

Uncertainty Assessment of Kinetic Model of Cyclohexane Oxidation, including PAH formation.

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Abstract

A reaction mechanism of cyclohexane is developed to study its oxidation at both low and high temperatures, including PAH precursor's routes. The mechanism is based on the previous works of the authors. Improvement is due to the addition of cyclohexene low temperature oxidation scheme, application of new rate parameters values, derived as the result of uncertainty analyses, specifically for sensitive reactions, and implementing new optimized sub models of acetylene and syngas for smaller species chemistry. Sensitivity analysis was performed on certain experimental targets in order to identify key routes. Uncertainty quantification is based on the available literature data and it was performed with the aid of an in house developed tool. The mechanism was successfully validated on the ignition delay data from rapid compression machines (RCM) and shock tube experiments, as well as laminar flame speed data. The concentration profiles of the soot precursor species from burner-stabilized premixed flames experiments with different mixture ratios and at different pressures and temperatures were also well reproduced by current model.

Introduction

Performance and in particular emissions of any combustion devices are strongly dependent on the fuel and their underlying chemistry. Conventional fuels, such as kerosene are a complex mixture of several individual species, but they can be classified into four hydrocarbon families, namely: normal and iso-paraffins, naphthenes (cyclic paraffins) and aromatics. Cycloalkanes (naphthenes) due to their cyclic structures, are an important chemical class of hydrocarbons found in commercial fuels mixtures, for instance by up to 35% in diesel, and around 20% in conventional kerosene formula, and about 10% in gasoline. This affects the ignition quality of the fuel, besides soot emission level. Therefore, kinetic investigation of cyclohexane (cyC₆H₁₂) as the simplest naphthene molecule has a great importance describing the oxidation behavior of conventional fuels, as well as understanding the effective paths of combustion emissions. Despite of the existing investigations on cyclohexane oxidation, the published reaction classes and their reference kinetic parameters from different kinetic models and available literature data show significant discrepancies in particular cases. As it is found, the uncertainty of reaction rate coefficients, for certain routes exceed more than 100%. In the present work, the former research of the authors [1] has been modified based on the outcome of the kinetic uncertainty analysis for each reaction class. Also the current sun-model contains extension of the secondary ignition of cyclohexene (cyC₆H₁₀) scheme in lower temperature.

Kinetic model

The current kinetic mechanism implements C₀-C₃ chemistry from the recent researches of Slavinskaya et al. [2-4]. The PAH formation sub-model from Chernov et al. [5] has been added to this reaction mechanism, to investigate sooting behavior of cyclohexane.

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The developed sub-model, similar to former study, is assumed to have two main different chemistry schemes, namely high and low temperature regimes. The cyclohexane high temperature oxidation proceeds through unimolecular initiation, H-atom abstraction by active radicals, β -scission decomposition and ring-opening steps, and cascading dehydrogenations. Whereas the low temperature scheme is mainly controlled by initiated cycloalkyl radical addition reaction with O_2 , isomerization of cyclic peroxy to hydroperoxy radical, decomposition of $cyC_6H_{10}OOH$ radicals via ring opening to linear and smaller species, or to form cyclohexanone and bicyclic ethers (Fig.1).

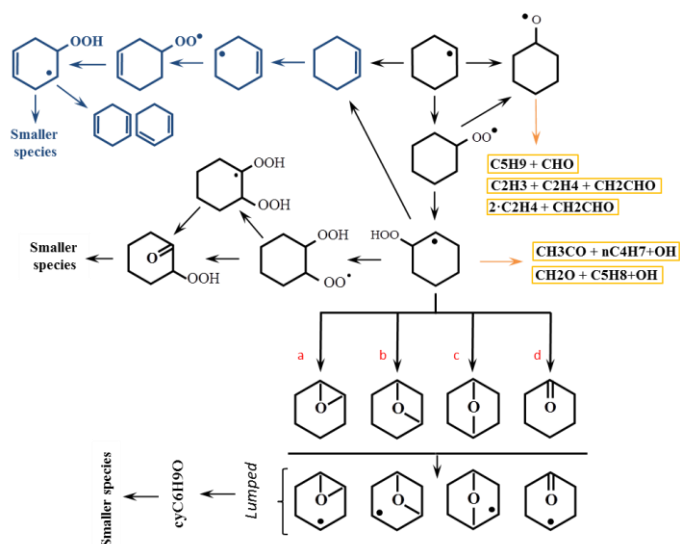


Fig. 2 Principal scheme of the low temperature oxidation of cyC_6H_{12} .

The new scheme contains certain number of new paths. For number of reactions, rate parameters coefficients have been justified through the approximation of literature data so that the resulted rate values over temperature remain in the feasible area, i.e. uncertainty intervals, and also show the better overall integrity with the entire mechanism. The approximation proceeds through:

- the review and justification of main reactions of the cyclohexane oxidation sub-models;
- the non-linear least squares method and its numeric realization FUMILI [6] to estimate the optimum values (overage rate values);
- evaluation of the uncertainty upper f_u and lower f_l boundaries:

$$Eq.1 \quad f_u(T) = \log \left[\frac{k_{upper}(T)}{k_0(T)} \right], f_l(T) = \log \left[\frac{k_0(T)}{k_{low}(T)} \right]$$

An in house developed tool, written by DLR (German Aerospace Center) at Stuttgart, named as “Reac-UQ”, was used for the mean of quantification of uncertainty intervals. Fig.2 represents an example of uncertainty analysis for one of the reactions of low temperature regime.

