An ignition delay time and chemical kinetic modeling study of the pentane isomers

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ABSTRACT

Ignition delay times of *n*-pentane, *iso*-pentane, and *neo*-pentane mixtures were measured in two shock tubes and in a rapid compression machine. The experimental data were used as validation targets for the model described in detail in an accompanying study [14]. The present study presents ignition delay time data for the pentane isomers at equivalence ratios of 0.5, 1.0, and 2.0 in 'air' (additionally, 0.3 in 'air' for *n*-, and *iso*-pentane) at pressures of 1, 10, and 20 atm in the shock tube, and 10 and 20 atm in the rapid compression machine, as well as data at an equivalence ratio of 1.0 in 99% argon, at pressures near 1 and 10 atm in a shock tube. An infrared laser absorption technique at 3.39 μm was used to verify the composition of the richest mixtures in the shock-tube tests by measuring directly the pentane isomer concentration in the driven section. By using shock tubes and a rapid compression machine, it was possible to investigate temperatures ranging from 643 to 1718 K. A detailed chemical kinetic model was used to simulate the experimental ignition delay times, and these are well-predicted for all of the isomers over all ranges of temperature, pressure, and mixture composition. In-depth analyses, including reaction path and sensitivity analyses, of the oxidation mechanisms of each of the isomers are presented. To the authors' knowledge, this study covers conditions not yet presented in the literature and will, in conjunction with the aforementioned accompanying study, expand fundamental knowledge of the combustion kinetics of the pentane isomers and of alkanes in general.

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1. Introduction

The combustion and chemical kinetics of *n*-pentane are of interest because it is a component of gas-turbine and gasoline engine fuel blends and is an intermediate species in the oxidation of higher-order hydrocarbons. For this reason, several studies have investigated its combustion characteristics and mechanism of oxidation. Literature data are scarcer concerning *iso*- and *neo*-pentane. While models for straight-chained alkanes have matured for species relevant to transportation fuels, much less work has been performed on branched alkanes, which are a large component in petrol and diesel fuels. Ignition delay time (IDT) data are particularly useful in the validation of kinetic mechanisms, and this study aims to increase the fidelity of the pentane isomer models utilizing these data. Several studies have been performed that examined the combustion of the pentane isomers, which include rapid compression machines (RCM) [1–4],

shock tubes (ST) [5–7], a well-stirred reactor [8], and an annular flow reactor study [9].

Dahm and Verhoek [5] explored the gas-phase oxidation of *n*-pentane in the low-temperature region, 595–732 K. A study by Burcat and co-workers [6] compared the IDTs of C_1–C_5 alkanes at stoichiometric conditions utilizing a shock tube at pressures between 8.27 and 9.46 atm over a temperature range of 1165–1400 K. Gonzalez and Sandler used an annular flow reactor to study the oxidation of an *n*-pentane/air mixture in the high-temperature, pre-ignition region in the temperature range of 773–893 K [9]. Westbrook et al. studied the oxidation of *n*-pentane at 1 atm and at temperatures ranging from 1068 to 1253 K using a well-stirred reactor [8]. Three RCM studies were published by Minetti et al. [3,4] and Westbrook et al. [1]. Minetti and co-workers studied the autoignition of alkanes in the intermediate temperature range from 630 to 920 K at equivalence ratios between 0.8 and 1.2, and at pressures between 3 and 16 bar, and concluded that the data were in relatively good agreement with the mechanism predictions. Minetti et al. also compared the pre-ignition chemistry of *n*-pentane and 1-pentene under stoichiometric conditions at pressures between 6.8 and 9.2 bar and at temperatures from 600 to 900 K. Autoignition, kinetic reaction mechanisms, and model

agreement were studied by Westbrook et al. for equivalence ratios between 0.5 and 2.0, at pressures from 8 to 20 bar, and temperatures from 675 to 980 K. Excellent agreement between computed and measured results was found [1]. An RCM study conducted by Ribaucour et al. compared the three isomers of pentane at stoichiometric conditions at initial pressures of 300 and 400 Torr and at temperatures ranging from 640 to 900 K [2]. A high-pressure shock tube study was performed by Zhukov et al. in which lean *n*-pentane IDTs were measured to aid development of a kinetic model [7]. Tests were performed at an equivalence ratio of 0.5 and over pressure and temperature ranges of 11–530 atm and 867–1534 K, respectively. It was concluded that the kinetic model was in good agreement with experimental data obtained therein. Oehlschlaeger et al. used a shock tube to measure IDTs of *iso*-pentane at equivalence ratios from 0.25 to 2.0 at pressures ranging from 1.10 to 12.58 atm and temperatures ranging from 1177 to 2009 K [10]. A flow reactor study of *neo*-pentane was carried out at a pressure of 8 atm, at an equivalence ratio of 0.3 and at temperatures ranging from 620 to 810 K by Wang et al. [11].

