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Combined kinetic modelling and experimental study of a fuel rich, premixed n-heptane flame

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Abstract

In this collaborative work a reaction scheme for n-heptane oxidation and emission formation was developed based on new experimental data obtained in a premixed fuel rich flame. It is based on our previous work on the flame chemistry of butane and butene isomers and follows the approach to continuously extend and improve an oxidation scheme by focusing on highly resolved species profiles in flames and include other combustion properties in the mechanism validation such as ignition delay time or laminar flame speeds. By this approach a comprehensive reaction scheme is provided that can be used in applications covering a wide parameter range, e.g. internal combustion engines.

Introduction

World's transportation is still driven by liquid fuels, this status will not be changed in near and mid-term future. A growing percentage of biofuels is mixed into crude oil based fuels. This is leading to formation of different types hazardous species. To understand and model new formation pathways, it is necessary to understand the formation of pollutants in pure hydrocarbon fuels.

The present study is focused on quantitative species measurements of a rich premixed burner stabilized low pressure flame, for which more species were quantified as in similar studies before [1] [2]. As in earlier works of our group [3] [4] the new experimental results are used to improve and extend an existing kinetic model. The final model consists of 350 species and 3783 reactions (forward and backward directions considered as individual reactions).

Approach

Experiments were carried out at Bielefeld University with a set-up described earlier in e.g. [4], [5]. In brief, the instrument provides a two-stage Wiley-McLaren ion source where ionization is operated by electron ionization. It is coupled to a reflectron time-of-flight (TOF) mass spectrometer which enables a mass resolution of $m/\Delta m$=4000. Thus,

determination of the elemental composition of C/H/O species by their exact mass is possible in the relevant mass range. A laminar flat flame of *n*-heptane with a composition of *n*-heptane/oxygen/argon (10.0 mol%/65.0 mol%/25.0 mol%) was investigated at 40.0 mbar. The resulting stoichiometry is $\phi = 1.69$, and the respective cold gas velocity was 65.7 cm/s at 300 K, equivalent to a total mass flux of 8.312 g/min. The flame was stabilized on a home-built flat-flame burner (McKenna-type) which features a sintered and water cooled bronze matrix with a diameter of 64.0 mm. The data quantification method was adapted from previous work [4], [5]. A detailed description of the procedure used in the data evaluation is given in the supplement of [4]. The preciseness is about 20-30% for directly calibrated species, but factors of 2-4 uncertainty are possible if cross sections must be estimated.

Temperature profiles were determined and used as input parameters for the kinetic modeling, recognizing that MBMS is an invasive technique and that the flow and temperature fields of the laminar flame are perturbed by the sampling probe.

The reaction scheme developed in this work is based on series of publications of our group in the past: A broadly validated reaction scheme for C1-C4 chemistry [6] which was extended for the combustion chemistry of toluene [7] for butane isomers [3] and for butene isomers [4].

The detailed mechanism for n-heptane oxidation follows the one published by our group in 2007 [8], which is based on rules described by Curran [9]. The main updates on the n-heptane sub mechanism are the following: First of all we consider more possible decomposition products due to the extended base chemistry. The addition of radical species to alkenes was implemented as developed in our previous work [4]. In contrast to the latter study we treat the H atom abstraction from formed alkenes similar to the H atom abstraction from the fuel molecules itself. The decomposition of alkenyl radicals is done more detailed as suggest by Mehl et al. [10]. The initial thermal decomposition reactions were revised and we do follow the suggestions of the work of El Bakali et al. [11]. Another major change concerns the decomposition of different fuel radicals. A literature review was performed and a new set of reaction rates is suggested.

