

A KINETIC MODELING STUDY OF THE OXIDATION AND COMBUSTION OF AROMATIC SPECIES

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Abstract

The aim of this work is to further validate a general and detailed kinetic model on very recent experimental data of the oxidation and combustion of aromatic compounds and also in the case of their blends with n-alkanes, both studied in a jet-stirred reactor. The comparisons between new experimental data and model predictions further confirm the validity and the broad applicability of the kinetic model.

Introduction

Benzene, aromatics and polycyclic aromatic hydrocarbons (PAH) are relevant intermediates of all practical combustion processes, and they are also key precursors to soot formation [1-3].

Because of real and commercial liquid fuels are complex mixtures of several hydrocarbon species, they are often made simpler and represented by surrogates, where aromatics are key components [4].

Therefore, the proper kinetic understanding of the primary steps in the chemistry of aromatic species is also a crucial point for the kinetic modeling of surrogate mixtures. Recently, new experimental data have been presented in literature [5,6].

Mixtures of benzene/toluene with n-decane, proposed as gasoline surrogates, were studied experimentally in a jet-stirred reactor (JSR) at 1 atm, at a constant mean residence time of 2 s, over the temperature range 500-1100 K, and for stoichiometric mixtures. Ethylbenzene oxidation has been performed also in a JSR, in operating conditions similar to the previous ones and at different equivalence ratios Φ . A general and detailed kinetic scheme of oxidation and combustion of aromatic species is here further validated in comparison with the new experimental data related to alkane/aromatic mixtures and to oxidation of ethylbenzene.

Kinetic Mechanism and Numerical Method

The detailed oxidation mechanism of hydrocarbons adopted herein [7], consisting of over 10000 reactions and more than 350 species, was developed based on hierarchical modularity [8]. Thermochemical data for most species were obtained from the CHEMKIN thermodynamic database. For those species whose

thermodynamic data are not available in the literature, the group additive method was used to estimate these properties. All numerical simulations were performed with the OpenSMOKE code, which is an upgraded version and extension of the well-tested DSMOKE code [9].

Comparison of experimental data and model predictions

Two different sets of recent experimental data related to combustion and oxidation of aromatic species are analyzed. The first refers to the oxidation of benzene/toluene mixtures with n-decane in a JSR [5], while the second set of experimental data refers to the oxidation of ethylbenzene [6].

Both these studies yielded a large set of experimental data consisting of concentration vs temperature profiles for reactants, stable intermediates and final products. These experiments constitute a further set of data very useful for the validation of the overall kinetic model.

1. Mixtures of benzene/toluene with n-decane[5]

The oxidation of benzene/toluene mixtures were studied experimentally in a JSR at 1 atm, at constant mean residence time of 2 s, over the temperature range 500-1100 K, and for stoichiometric mixtures.

Figure 1 and 2 show the main characteristics of the conversion behavior of the 75/25 mixtures of benzene and toluene with n-decane, respectively.

In these experiments, it is relevant to observe the major reactivity of toluene in respect of benzene. The difference of behavior between the two aromatic reactants is significant and related to the formation of the products below 800 K. Benzene in the mixture does not express low temperature reactivity, while the predicted n-decane conversion correctly exhibits the experimental Negative Temperature Coefficient (NTC) behavior. On the other hand, the model slightly underestimates the reactivity of toluene and overestimates the one of n-decane in the temperature range 700-800 K.

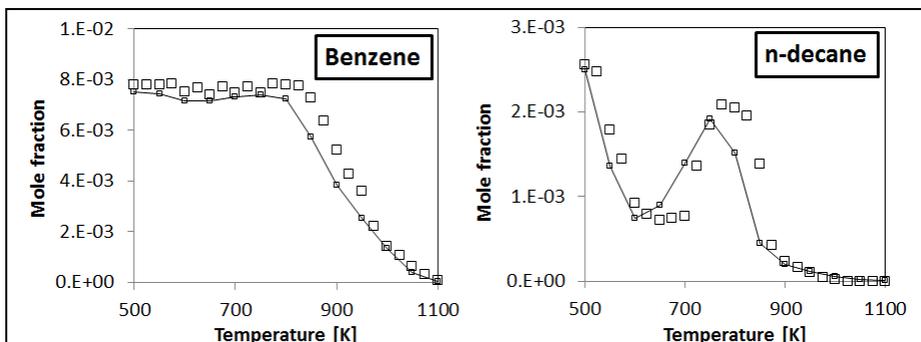


Figure 1. Main characteristics of the conversion behavior of the 75/25 mixtures of benzene/n-decane.

