

A Skeletal Mechanism for the Oxidation of *n*-Heptane / *iso*-Octane generated by the Chemistry Guided Reduction Approach

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1 Introduction

Combustion of fossil fuels is the major human energy source, a status that will last at least for the near and mid-term future. However, the fossil hydrocarbon supplies will diminish and therefore a movement towards the generation of renewable energy [1-3] is under way to help meet the increased global energy needs. Detailed chemical reaction mechanisms have proven to be powerful tools to model and analyse the chemical process of fuel degradation. Such mechanisms help to deepen the understanding of the chemical part of the combustion process; they provide information about ways to improve fuel qualities and are practical modelling tools in engineering research. However, the direct incorporation of chemical reaction mechanisms in simulations with complex reactor models is limited by the large number of species and elementary steps that are introduced with detailed reaction mechanisms, especially for liquid reference combustibles such as *n*-heptane and *iso*-octane that are commonly used to model the ignitability of practical fuels. Considering that future model fuels will become multi component mixtures both comprehensive and compact models are needed for the pure components to achieve predictive power for combustion characteristics of mixtures at affordable computational costs.

n-Heptane and *iso*-octane are PRF (Primary Reference Fuel) components used for engine knock rating of spark-ignition engines. They will be standard components also in future model fuel blends that additionally contain aromatic fuels such as toluene [4].

Recently, we presented the chemistry guided reduction (CGR) approach [5], which aims at a mechanism reduction to the skeletal level conserving the predictive power of the detailed starting mechanism. CGR is based on chemical lumping and species removal with the necessity analysis method, a combined reaction flow and sensitivity analysis [6]. A defined sequence of simplification steps, consisting of the compilation of a compact detailed chemical model, the application of linear chemical lumping and finally species removal based on species necessity values allows a significantly increased degree of reduction compared to the simple application of the necessity analysis or similar species or reaction removal methods. The lumping approach we used is discussed in detail in [5,7]. For *n*-heptane we derived a skeleton model by CGR, which consists of 110 species, 1174 forward and backward reactions and is validated against the full range of combustion conditions. In the present study we show that the lumping rules derived for *n*-heptane can be applied to the branched peroxy radical isomers formed by *iso*-octane oxidation with minor modifications. Moreover, a comprehensive skeletal level of reduction can be achieved by applying the necessity analysis analogously [5].

2 Chemical Model

The *n*-heptane/*iso*-octane mechanism is based on the baseline chemistry of Hoyermann et al. [8], which includes benzene build up and destruction reactions of Wang and Frenklach [9] and detailed oxidation mechanisms for *n*-heptane and *iso*-octane from the Lawrence Livermore National Laboratory (LLNL) [10,11].

In the first step a detailed *n*-heptane/*iso*-octane mechanism was compiled using the detailed *n*-heptane mechanism of Ahmed et al. [7] and the *iso*-octane oxidation mechanism of Curran et al. [11]. The detailed mechanism consists of 390 species and 3521 irreversible reactions, which is a compact size, compared to the LLNL models. According to the CGR method such compact mechanisms are suitable starting points for the next reduction stage.

In the second step chemical lumping was applied to the *n*-heptyl, *n*-heptylperoxy and -oxy radicals as described in [5,7]. For *iso*-octyl we applied a more detailed lumping due to presence of tertiary C-atoms. The 4 *n*-heptyl radicals and heptyl-peroxy species were lumped to one species in case of *n*-heptane. For *iso*-octyl we introduced three lumped species with primary, secondary or tertiary C-atoms at the radical position. For the isomeric species formed by internal H-atom abstraction we lumped species with a function at the primary site (radical or OOH group) separately from the other isomers. Those species were lumped in the same manner as described in [5]. The remaining 2 isomers with the functionality on the inner C-atoms of the main chain are not lumped and their isomerisation and subsequent decomposition reactions are described in detail.

In the third stage according to the CGR approach a skeletal mechanism was generated by the application of the necessity analysis to the lumped mechanism. First the species were removed, which have been identified to be redundant for *n*-heptane oxidation in the preceding study [5]. In this work we derived and discussed criteria for maximum and integrated necessity values that were applied to discriminate the redundant species. Only slightly modified criteria were used in the present study to reduce the lumped *iso*-octane oxidation model to the skeletal level. A detailed discussion of the procedure is given in [5]. The derived skeletal mechanism consists of 200 species and 1800 irreversible reactions. Only one lumped *iso*-octyl-hydroperoxy radical became redundant in the necessity analysis, because a comprehensive description of the low temperature *iso*-octane oxidation necessitates a rather high level of detail. This is similar to our findings and the results of Kazakov et al. for *n*-heptane reduction being discussed in [5,14].

3 Mechanism Validation

Shock Tubes

The autoignition of *iso*-octane and *n*-heptane/*iso*-octane mixtures can be studied for high and intermediate temperatures and different pressures in shock tube experiments. We have used the *n*-

heptane/*iso*-octane mechanism assuming constant-volume and homogeneous adiabatic conditions behind the reflected shock wave to simulate high [15,16] and intermediate [12] temperature shock tube experiments. The predicted ignition delay time was determined from the CH-profile for [15,16] and from the pressure profiles for [12]. The modelling results are compared in Fig. 1 with the experimental data. For all conditions we found a good agreement. Moreover, we can state that only minor deviations are found between the skeletal and the detailed models.

