THEORETICAL AND KINETIC MODELLING STUDY OF THE OXIDATION OF OXYGENATED AROMATIC HYDROCARBONS: REACTION CLASSES AND RATE RULES

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Abstract
Oxygenated aromatics are of interest both as components of bio-oils derived from fast pyrolysis of biomass, and for their potential use as anti-knocking additives. In this work, we propose a list of reaction classes for the pyrolysis and combustion of oxygenated aromatics in order to systematize the development of kinetic mechanisms, along the same line of the traditional approach for n- and iso-alkanes. Based on our list of reaction classes, we are performing ab initio Transition State Theory (TST) based Master Equation (ME) calculations of rate constants of relevant oxygenated aromatic hydrocarbons to derive rate rules. The latest version of the CRECK kinetic model (1905) was updated and validated on a large variety of experimental data for phenol and anisole.

Introduction

Bio-oils represent one of the most suitable near-term alternatives to fossil fuels. Bio-oils are obtained from fast pyrolysis of biomass, producing mostly liquid fuels with some residual char and fuel gas. The use of vegetables and sugar oils for fuel production has raised ethical concerns about its competition with food stocks and its impact on the price of food. Thus, lignin emerged as a promising route for the production of renewable oxygenated fuels. The complex structure of lignin potentially leads to the generation of a variety of oxygenated compounds, including oxygenated aromatics such as anisole, phenol, guaiacol, and catechol. In addition to bio-fuels, oxygenated aromatics are key intermediates in the oxidation of mono-aromatic hydrocarbons (MAHs) (e.g. benzene, toluene, xylene, etc.), which are key components in gasoline, diesel, and jet-fuels surrogate, as well as key building blocks for PAHs kinetics, leading to soot formation. However, despite the relevant role of MAHs in combustion systems, the knowledge of their combustion characteristic is still limited compared to linear fuels. It is therefore necessary to establish a systematic approach to the kinetic modelling of these species [1]. Therefore, we started classifying the kinetic mechanism into reaction classes as the first step to identify most of the possible routes of decomposition/oxidation of the

reactants. Once these classes were identified, we performed ab initio calculations for each class and each molecule using EStokTP in order to obtain rate rules. The updated kinetic model was then validated with kinetic simulations using OpenSMOKE++.

Reaction classes

Reaction classes identify the different paths of decomposition/oxidation of a molecule. The list of the main reaction classes for MAHs oxidation are shown in Table 1, taking phenol as example.

Table 1. Reaction classes for phenol.

Reaction Class	**Example**
Initiation reactions	C6H5OH+M=C6H5O•+H• C6H5OH+M=C6H4OH+H•
H-abstraction reactions	C6H5OH+R•=C6H4OH•+RH C6H5OH+R•=C6H5O•+RH
Ipso-addition reactions	C6H5CH3+OH•=C6H5OH+CH3•
Radical addition/recombination and decomposition reactions via ring opening	C6H5O+OH•=C4H5+CO+HCO
Radical isomerization	C6H5O•=C6H4OH•
Radical decomposition	C6H4OH•=C6H4+OH•
Resonance stabilized recombination	2C6H5O•=DIBZUFR+H2O
Radical recombination	C6H5O•+CH3•=C6H5OCH3
Oxidation reactions	C6H5O•+O2=C6H5CH2O+OH•

Based on the current version of the CRECK kinetic model, about 36 sub-classes were identified. We started to tackle the main reaction classes, namely H-abstractions and ipso-additions.

Computational method

All the kinetic constants were determined using EStokTP [2], a modular computational environment designed to perform electronic structure, transition state theory (TST), and master equation (ME) calculations to obtain automatically a priori predictions of temperature and pressure dependent rate constants. EStokTP relies on commercial softwares such as Gaussian G09 and Molpro 2010 for electronic structure calculations, and MESS for Master Equation simulations. A sketch of the protocol adopted is shown in Figure 1 and explained below. The code requires as input a guess for the geometries of reactants and products, the type of transition state to be searched and the theoretical methods to adopt in each step. After a first optimization of reactants and products, the reaction path is explored by identifying first the transition state and then the intermediate wells, if present. Structures, frequencies and hindered rotors are determined for each state at Level 1, typically using DFT methods. High level single point energies calculations are then

performed. This is typically the limiting step in terms of computational costs. Finally, before evaluating the rate constants, an intrinsic reaction coordinate (IRC) scan is performed both to check the TS and to implement variational TST. Master equation calculations are then performed with MESS so as to obtain temperature and pressure dependent rate constants k(T,P).

