RATE RULE MODELING OF PAH GROWTH

Niccolò Fanari, Luna Pratali Maffei*, Tiziano Faravelli
*luna.pratali@polimi.it

The kinetic modeling of the pyrolysis and combustion of polycyclic aromatic hydrocarbons (PAHs) is crucial to address practical challenges in the current energy transition, such as the evolution of carbonaceous nanoparticles formation that is also interesting for the synthesis of high-value carbon materials [1].
Quantum mechanical calculations are extensively used to develop fundamentally-based kinetic models, however a fully detailed approach is impractical for large PAHs. In this work, we apply a theory-based lumped approach for the definition of reaction classes and rate rules to describe the kinetics of PAHs growth through two relevant reaction classes i.e., the HACA mechanism and the recombination of benzyl-like radicals with propargyl [2]. Based on literature theoretical calculations, our in-house master equation based lumping tool was combined with PSSA to obtain rate constants of global reactions to be implemented in CRECK kinetic model. First, we refined the rate rule definition for the rate constants for 1-ring to 4-ring aromatics. Then, we updated the model with the newly derived rate constants.
The left panel of Fig. 1 depicts the new HACA rate rule adopted with respect to the one previously adopted in the model at 1 atm. The new estimates decreases at high temperatures. Fig. 1 also shows the impact of the new rate rule on the predictions of $C_{10}H_8$ and $C_{12}H_8$ experimental profiles from C_2H_4 pyrolysis [3]. As expected, the $C_{10}H_8$ formation is lower due to the lower rate, while the mole fraction of $C_{12}H_8$ increases due to the slightly higher concentration of its precursor ($C_{10}H_7$).

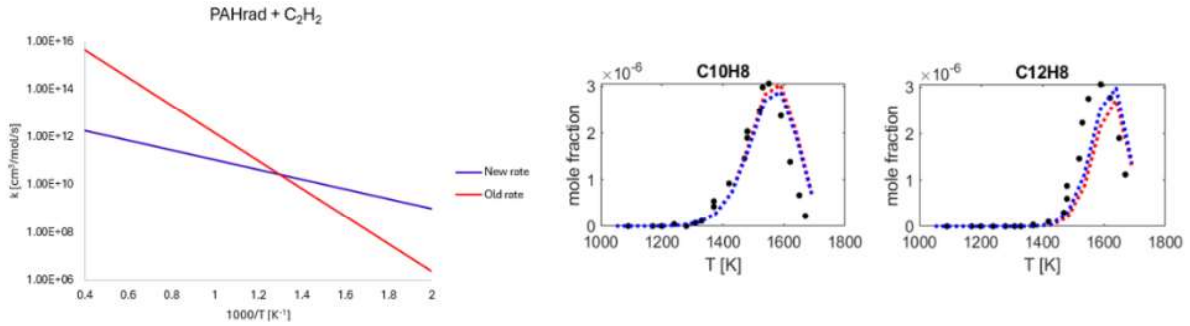

Figure 1: Comparison of the new and old rate rules for the HACA mechanism (left) and associated impact on kinetic simulations of C2H4 pyrolysis (right).

References

[1] N. Islam and B. K. Saikia, Chemosphere, vol. 303, p. 135027,2022
[2] L. Pratali Maffei , PhD thesis, 2022.
[3] W. Sun, A. Hamadi, S. Abid, N. Chaumeix, and A. Comandini,Combust Flame, vol. 220, pp. 257–271, 2020