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Comprehensive kinetic modeling and experimental study of a fuel-rich, premixed *n*-heptane flame

Lars Seidel^b, Kai Moshhammer^{a,1}, Xiaoxiao Wang^b, Thomas Zeuch^c, Katharina Kohse-Höinghaus^{a,*}, Fabian Mauss^{b,*}

^a Department of Chemistry, Bielefeld University, Universitätsstraße 25, D-33615 Bielefeld, Germany

^b Thermodynamics and Thermal Process Engineering, Brandenburg University of Technology, Siemens-Halske-Ring 8, D-03046 Cottbus, Germany

^c Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstraße 6, D-37077 Göttingen, Germany

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ABSTRACT

An existing comprehensive kinetic hydrocarbon oxidation model has been augmented and revised for a detailed analysis of *n*-heptane flame chemistry. The analysis was enabled by experiments in which the detailed species composition in a fuel-rich flat premixed ($\phi = 1.69$) *n*-heptane flame at 40 mbar has been studied by flame-sampling molecular-beam mass spectrometry using electron impact ionization. Mole fraction profiles of more than 80 different species have been measured and compared against the new detailed kinetic model consisting of 349 species and 3686 elementary reactions. For all major products and most of the minor intermediates, a good agreement of the modeling results with the experimentally-observed mole fraction profiles has been found. The presence of low- and intermediate-temperature chemistry close to the burner surface was consistently observed in the experiment and the simulation. With the same kinetic model, *n*-heptane auto-ignition timing, flame speeds and species composition in a jet-stirred reactor have been successfully simulated for a broad range of temperatures (500–2000 K) and pressures (1–40 bar). The comprehensive nature and wide applicability of the new model were further demonstrated by the examination of various target experiments for other C₁ to C₇ fuels.

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1. Introduction

World's transportation is still driven by liquid fuels. Despite efforts to promote electric vehicles, this status is not likely to be changed in the near or mid-term future. A growing percentage of biofuels in blends from crude-oil-based fuels is one approach to reduce the fossil fuel dependence. However, this may lead to emission of different types of biofuel-specific hazardous species [1] such as aldehydes. To understand and model their formation pathways, it is necessary to understand the formation of pollutants in pure hydrocarbon fuels first.

n-Heptane is a major component in reference and surrogate fuels for internal combustion engines. The primary reference fuel (PRF) for octane rating is defined as a blend of *n*-heptane and *iso*-octane. Pure *n*-heptane is the simplest surrogate for diesel fuels. The surrogate ETRF (ethanol toluene reference fuel) has been

proposed as the future reference fuel for ethanol-containing gasoline fuels with a significant amount of *n*-heptane. Moreover, the degradation pathways for larger *n*-alkanes are analogous to *n*-heptane degradation. For these reasons, a vast interest arose in the combustion community to explore the combustion chemistry of *n*-heptane, which has become one of the most extensively studied hydrocarbons. However, even for *n*-heptane, the formation pathways of hazardous aldehyde, polycyclic aromatic hydrocarbon (PAH) or particulate emissions are still not fully understood and further research is needed that concentrates on these details.

One approach to unravel *n*-heptane combustion chemistry is to study the full species set as a function of reaction time in burner-stabilized flames. The first detailed study in this direction was reported in 1997 by Douté et al. [2]. The flame experiment was conducted at 60 mbar and equivalence ratios of $\phi = 0.7$ –2.0 (diluted by argon); molecular-beam-mass spectrometry (MBMS) was used as the analytical method. This work was later extended to a fuel-rich flame ($\phi = 1.9$ with N₂ dilution) at atmospheric pressure by the same group [3], while Ingemarsson et al. [4] investigated a stoichiometric flame (in air) at atmospheric pressure. Recently, stoichiometric low-pressure flames were investigated using molecular-beam mass spectrometry with synchrotron

* Corresponding authors.

E-mail addresses: kkh@uni-bielefeld.de (K. Kohse-Höinghaus), Fabian.Mauss@tdvt.de (F. Mauss).

¹ Current address: Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA.

radiation for photoionization (PI-MBMS) [5–7], in these studies, the mole fraction profiles including many oxygenated species were reported. The influence of blending *n*-heptane with oxygenated fuels in premixed low-pressure flames ($\phi = 1.6$) was studied by Chen et al. [8].

In the experimental part of the present study, quantitative species measurements were conducted in a fuel-rich, premixed burner-stabilized low-pressure flame, in which significantly more species were quantified as in similar studies before [2–8]. A special emphasis was placed on the measurement of mole fraction profiles of important intermediates of PAH and soot formation pathways. Similarly, mole fraction profiles of many oxygenated intermediates were recorded that provide critical information for kinetic model development, also with regard to the oxidation of partially oxygenated compounds during biofuel combustion.

