



# Experimental and kinetic modeling study of 1-hexene combustion at various pressures



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## ARTICLE INFO

### Article history:

Received 2 April 2016

Revised 25 July 2016

Accepted 28 July 2016

Available online 12 September 2016

### Keywords:

1-Hexene

Flow reactor pyrolysis

Laminar flame speeds

Kinetic model

Model validation

## ABSTRACT

The pyrolysis of 1-hexene was studied in a flow reactor by synchrotron vacuum ultraviolet photoionization mass spectrometry and gas chromatography combined with mass spectrometry at 0.04, 0.2, and 1 atm. Laminar flame speeds of 1-hexene/air mixtures at various pressures (1, 2, 5, and 10 atm) were measured at an initial temperature of 373 K and equivalence ratios from 0.7 to 1.5. A kinetic model of 1-hexene combustion with 122 species and 919 reactions was developed to investigate the key pathways in the decomposition of 1-hexene and the formation and consumption of products, as well as the chemical kinetic effects on the laminar flame propagation. The presence of double bond in 1-hexene molecule leads to the enhanced formation of resonantly stabilized radicals and unsaturated intermediates. The model was also validated against the experimental data of 1-hexene combustion from literature, including ignition delay times and species profiles in jet-stirred reactor oxidation and laminar premixed flames. The extensive validations demonstrate the applicability of the present model over a wide range of conditions, such as low to high pressures, intermediate to high temperatures, and pyrolysis to oxidation circumstances.

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## 1. Introduction

Alkenes are an important component family in gasoline [1–3]. As the octane numbers of alkenes are higher than those of *n*-alkanes with the same carbon number [4], alkenes are also known to be good octane boosters and can be used as surrogate components for gasoline [5–8]. Alkenes are also important intermediates in the pyrolysis and combustion of large alkanes, cycloalkanes and alcohols [9–12]. Thus the sub-mechanism of alkenes plays an important role in the combustion of large alkanes, cycloalkanes and alcohols. Besides, the research of alkene combustion can provide specific insight into the chemistry of C–C double bond which also widely exists in biodiesel molecules [13–15]. Some previous studies [4,13,16–18] also showed that the chain length and position of the C–C double bond in alkene molecule have significant influence on fuel decomposition and oxidation chemistry and consequently affect the combustion characteristics such as ignition delay times. Therefore investigations on the combustion of alkenes will not only

increase our knowledge of alkene combustion chemistry, but also benefit the understanding of the combustion chemistry of other related fuel types.

There are some previous investigations [13,17–28] on the combustion of C<sub>5</sub> and larger alkenes which are in liquid phase under the standard condition. Among large alkenes, 1-hexene (C<sub>6</sub>H<sub>12</sub>) is a representative one due to its moderate molecular weight and length of carbon skeleton. Previous studies of 1-hexene combustion focused on the measurements of ignition delay times [13,17–20] and species profiles in jet-stirred reactor (JSR) oxidation [19,21] and laminar premixed flames [22–24]. For the pyrolysis study of 1-hexene, only Zhao et al. [25] investigated the pyrolysis of 1-hexene in a quartz tube at 873, 923, and 973 K, but they did not provide the concentration information of pyrolysis species. For the measurement of laminar flame speeds, only Burluka et al. [26] measured the laminar flame speeds of 1-hexene/air mixture at 5 atm and 360 K. Therefore, the experimental study in pyrolysis with comprehensive speciation and laminar flame speeds of 1-hexene over a wide pressure range are still limited. Several kinetic models have been developed based on the above oxidation data. Mehl et al. [4] developed a kinetic model for the oxidation of hexene isomers according to the data of ignition delay times. Yahyaoui

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et al. [19,20] and Touchard et al. [29] generated kinetic models of 1-hexene using the EXGAS program and validated the models on the ignition delay times [18–20] and the species profiles in JSR oxidation [19]. Besides, Nawdiyal et al. [24] also developed a kinetic model of 1-hexene and validated it on the species profiles in laminar premixed flames of 1-hexene under stoichiometric and rich conditions.

In this work, the main target is to investigate the combustion chemistry of 1-hexene under pyrolysis and intermediate-to-high temperature oxidation circumstance at various pressures. In the experimental study, the pyrolysis of 1-hexene was performed in a flow reactor over the temperature range of 800–1350 K at a variety of pressures (0.04, 0.2, and 1 atm), and the laminar flame speeds of 1-hexene at various pressures of 1, 2, 5, and 10 atm were also measured using a single-chamber cylindrical combustion vessel. The pyrolysis species were detected using both synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) at 0.04 atm and gas chromatography combined with mass spectrometry (GC-MS) at all pressures. In the modeling study, a kinetic model of 1-hexene was developed and comprehensive validation of the model was performed on both the new experimental data in this work and the literature data at intermediate-to-high temperature region, including species profiles in jet-stirred reactor oxidation [19], species profiles of laminar premixed flames [22–24] and ignition delay times [13,17,19,20]. Experimental data used to validate the present model were summarized in Table S1 of the Supplementary materials.