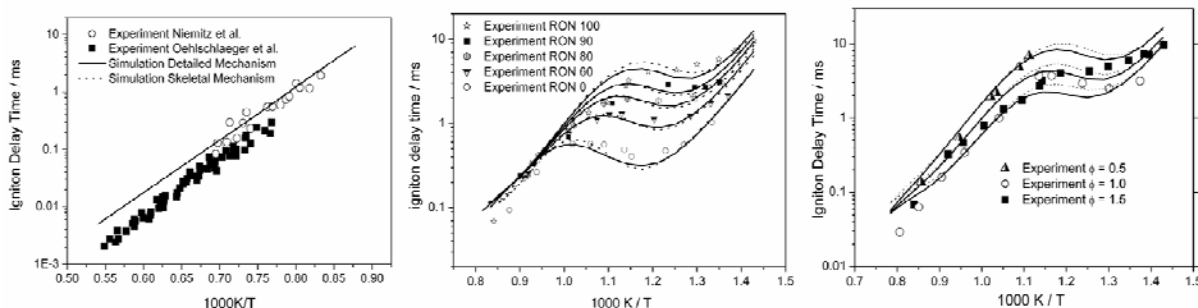


Figure 1. Experimental (symbols) and predicted (black line detailed, dotted line skeletal mechanism) ignition delays. Left Panel: High temperature ignition, all data normalized to 1 atm, $\phi = 1$, and 21% O_2 . Circles: Niemitz et al. [16]; Squares Oehlschlaeger et al. [15]. Middel panel: Ignition delay times in shock tube experiments [12] at 40 bar, dependence on the *n*-heptane/*iso*-octane mixture composition. Right panel: Dependence on mixture strength for *iso*-octane [12].

Jet Stirred Reactor

In Fig. 2 the results of the model predictions using the detailed and the skeletal mechanisms are shown together with the experimental results for the jet stirred reactor oxidation of *iso*-octane [17]. A reasonable agreement between simulations and experiment is found.

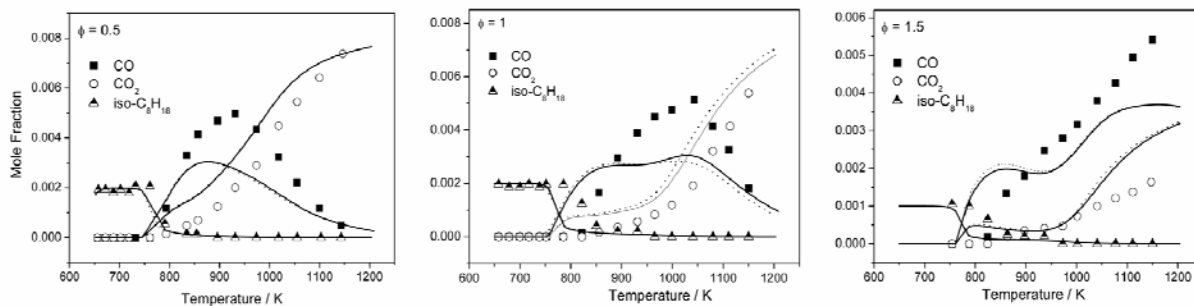


Figure 2. Oxidation of 0.1% *iso*-octane in O_2/N_2 in a jet stirred reactor at $p = 10$ bar, for $\phi = 0.5$ (left panel), $\phi = 1$ (middle panel), and $\phi = 1.5$ (right panel). Experimental results (Ref. 17, symbols) versus model predictions (black lines detailed, dotted skeletal mechanism).

Flames

The results of the model predictions using the detailed and the skeletal mechanisms are shown together with the experimental results in Fig. 3. We see that simulated flame speeds show nice agreement with the experimental data over the whole fuel-air-mixture range.

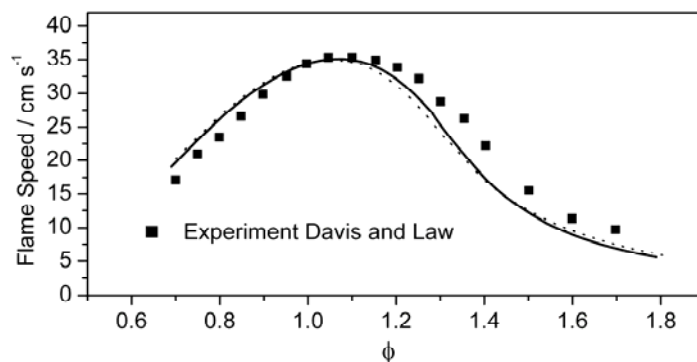


Figure 3. Numerically and experimentally determined laminar flame speeds, S_u^0 , for iso-octane/air mixtures. $p = 1$ bar, $T_u = 298$ K. Lines: Calculations performed with the detailed (black) and skeletal (dotted) mechanisms. Experiments (squares) are performed by Davis and Law [18].

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