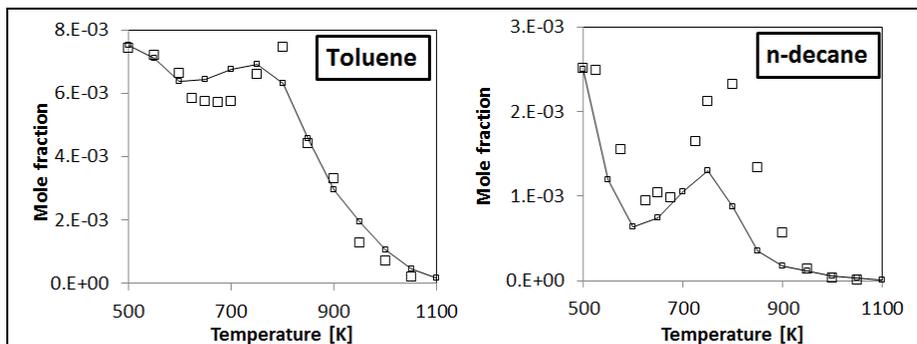


Figure 2. Main characteristics of the conversion behavior of the 75/25 mixtures of toluene/n-decane.

Figure 3 shows the sensitivity analysis performed at intermediate temperature for the mixture toluene/n-decane. The most sensitive reactions are the H-abstraction reactions on n-decane, where OH accounts for 86% of the total reactions. Phenoxy and benzyl radicals significantly sustain the radical pool. The recombination reaction:



transforms the stable benzyl and hydroperoxy radicals in the very reactive phenyl and OH radicals.

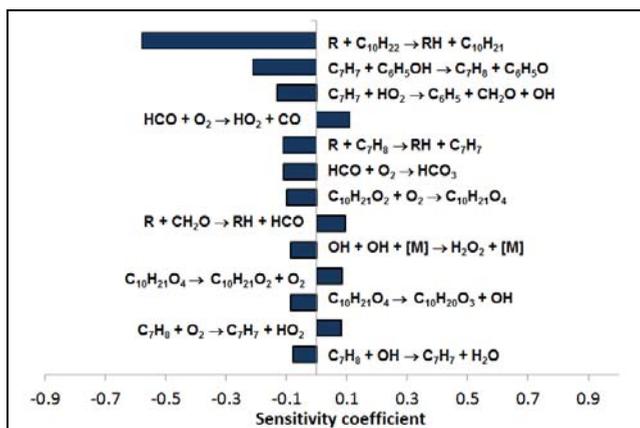


Figure 3. Sensitivity analysis of toluene/n-decane mixture at 750 K.

Figure 4 shows respectively in the panels A and B the formation of phenol and cresol during the oxidation of mixtures of benzene/toluene with n-decane. The phenol is underestimated, while the cresol yields are accurately predicted in both mixtures.

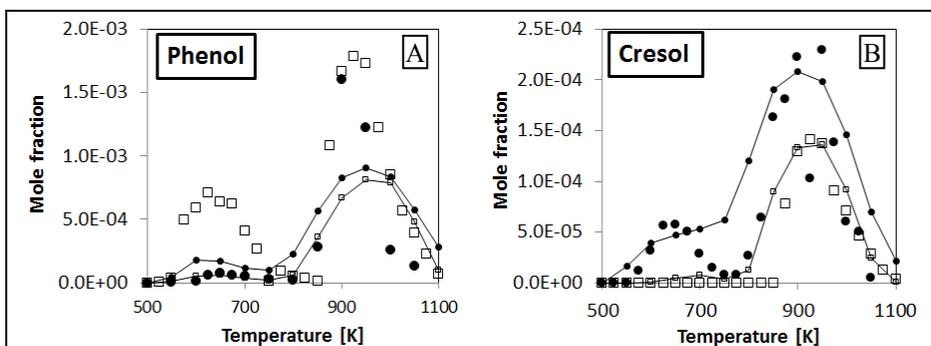


Figure 4. Products formation of phenol (Panel A) and cresol (Panel B) in benzene/n-decane mixture (exp: open square, model: line with open square) and toluene/n-decane mixture (exp: solid circles, model: line with solid circles).

2. Oxidation of ethylbenzene[6]

The oxidation of ethylbenzene was studied experimentally in a JSR at quasi-atmospheric pressure (800 Torr), at constant mean residence time of 2 s, over the temperature range 750-1100 K, and at three equivalence ratios Φ (0.25, 1 and 2).

Figure 5 shows the conversion of ethylbenzene in lean, stoichiometric and rich conditions. The experimental and predicted ethylbenzene behavior is similar for all the three mixtures. The model overestimates the reactivity of ethylbenzene mainly in the temperature range of 800-900 K, while there is a slight underprediction at higher temperatures.