This study adds to the literature by extending the range of conditions for each of the fuels, most notably for *iso*- and *neo*-pentane for which there have been few experimental studies compared to *n*-pentane. However, this study represents more than simply extending a matrix of experimental conditions. The three isomers, although relatively small, exhibit significant structural diversity, and are the smallest isomeric set of alkanes containing linear, singly-branched, and doubly-branched species. Knowing the effects that these structural differences have on the reactivity of the fuels is of importance, especially for typical transportation fuels which contain a large amount of alkanes with various amounts of structural branching. Also, between the isomers there should be adequate structural variation to be representative of all larger alkanes. An example is observed in the similarity between *iso*- and *neo*-pentane and the varyingly branched portions of *iso*-octane. *n*-Pentane may also be an ideal analogue for larger normal alkanes due to the proximity of its outermost secondary carbons. The relatively fast isomerization reactions of alkyl-peroxyl and hydroperoxyl-alkyl-peroxyl radicals via 6-membered transition state rings can occur between these two secondary carbons. This is the smallest normal alkane for which this fast isomerization can occur, and it is the dominant kind of pathway for larger alkanes at low temperatures (600–900 K). This makes it a better archetype for low-temperature alkane oxidation chemistry than propane or *n*-butane, for example, neither of which have a long enough alkyl chain to be truly representative of longer normal alkanes.

As well as being representative of larger highly branched alkyl structures, *neo*-pentane itself shows interesting combustion characteristics. It is the smallest alkane that contains only primary and quaternary carbons, with the next smallest alkane of this type being *neo*-octane (2,2,3,3-tetramethylbutane). As discussed in Section 3.3, this uncommon structure results in the lack of a major unimolecular pathway of the alkyl-peroxyl radical, which is present for all but the *neo*-alkanes. This causes *neo*-pentane to show abnormal trends in reactivity as a function of temperature. Its highly symmetric nature also means that the amount of different types of species and reactions involved in its oxidation pathways is greatly reduced compared to its isomers. In terms of kinetic modeling, this introduces an extra layer of constraint on model parameters, due to there being far less possible combinations of input values. This helps ensure that a situation does not occur in which a series of compensating errors in thermochemical and reaction rate assignments can approximate accurate predictions for a given set of validation targets.

In this study, data were collected experimentally using shock tubes and an RCM at elevated pressures and temperatures, as presented below. The proposed model is presented in comparison to the data for validation. Provided first are details of the experiments, followed by a presentation of the extensive results and corresponding

Table 1
Experimental conditions studied here in shock tubes and an RCM.

Fuel	T (K)	p (atm)	φ	Dilution (%)
n-C$_5$H$_{12}$	643–1555	1–20	0.3–2.0	∼75–99
iso-C$_5$H$_{12}$	663–1675	1–20	0.3–2.0	∼75–99
neo-C$_5$H$_{12}$	651–1718	1–20	0.5–2.0	∼75–99

discussion. Comparisons with the chemical kinetic model are provided in the same plots with the experimental data.

2. Experimental

Fuel/'air' mixtures were studied for *n*- and *iso*-pentane at equivalence ratios of 0.3, 0.5, 1.0, and 2.0, and at equivalence ratios of 0.5, 1.0, and 2.0 for *neo*-pentane. 'Air' in the case of the experiments presented in this study refers to nitrogen (or argon/carbon dioxide) and oxygen in a 79-to-21 ratio, respectively. New data are also presented for each of the isomers at stoichiometric, highly dilute (99% argon) conditions at pressures near 1 and 10 atm. Experiments were performed at pressures near 1, 10, and 20 atm, and at temperatures ranging from 778 to 1718 K in the shock tubes, and at 10 and 20 atm in the RCM at temperatures between 643 and 1065 K. The ST experiments were carried out in the high pressure ST at Texas A&M University (TAMU) and the high pressure ST at NUI Galway's (NUIG) Combustion Chemistry Centre. All RCM experiments were carried out in one of the twin-opposed piston RCMs at NUIG. Experimental data were used to make improvements to the chemical kinetic mechanisms previously developed by Healy et al., Curran et al. and Wang et al. [11–13], as detailed in the partner study to this one [14]. Mixtures were composed of spectrophotometer grade (≥99%) *n*-pentane, *iso*-pentane, and *neo*-pentane; and high purity (≥99.5%) oxygen and nitrogen. The experimental conditions investigated in this study are outlined in Table 1. The ignition delay times reported in this study along with associated pressure and temperature conditions are available as Supplementary material, as well as plots of model performance against other literature targets.

2.1. TAMU shock tube hardware

The shock tube is constructed of 304 stainless steel. The driven section is 4.72 m in length, and the driver section is 2.46 m long. The shock-tube diameter is 15.24 cm, and the inner surface is polished to 1 μm RMS to reduce boundary layer formation. Five PCB 113 pressure transducers along the driven section of the tube are used to measure the incident-shock velocity. The pressure transducer signal is fed to four Fluke PM 6666 timer counter boxes to measure the time it takes the shock to pass from one transducer to the next. The time intervals are then extrapolated to find the incident-shock velocity at the endwall. As a result, the experimental reflected-shock temperature is known to within 15 K. Helium was used as the driving gas throughout. For the 1 and 10 atm experiments, polycarbonate diaphragms were used to separate the driving gas from the test mixture, and scored aluminum diaphragms were used for the 20 atm experiments. All experiments were performed behind the reflected shock wave. Small viewing ports adjacent to the endwall allow for the capture of light emission during combustion. More details on the shock tube are available in Aul et al. [15].

A mixing tank was evacuated to less than 5×10^{-5} Torr and filled to the proper species concentration using the partial pressures method. Gases were passed through a perforated stinger traversing the center of the mixing tank to allow for rapid, turbulent mixing. At least 24 h was allowed to pass between the creation of the mixture and experimental runs, to allow for complete homogeneous mixing of the gases.

During the preparation of large fuel-rich mixtures, some fuel condensation was observed. To minimize this condensation, mixtures