Results
The developed reaction scheme was validated against the measured new species concentration profiles of the studied n-heptane flame and many other experimental targets from earlier work. The study is work in progress and figures show therefore preliminary results. The experimental temperature profile was used as input for modelling the flames. It was found that the calculated temperature profile predicts a peak temperature close to the measured value. The model shows a good agreement for all major species (Figure 1a) and a most of the measured intermediates such as C_3H_4 (Figure 2a), C_4H_6 (Figure 2b) and aromatic species. A good agreement with measured ignition delay times (Figure 3a) and speciation in jet stirred reactors (Figure 3b) was found.
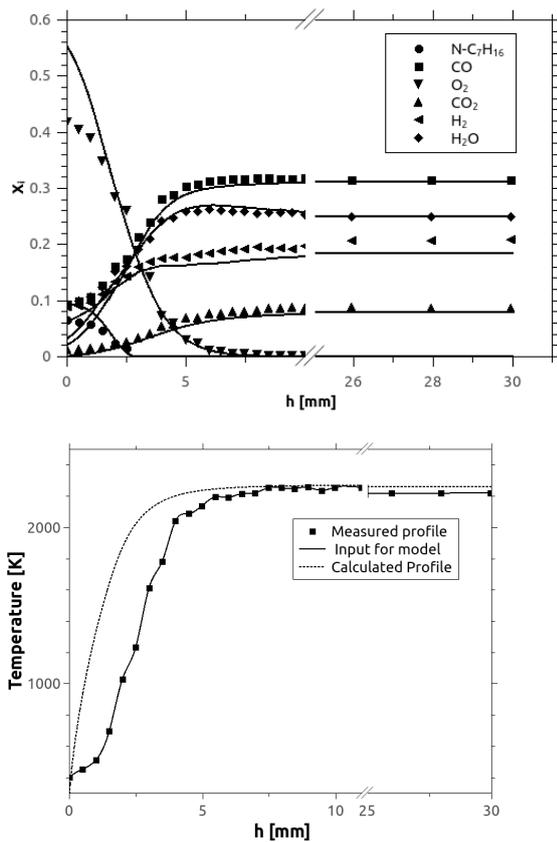
Figure 1a (left): measured (dots) profiles for the major species and the model prediction.
1b (right): measured temperature profile (dots), calculated temperature profile (dotted line) and the profile used as model input (solid line).
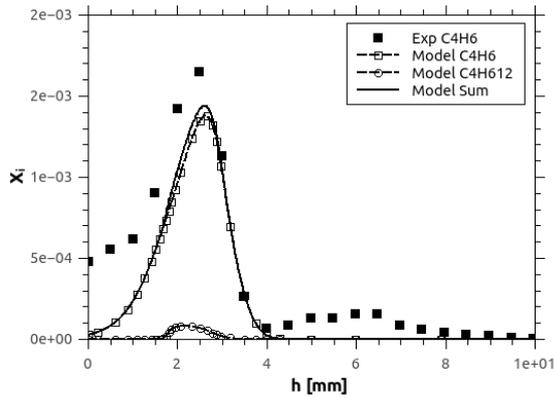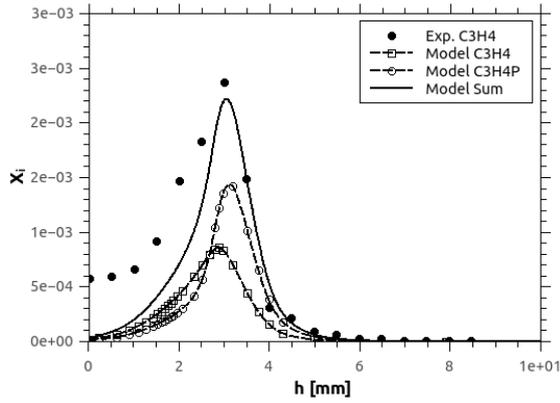
Figure 2a (left): measured profile for C_3H_4 (dots) and the model prediction for the two isomers C_3H_4 and C_3H_4P (dotted line) and there sum (solid line).
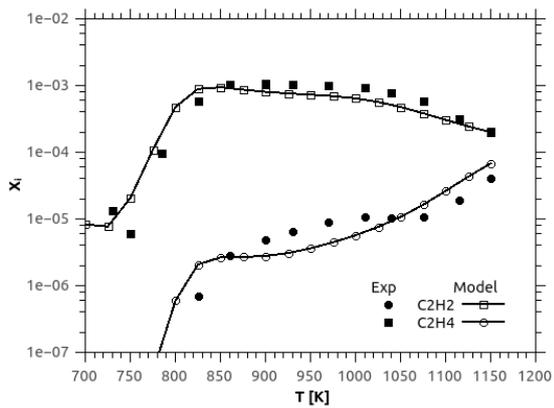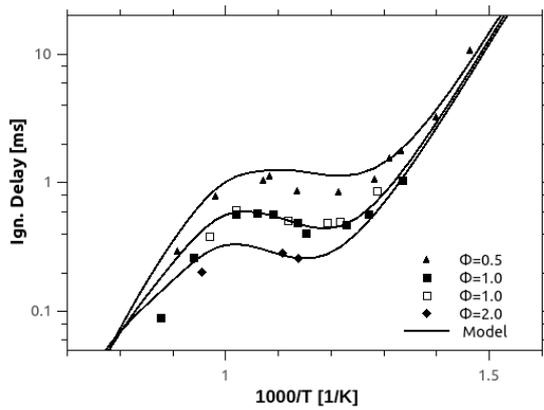
Figure 3a (left): Ignition delay times for n-heptane/air in a shock tube at 40 bar. Experiments: solid symbols for Φ=0.5 and 1.0 [Fieweger 1997], for 2.0 [Ciezki 1993], open symbols [Heufer 2010]; solid line corresponds to model prediction. Figure 3b (right): Experimental species profiles and model prediction in a jet stirred reactor at 10atm, fuel / equivalence ratio = 1.5 [Dagaut 1993].

Conclusion

In the present work new experimental data for a burner stabilized n-heptane flame were obtained, containing several oxygenated species, and used to improve existing reaction schemes developed in previous works. The developed model is consistent with previous works on the flame chemistry of other fuels and was validated against a wide range of experiments. The measured species profiles were further used to investigate the different decomposition pathways of fuel radicals. The developed reaction scheme shows a good prediction of the flame structure and is able to predict at the same time other combustion features such as ignition delay times or speciation in jet stirred reactors.

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