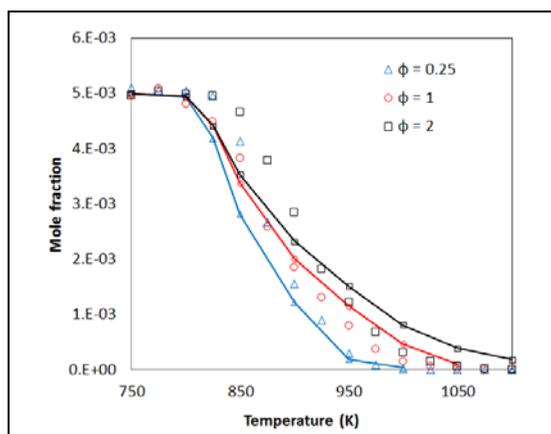


Figure 5. Ethylbenzene conversion at three different equivalence ratio ($\Phi = 0.25$: blue triangles and line; $\Phi = 1$: red circles and line; $\Phi = 2$: black squares and line).

Figure 6 represents the rate of production analysis at 850 K, for a stoichiometric mixture and in the conditions corresponding to a 38% conversion of ethylbenzene.

The decomposition of ethylbenzene is dominated by the H-abstraction reactions, which lead to the primary formation of styrene, ethylene and phenyl radical. Moreover, an important role is assumed by the dealkylation reactions by radicals H, OH and CH₃ to form respectively benzene, phenol and toluene.

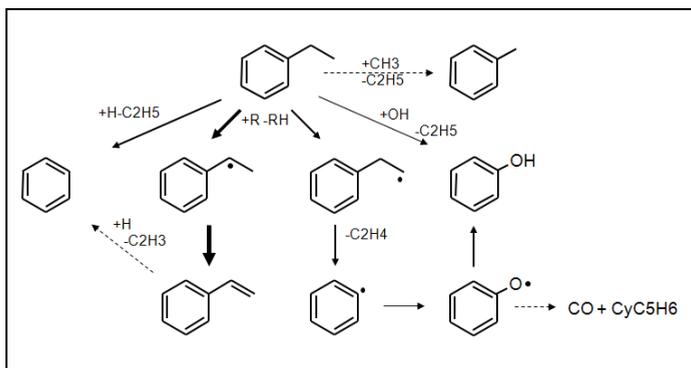


Figure 6. Flow rate analysis of ethylbenzene oxidation in a JSR at 850 K and 1 atm, for a stoichiometric mixture at 38% conversion.

Figure 7 presents a comparison of experimental and predicted yields at $\Phi=1$. Not only the main primary products, such as styrene and ethylene, but also the minor and secondary ones, as benzene, toluene, phenol and cresol, are properly predicted.

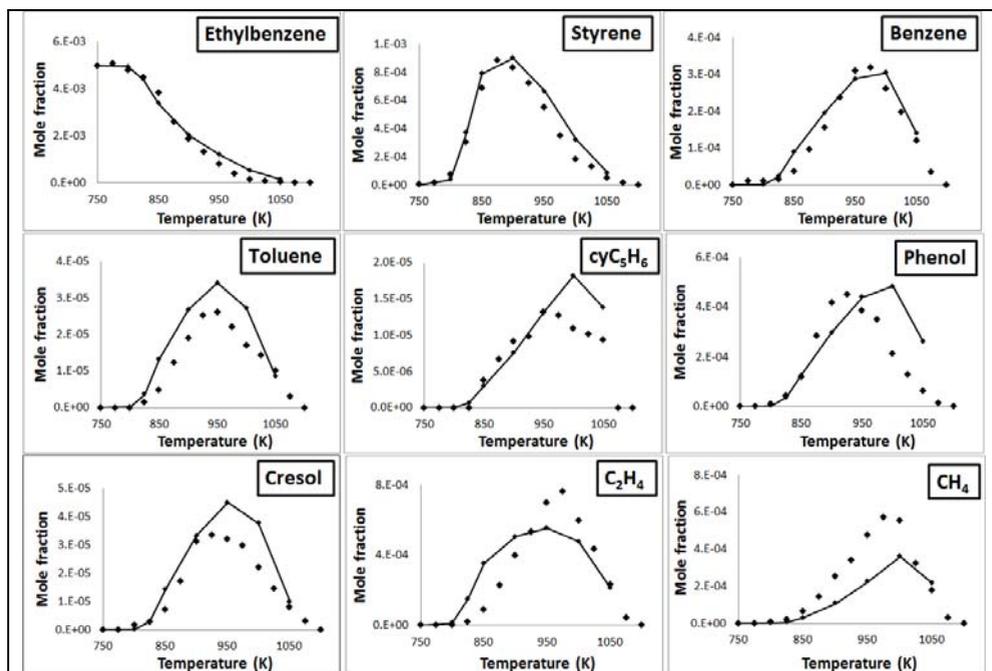


Figure 7. Mole fractions of the major products vs. temperature at $\Phi=1$.

Conclusions

The proposed kinetic mechanism represents fairly well the experimental measurements of the oxidation of alkane/aromatic mixtures and ethylbenzene under the reported conditions.

The refined kinetics of aromatics oxidation and combustion further confirms the reliability of the model and allows the successive extension of the scheme towards heavier aromatic fuels, polycyclic aromatic hydrocarbons and soot growing processes.

Acknowledgements

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