## 2. Experimental methods

### 2.1. Flow reactor pyrolysis

In this work, the SVUV-PIMS experiments of flow reactor pyrolysis were performed at the National Synchrotron Radiation Laboratory (NSRL), Hefei, China. Detailed information on the synchrotron VUV beamline and the pyrolysis apparatuses using both SVUV-PIMS and GC-MS can be found in our previous work [30–35]. Schematic diagrams of the apparatuses are presented in Figs. S1 and S2 of the Supplementary materials. The flow rate of carrier gas Ar was controlled by a mass flow controller with the flow rate of 980 standard cubic centimeters per minute (SCCM). The liquid flow rate of 1-hexene (purity  $\geq 99.5\%$ ) was controlled by a high performance liquid chromatography pump at 0.111 mL/min (equal to 20 SCCM in gas phase). The total flow rate of the mixture of Ar and pre-vaporized 1-hexene was 1000 SCCM. Therefore the inlet mole fractions of fuel and Ar are 2% and 98%, respectively. During the experiment, the mixture was fed into a 0.7 cm inner diameter and 22.9 cm length flow tube with 15 cm length heated region in the furnace. The flow tube was made of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> to minimize wall catalytic effects [36,37]. The small inner diameter (0.7 cm) was selected to ensure strong radial diffusion effects, reduce radial concentration gradients, and achieve adequately homogeneous reaction circumstances based on the experience in previous laminar flow reactor experiments, e.g. Cathonnet et al. [38] and Glarborg et al. [39]. The temperature profiles along the flow tube centerline under different furnace temperatures were measured by an S-type thermocouple. Detailed introduction of the methods of centerline temperature measurement and pressure calculation can be found in our previous work [10,31,40].

In the SVUV-PIMS pyrolysis experiments, two experimental modes were used, including the measurement of photoionization efficiency spectra to identify pyrolysis species and the measurement of mass spectra at a variety of furnace temperatures to determine the mole fractions of pyrolysis species. The data evaluation method has been introduced in detail elsewhere [30,31], and will not be repeated here. The photoionization cross sections (PICSSs)

were taken from the online database [41]. The experimental uncertainties were estimated to be  $\pm 10\%$  for major species,  $\pm 25\%$  for intermediates with known PICSSs, and a factor of 2 for intermediates with estimated PICSSs [42,43]. In the GC-MS pyrolysis experiments, the identification of pyrolysis species was performed using an online GC coupled with a mass spectrometer. For the purpose of avoiding gas condensation, both the transfer line and six-port valve were heated to 473 K. A HP-PLOT Q capillary column was used to separate the pyrolysis species. Quantification of products was performed by direct calibration of standard gas mixtures of known compositions, and indirect calibration by effective carbon number based on the response of the flame ionization detector (FID). The experimental uncertainties were estimated to be  $\pm 10\%$  for species with direct calibration and  $\pm 20\%$  for others [33,44,45]. The errors of carbon balance were both within 10% in the SVUV-PIMS and GC-MS pyrolysis experiments.

### 2.2. Laminar flame speeds

The laminar flame speeds of 1-hexene/air mixture at 1–10 atm and 373 K were measured from spark-ignited, outwardly-propagating spherical flames using a cylindrical combustion vessel. Combustion vessel has many advantages in measuring laminar flame speeds at elevated pressures [46]. The experimental apparatus consists of a sample inlet system, a premixing vessel (inner volume 9.06 L), a constant-volume single-chamber combustion vessel (inner volume 2.77 L), and a schlieren system. Schematic diagram of the apparatus is presented in Fig. S3 of the Supplementary materials. The combustion vessel is made of 304 stainless steel and can be operated at static pressures up to 200 atm. The uniformity of the temperature inside the combustion vessel was measured to be within  $\pm 1$  K. Synthetic air consisting of 21% O<sub>2</sub> and 79% N<sub>2</sub> was used as the oxidizer, and the liquid 1-hexene was vaporized in an electrically heated vaporizer. The combustible mixtures were prepared in the premixing vessel using the partial pressure method and a magnetic stirrer was used to ensure good mixing. For a specific equivalence ratio, one preparation can provide enough combustible mixture for all measurements at different pressures. The prepared mixture was then charged into the combustion vessel and was ignited by two horizontally assembled tungsten electrodes (diameter 500  $\mu$ m). The images of outwardly propagating spherical flame were recorded by the schlieren system after the ignition. The resolution was set at 480  $\times$  480 pixels to map a region of 75  $\times$  75 mm<sup>2</sup>. Each experiment was carried out three times, and the average value was reported and used to validate the kinetic model. The data processing method in this work is referred to the nonlinear extrapolation methods developed by Kelley et al. [47] and Halter et al. [48]. The evaluated uncertainties of measured flame speeds are between  $\pm 0.81$  and  $\pm 1.61$  cm/s depending on the equivalence ratios ( $\phi$ ) and initial pressures.

## 3. Kinetic modeling

A kinetic model of 1-hexene with 122 species and 919 reactions was developed in the present work. The C<sub>0</sub>–C<sub>4</sub> sub-mechanism was mainly taken from our previous models of butanol isomers [9,31,49]. Names, nomenclatures, and structures of some important species discussed in this work are shown in Table S2 of the Supplementary materials. Most thermodynamic and transport data in the present model are taken from the butanol models [9,31,49] and the database of Goos et al. [50]. The reaction mechanism, thermodynamic data and transport data files are provided in the Supplementary materials. The simulation work was performed using the Chemkin-PRO software [51].

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