Due to its early definition as a reference fuel component in the 1930s for gasoline, *n*-heptane was and is an important target also in the field of combustion chemistry modeling. The first reaction scheme used for kinetic simulations was published in 1979 by Coats and Williams [9], followed by the work of Westbrook et al. [10,11] and Chakir et al. [12]. The first rule-based and automatically generated reaction mechanisms by Chevalier et al. [13] was also directed toward *n*-heptane modeling and included high- and low-temperature oxidation. This work was followed in the 1990s by Ranzi et al. [14] and Côme et al. [15]. Their models were examined against experiments in shock tubes and jet-stirred reactors. Later, Curran and co-workers published an extensively validated model for *n*-heptane oxidation [16], introducing 25 major classes of elementary reactions. Recent publications focused on the development of mechanisms comprising multiple fuels [17–19] or fuel blends [20,21]. The latest published kinetic model by Pelucchi et al. [22] focuses introducing additional reaction classes for the low-temperature chemistry by introducing additional reactions for hydroperoxide species. However, in all previous studies, the detailed modeling of species profiles in *n*-heptane flames has not been combined with a broad validation of the provided mechanisms against shock tube and jet-stirred reactor experiments that cover low-temperature oxidation chemistry; other fuels than *n*-heptane are not normally included in this validation either. Moreover, the modeling of *n*-heptane flame speeds proved to be difficult in early studies [23].

In 2007 some of the present authors reported the first detailed kinetic model for *n*-heptane oxidation, which was validated for the full range of combustors, pressures, fuel/oxidizer ratios and temperatures (500–2000 K) including shock tube experiments, jet-stirred and flow reactor measurements, ignition timing in a homogeneous charge compression ignition engine (HCCI), burner-stabilized flames and flame speed measurements. The widespread applicability of this reaction mechanism was demonstrated later in several studies that explored combustion processes beyond the initial target range [18,24–26] and for simulations of internal combustion engines [27,28]. This reaction mechanism [18] is the starting point for the modeling part of the present work. The detailed species measurements provided in this study enable a significantly deeper validation of the *n*-heptane flame chemistry compared to the original work, now including oxygenated species. This analysis was further supported by recent collaborative studies on the flame chemistry of butane and butene fuels [29,30] in which the C_4 chemistry of the original mechanism was significantly augmented. In this work the low-temperature *n*-heptane oxidation chemistry of the kinetic model has been critically inspected and revised.

Consequently, the reaction mechanism derived here provides a significant step beyond just another *n*-heptane flame chemistry model, validated against some newly measured flame data. The kinetic model augmented and presented in this work is a

comprehensive C_1 – C_7 hydrocarbon oxidation mechanism and its range of validation targets comprises a large number of fuels and fuel mixtures including methane, ethane, ethene, acetylene, propane, propene, acetylene/propene, *n*-butane, *iso*-butane, 1-butene, 2-butene, *iso*-butene, 1-hexene, *n*-heptane, toluene in flames and reactor experiments. This broad validation ensures that the mass flow analysis provides a realistic picture of *n*-heptane flame chemistry; especially with regard to pollutant formation (see discussion in [31]). The current hydrocarbon oxidation model, provided in the Supplement Material, consists of 349 species and 3686 reactions where forward and backward reactions are considered as individual reactions.

2. Experiment and data evaluation

2.1. Molecular-beam mass spectrometry (MBMS)

Experiments were carried out at Bielefeld University with a set-up described earlier in [30,32]. In brief, the instrument provides a two-stage Wiley-McLaren ion source equipped for 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 (separation of oxygenated and non-oxygenated species is possible). The burner is mounted in an upright fashion in the center of a flame chamber (320 mm diameter, 550 mm height). The flame gases were sampled via a quartz nozzle with a 25° cone angle and a $\sim 500 \mu\text{m}$ orifice diameter at the tip. A pressure reduction from 40 mbar in the flame chamber to $\sim 10^{-4}$ mbar in the 1st pumping stage interrupted further reactions and led to the formation of a molecular beam which passed through a copper skimmer (2 mm diameter) into the ionization chamber of the mass spectrometer at 10^{-6} mbar. Ionization relied on a pulsed electron beam of $\sim 10^9$ electrons/pulse with an energy distribution of 1 eV (Full Width at Half Maximum, FWHM) which permitted to detect all species in the same mass spectrum. Soft ionization using electron energies in the range between 10 and 18 eV were applied to minimize undesirable fragmentation processes. Measurements of intermediate species were performed at nominal energies of 10.5 eV, 12.0 eV, 13.5 eV, whereas an energy of 16.5 eV was applied for the determination of the major species, namely H_2 , H_2O , CO, O_2 , Ar, CO_2 , and *n*-heptane.

2.2. Flame and burner

A laminar flat premixed 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 flow rates of oxygen and argon were regulated by calibrated mass-flow controllers (MKS, Aera) with a precision of $\pm 5\%$ since gas conversion factors were applied. The dosage of liquid *n*-heptane was realized by a syringe pump that injected the fuel into a heated vaporizer (130 °C). The entire Ar stream was fed through the vaporizer to ensure stable evaporation, thus an uncertainty of $\pm 5\%$ is also assumed for the *n*-heptane flow. In due consideration of these uncertainties, the stoichiometry of the flame covers a range from 1.61 to 1.78.

The flame was stabilized on a home-built flat-flame burner which features a sintered and water-cooled bronze matrix with a diameter of 64.0 mm. The burner was mounted on a translational stage that is movable in vertical and horizontal directions. By varying the distance to the nozzle, species mole fraction profiles were obtained along the centerline of the flame as a function of height

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