Results and discussions

A. Ignition-delay-time

The simulation of experimental data for ignition delay times of Lemaire et al.[12] and Daley et al. [13] in various temperature range, pressure and stoichiometric condition are shown in Fig. 3a,b.

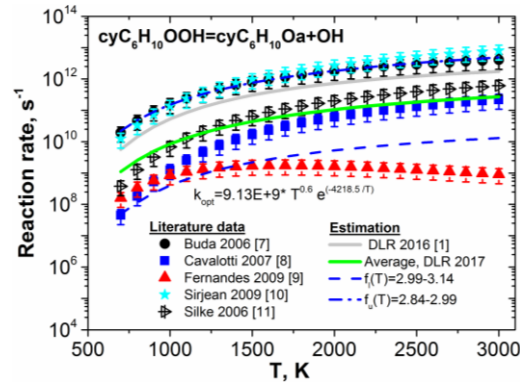


Fig. 2 Uncertainty estimation and analysis of reaction rate vs. temperature, based on the available literature data for the reaction $cyC_6H_{10}OOH = cyC_6H_{10}Oa + OH$

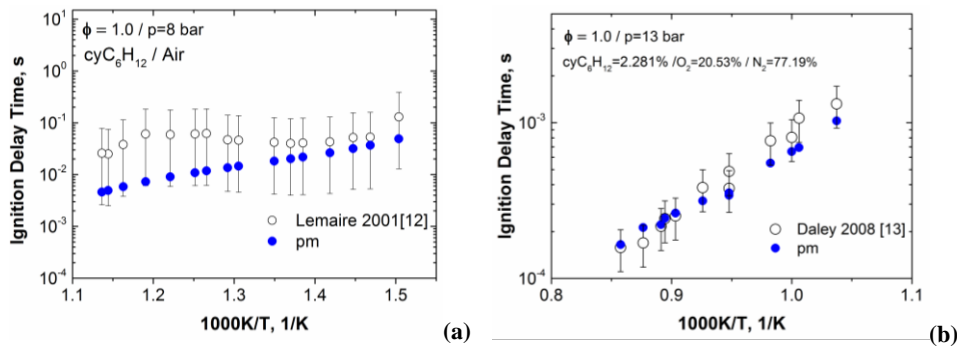


Fig. 3 Cyclohexane ignition delay time from: a) RCM experiments [12] for $\phi=1$, $p=8$ atm and b) shock-tube experiment [13] at $\phi=1$ and $p=13$ atm. Closed symbols: Simulations, open symbols: experimental data.

B. Ignition-delay-time

Results of modeling the mole fraction profiles of certain important PAH precursors, namely CH_4 , C_2H_2 , C_2H_4 , C_4H_6 and C_6H_6 (benzene) from a premixed fuel-rich $\phi=2.0$ flame of Ciajolo et al. [14] at $p=1$ atm are shown in Fig.4a-c and also compared with last previous work [1]. They show a good overall consistency between prediction and observation, and shows improvement, predicting formation of benzene molecule, known as primary aromatic structure.

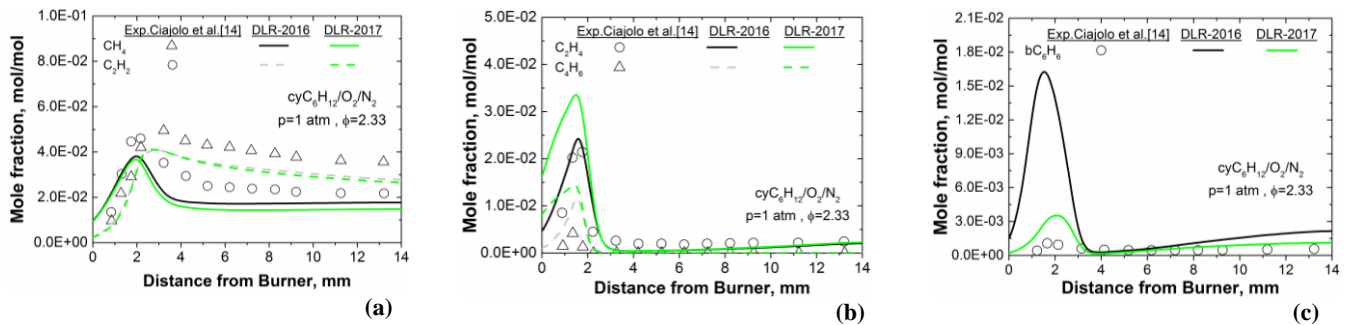


Fig.4 Simulated and experimental [14] concentration profiles of the soot precursors species. Symbols are experiments, lines for predicted profiles by two models.

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