

Reaction class-based kinetic model development and automated validation: polycyclic aromatic hydrocarbons growth in toluene and methylnaphthalene oxidation

Luna Pratali Maffei^{1*}, Niccolò Fanari¹, Timoteo Dinelli¹, Tiziano Faravelli¹

1 Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Italy

**Corresponding author: luna.pratali@polimi.it*

Highlights

- Reaction classes definition for the kinetics of oxidation and growth of aromatic hydrocarbons
- Rate rules development from 1 to 2-ring aromatics
- New reaction class updated: growth of C7 rings through propargyl addition
- Systematic model validation and analysis: reaction fluxes grouped by class in heat maps

1. Introduction

The kinetic modeling of pyrolysis and oxidation of hydrocarbons aids to tackle practical challenges of the current energy transition such as the selection and formulation of new renewable fuels or the development and optimization of alternative processes for energy production (e.g., hydrocarbon pyrolysis coupled with hydrogen and added-value carbon materials production). Quantum chemical calculations are widely used to construct fundamentally-based kinetic models, however they result in an exponential increase in the model complexity especially for large species such as polycyclic aromatic hydrocarbons (PAHs). Hence, a fully detailed approach is impractical (and inapplicable) for aromatic species with more than 1-2 rings and therefore to e.g., predict the growth of the aromatic species into solid carbon. This calls for a more coarse-grained (lumped) approach to the description of the kinetics, which should however retain physical consistency with the reaction mechanism of small aromatic hydrocarbons. Systematic model development can be achieved through the definition of reaction classes and rate rules from small to large species. Based on the lumping and rate rule procedures developed in CRECK modeling group in the past decades [1, 2], we recently built a tool to lump automatically complex sets of rate constants from quantum chemical calculations [3]. Additionally, we started a thorough reaction classification and rate rule development for aromatic species which is currently missing in the literature. This work presents the systematic reaction class and rate rule approach for the case of toluene and α -methylnaphthalene, chosen as model systems for methylated aromatics. Building on previous work [4], we refine the rate rule definition for the scaling from 1-ring to 2-ring aromatics and we update the model with recent theoretical findings on relevant pathways for aromatics growth [5].

2. Methods

The rationale behind reaction classes definition is shown in Figure 1. A reaction class is defined through the species type, i.e., the functional group participating in the reaction, and the class type, i.e., a global reaction pathway possibly including multiple channels such as the addition of HO₂. Then, reaction types identify individual pathways. The classification is hierarchical: for instance, the reactivity of the aromatic ring A1 is defined by a single class independent of the species it belongs to. Within each class, rate rules allow for the scaling between different species. For instance, the rate constant for an H-abstraction reaction from the aromatic ring can be scaled from toluene to α -methylnaphthalene (AMN) by the symmetry factor and the number of abstracted hydrogen atoms (i.e., 7/10). For other reaction classes, the presence of the lateral aromatic ring in AMN further decreases the rate constant [4]. In this work, additional theoretical calculations for H-abstraction reactions were performed to enhance the accuracy of such scaling parameters. Then, the recently computed benzyl + propargyl growth reaction [5] leading to the formation of naphthalene was lumped [3] and included in the kinetic model for both species. Model testing and analysis were performed with SciExpeM [6], a recently developed data ecosystem that includes thousands of datapoints for ideal and real reactor experiments of various fuel types. Performance analysis was aided by rate of production analysis visualized through heat maps that automatically group together the reaction classes defined in this work.

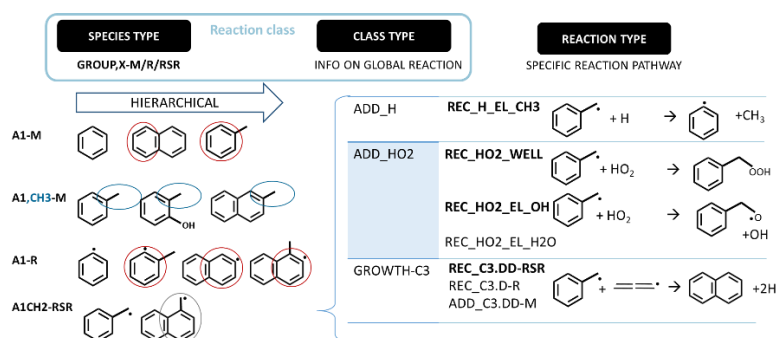


Figure 1. Definition of reaction classes in this work with examples for A1CH2 species type.

