

## II. Abstract

The aim of this work was to determine the kinetic parameters of the hydrogen abstraction reactions (H-abstraction) involved in the initiation of combustion processes. The study was focused mainly on reactions between polycyclic aromatic hydrocarbons (PAHs) and OH<sup>•</sup> radical, as well as those related to aliphatic compounds, for which the H-abstracting agent was either molecular oxygen O<sub>2</sub> or hydroperoxyl radical HO<sub>2</sub><sup>•</sup>.

Calculations of the electronic structures along the entire reaction pathways were used to determine the rate constants of the reference reactions. The recrossing effect, quantum tunneling and explicit treatment of anharmonicity of low-frequency vibrations were also taken into account. Results from these calculations were then applied to extrapolate the reaction rate constant of the reference reaction to other processes within a given class, in accordance with the Reaction-Class Transition State Theory (RC-TST) framework. This method allows for a quick approximation of rate constants with accuracy, which is comparable to the variational versions of TST, with much less computational cost.

Next subject that was considered in this dissertation, was the analysis of the substituent effects in monosubstituted PAHs on the H-abstraction reactions by hydroxyl radical. A set of variables was obtained from electronic structure calculations, as well as thermodynamic and kinetic parameters of each reaction, to define the quantitative structure-activity relationship (QSAR). A multiple linear relationship (MLR) model was constructed, that provides means to estimate reaction rate constants using the attributes of reagents and products of a given reaction.

Results reported here, along with those published previously, provide a coherent description of the early stages of hydrocarbon combustion. They can be used to model real-life combustion processes occurring in internal combustion engines.

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