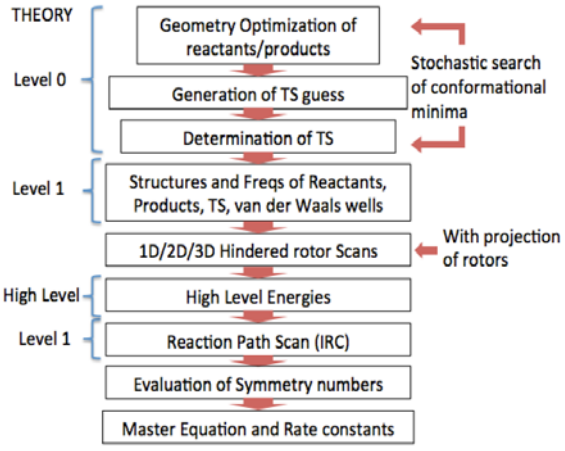

Figure 1. EStokTP program structure.

Calculations of H-abstractions and ipso-additions for phenol, toluene, benzene and anisole are in progress (~100 rate constant calculations in total). Once all the rate constants are evaluated, it will be possible to state general rules so that rate constants for more complex aromatic hydrocarbons (multiple rings, multiple substitutions) may be derived based on analogy, ensuring consistency within the kinetic model.

H-abstraction reactions

H-abstraction reactions are relevant in defining the reactivity of the system and the selectivity to products. Rate constants of the generic reaction R•+ R'H ↔ R'•+ RH depend on the properties of the abstracting radical and on the type of abstracted hydrogen, namely the type of bond and the effect of the neighboring moieties.

The potential energy surface of H-abstraction of phenol on OH group and on the ring is shown, as an example, in Figure 2.

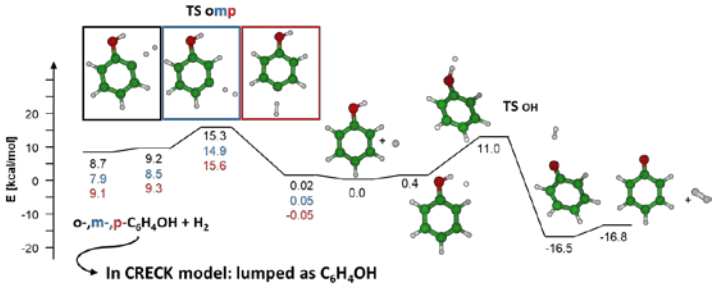

Figure 2. PES of H-abstraction on phenol.

The rate constants obtained for phenol, toluene, anisole and benzene are illustrated in Figure 3. In particular, H-abstraction on OH differ by less than a factor 2 on the hydroxyl moiety and less than a factor 1.3 on the ring side with respect to previous estimates [3,4]. Furthermore, the constants become comparable around 1500 K.

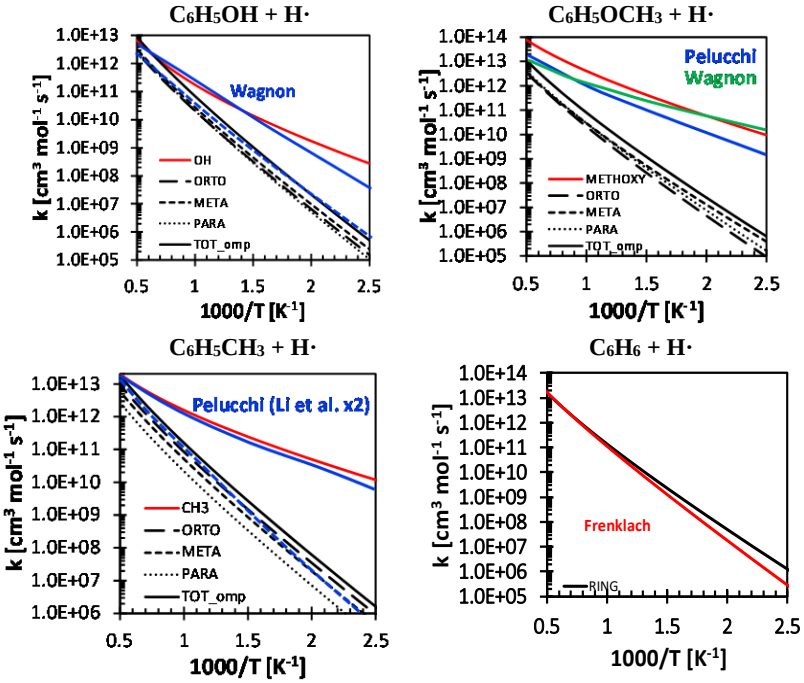

Figure 3. Rate constants dependence on temperature for phenol, toluene, anisole and benzene.