3. Results and discussion

Toluene and AMN share very similar reactivity. However, the global oxidation reactivity of the latter is slower (e.g., see the laminar burning velocities displayed in Figure 2a) mostly due to the smaller rate constants for H-abstractions and to the presence of the second aromatic ring that leads to the formation of more stable products. Theoretical calculations revealed substantial decrease in the rate constants for abstraction reactions from AMN by bulky radicals (e.g., OH, O₂, CH₃). The analogy between toluene and AMN is for instance evident in the reaction class-based analysis of Figure 2b (co-pyrolysis with propyne in a batch reactor, 50% conversion). AMN is consumed less by H-abstractions and more by ipso substitutions, producing more CH₃. The benzyl-like radicals formed (A1CH2) also behave similarly, however benzyl also forms C₇H₆ through β-scission, while C₁₀H₇CH₂ recombines with methyl to form naphthalene and C₂H₄, as reflected in the flux of add_ch3 class for A2-amn. In both systems, the formation of the second (A2-tol) and third (A3-amn) aromatic ring is mostly driven by propargyl addition (growth-c3 class).

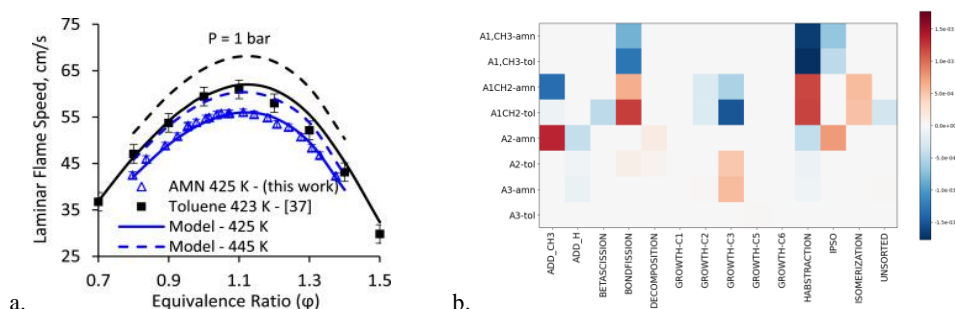


Figure 2. a. Laminar burning velocity of toluene and AMN b. heat maps with the rate of production analysis for the reactants, their benzyl-like radicals, and A2/3 aromatics in the copyrolysis of propyne and toluene (“tol”) and that of propyne and AMN (“amn”). Reaction rates are grouped by class type.

4. Conclusions

This work presents a systematic model development for the kinetics of pyrolysis and oxidation of aromatic hydrocarbons, focusing on the rate rules to derive the kinetics of 2-ring aromatics (α-methylnaphthalene) from monoaromatics (toluene). Scaling factors ensure physical consistency between the two systems. Automated tools for model analysis provide an immediate visualization of the similarities and differences between analogous species in the pyrolysis of toluene and AMN, for instance showing slower consumption by H-abstractions in AMN and similar growth rates through C3 species.

References

- [1] E. Ranzi, M. Dente, A. Goldaniga, G. Bozzano, T. Faravelli, Prog. Energy Combust. Sci. 27 (2001) 99–139.
- [2] E. Ranzi, M. Dente, T. Faravelli, G. Pennati, Combust. Sci. Technol. 95 (1993) 1–50.
- [3] L. Pratali Maffei, M. Pelucchi, C. Cavallotti, A. Bertolino, T. Faravelli, Chem. Eng. J. 422 (2021) 129954.
- [4] A. Nobili, L. Pratali Maffei, M. Pelucchi, et al., Proc. Combust. Inst. 39 (2023) 243–251.
- [5] H. Jin, A. Farooq, Combust. Flame. 253 (2023) 112816.
- [6] E. Ramalli, T. Dinelli, A. Nobili, et al., Chem. Eng. J. 454 (2023) 140149.

Keywords

Kinetic modeling; rate rules; automated validation; toluene