$$

$$- \sum_{P_r} k^i_{P_r}(E)\, n_i(E) + k^i_R(E)\, K^{eq,i}_R\, n^{eq}_i \cdot n_{R1}\, n_{R2} \quad \textit{Chemical Reaction}$$

PAHs Model

Reaction classification:

- Each **reaction class** is identified by the **type of species** and the **class type** corresponding to an elementary reaction.
- Within each reaction class, different **reaction types** identify specific reactions associated to reference kinetic parameters which may be extended through rate rules.

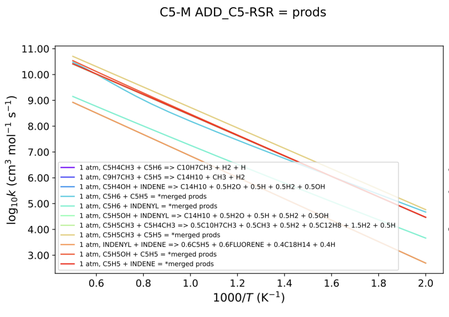


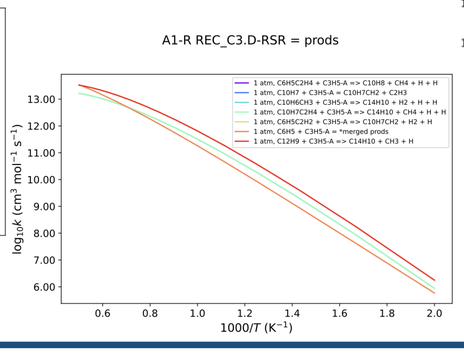
Results & Model Validation

- Several reaction classes were updated and *scaled* from small to larger PAHs:
  ***Reference reactions** come from literature or in-house calculations
  ****Scaling factors** account for molecular symmetry or calculated extend kinetics to larger PAHs.

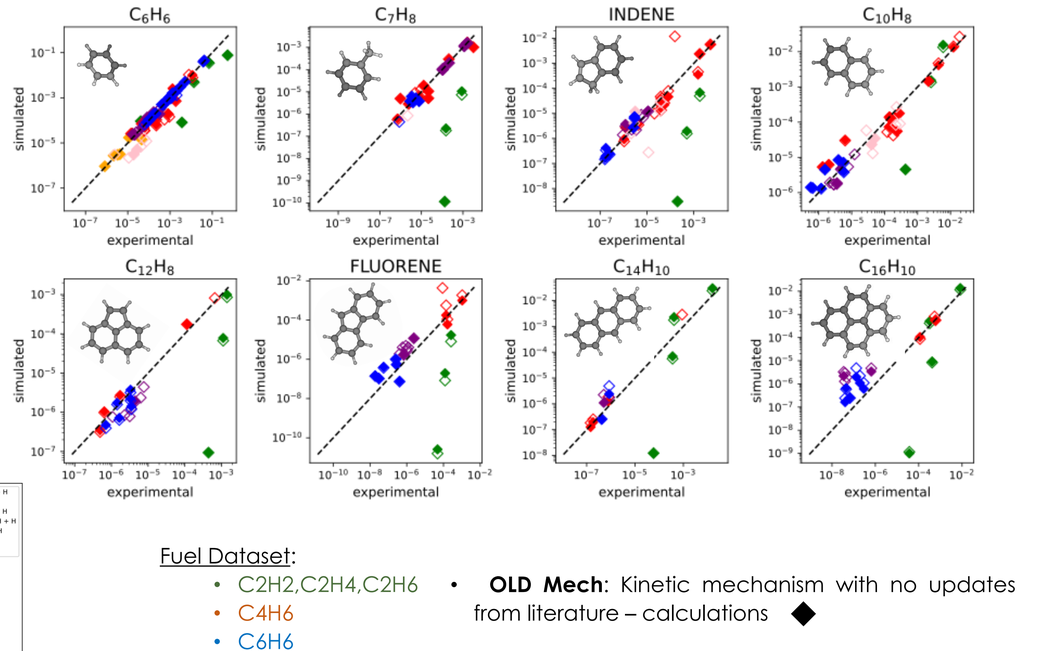
Reaction Class	Reaction	A [mol,cm,s]	n [-]	Ea [cal/mol]	**Scaling
[C5-RSR][ADD_C4.DT-M]	*C4H4+C5H5 [4] C4H4+INDENYL	5.61E+09 3.37E+09	0 0	23680 23680	* 3/5
[A1CH2-RSR][ADD_C4.DT-M]	C4H4+C7H7 C4H4+C10H7CH2	1.12E+09 1.12E+09	0 0	23680 23680	1/5 1/5
[A1,CH2-M][ADD_A1-R]	*C6H5C2H+C6H5 [5] C6H5C2H+C10H7 [6]	4.6E+09 9.2E+09	0 0	4300 4300	* 2
[A1-R][ADD_C2.T-M]	*C6H5+C2H2 C10H7+C2H2	1.3E+13 1.3E+13	0 0	9450 9450	* 1
[C5-RSR][ADD_C4.TT-M]	*C5H5+C4H2 INDENYL+C4H2	5.72E+64 5.72E+64	-14.5 -14.5	58800 58800	* 1
[A1CH2-RSR][ADD_C4.TT-M]	C7H7+C4H2 C10H7CH2+C4H2	1.14E+64 1.14E+64	-14.5 -14.5	58800 58800	1/5 1/5
…	…	…	…	…	…

- **Consistency** across reaction classes is ensured by requiring similar rate parameters for reactions involving species with comparable structures and reactivity.





- **Parity Plots**: impact of implemented kinetics on species formation compared to experimental data for CRECK database.
- Model testing was performed with **OpenSMOKE++** and **SciExpeM**, then post-processed for creating Parity Plots.



Fuel Dataset:

- C2H2,C2H4,C2H6
- C4H6
- C6H6
- C7H8
- C10H7CH3

- **OLD Mech**: Kinetic mechanism with no updates from literature – calculations ◆
- **NEW Mech**: Updated kinetic mechanism from literature - calculations ◇

References:

[1] N. Islam and B. K. Saikia, Chemosphere, vol. 303, 2022.
[2] A. Mebel et al., J. Phys. Chem. A 2019, 123, 9, 1720–1729.
[3] L. Pratali Maffei , PhD Thesis, 2022.
[4] S. Fascella, PhD Thesis, 2004.
[5] J. Hanfeng, Y. Lili, et al., Combustion and Flame, vol. 243, 2022.
[6] Personal communication. Under review.

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