Ipso-addition reactions

An example of dependence on temperature of ipso-addition reactions is reported in Figure 4.

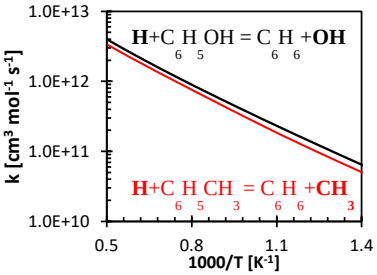

Figure 4. Temperature dependence of ipso-addition reactions.

Ipso-addition reactions of H on phenol and toluene can form benzene via subsequent elimination of OH or CH_3. According to similar steps, catechol can form phenol, and guaiacol can form phenol or anisole.

Kinetic simulations

The experimental mole fractions and the simulated profiles for phenol pyrolysis in nitrogen, (at 1 atm, 1170 K) [5] are shown in Figure 5.

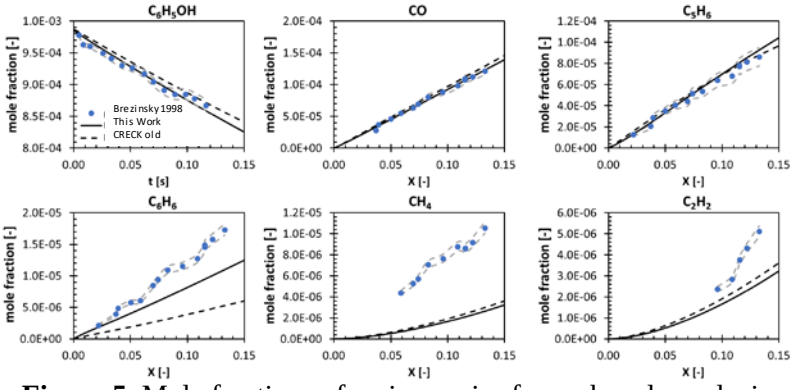

Figure 5. Mole fractions of main species from phenol pyrolysis.

The current model reproduces well the decay of phenol and of the main products, but it still underestimates CH_4, C_2H_2 and C_6H_6. The benzene profiles, nevertheless, presents significant improvement due to updated phenol reactivity. It should be noted that a very limited amount of data is available for phenol pyrolysis and oxidation in the literature, thus preventing wide range validations and further encouraging a theory based approach.

The experimental mole fractions [3] and the simulated profiles for anisole oxidation (φ=0.5, 1 atm) are shown in Figure 6. The improvements brought by the update of the model with the new kinetic parameters is indeed remarkable. However, the concentration of benzene is still underestimated.

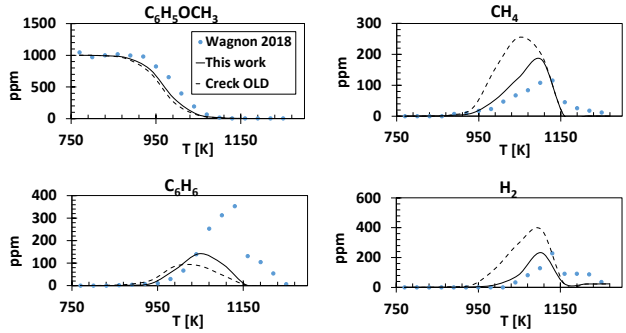

Figure 6. Mole fractions of main species from anisole oxidation in JSR [3].

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Conclusion and further developments

This work discusses the approach to the systematic investigation of MAHs kinetics. The definition of reaction classes together with theoretical calculations allow the determination of rate rules that can be extended to more complex systems such as PAHs, or MAHs with multiple substitutions (e.g. catechol, guaiacol, vanillin, etc.). The improved performances of the CRECK model updated with our new calculations supports the robustness of the proposed approach.

Acknowledgements

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