RATE RULE MODELING OF PAHs GROWTH

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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 becomes impractical for large PAHs. In this work, we adopt a theory-guided lumped approach to define reaction classes and rate rules for describing PAH growth kinetics [2]. Using theoretical data from literature, we coupled our in-house master-equation-based lumping tool with the PSSA to derive rate constants for global reactions, which were then implemented into the CRECK kinetic model. Initially, we refined the rate rule definitions for reactions involving 1-ring to 4-ring aromatics by applying symmetry and analogy considerations. The model was subsequently updated with these newly derived rate constants. Reaction classes are designed to be self-consistent: reactions involving different moieties, such as C_4H_4 additions to C5-RSR and A1CH2-RSR, belong to different classes but show similar reactivity when scaled via symmetry and analogy. Self-consistency also holds within a single class; for instance, $C_6H_5C_2H$ adds to both C_6H_5 and $C_{10}H_7$ within the same class, but theoretical studies show the rate for C_6H_5 is half that of $C_{10}H_7$. Such differences are captured by scaling rules or fitted correlations based on quantum chemical data.

Reaction Class	Reaction	A [mol,cm,s]	n [-]	Ea [cal/mol]	Scaling
[C5-RSR][ADD_C4.DT-M]	*C4H4+C5H5 [3] 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,C2H-M][ADD_A1-R]	*C6H5+C6H5C2H [4] C6H5C2H+C10H7 [5]	4.6E+12 9.2E+12	0 0	4300 4300	* 2

Table 1: Example of reaction classes scaling parameters adopted on the basis of reference reaction (*).

References

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