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Autoignition of *trans*-decalin, a diesel surrogate compound: Rapid compression machine experiments and chemical kinetic modeling

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ABSTRACT

Decahydronaphthalene (decalin), with both *cis* and *trans* isomers, is a bicyclic alkane that is found in aviation fuels, diesel fuels, and alternative fuels from tar sands and oil shales. Between the two decalin isomers, *trans*-decalin has a lower cetane number, is energetically more stable, and has a lower boiling point. Moreover, *trans*-decalin has often been chosen as a surrogate component to represent two-ring naphthenes in transportation fuels. Recognizing the importance of understanding the chemical kinetics of *trans*-decalin in the development of surrogate models, an experimental and modeling study has been conducted. Experimentally, the autoignition characteristics of *trans*-decalin were investigated using a rapid compression machine (RCM) by using *trans*-decalin/O_2/N_2 mixtures at compressed pressures of $P_C = 10–25$ bar, low-to-intermediate compressed temperatures of $T_C = 620–895$ K, and varying equivalence ratios of $\phi = 0.5$, 1.0, and 2.0. These new experimental data demonstrate the effects of pressure, fuel loading, and oxygen concentration on autoignition of *trans*-decalin. The current RCM data of *trans*-decalin at lower temperatures were also found to complement well with the literature shock tube data of decalin (mixture of *cis* + *trans*) at higher temperatures. Furthermore, a chemical kinetic model for the oxidation of *trans*-decalin has been developed with new reaction rates and pathways, including, for the first time, a fully-detailed representation of low-temperature chemical kinetics for *trans*-decalin. This model shows good agreement with the overall ignition delay results of the current RCM experiments and the literature shock tube studies. Chemical kinetic analyses of the developed model were further conducted to help identify the fuel decomposition pathways and the reactions controlling the autoignition at varying conditions.

1. Introduction

Decahydronaphthalene (decalin) is a bicyclic alkane with two fused six-membered rings. It is commonly found in aviation fuels, diesel fuels, and alternative fuels from tar sands and oil shales [1–4]. Moreover, as decalin possesses some advantageous characteristics in terms of thermal stability, combustion properties, and energy density, it has been shown to be one of the most thermally stable and endothermic fuel components for jet fuels [5]. In addition, it has shown favorable combustion characteristics in both gas turbines and diesel engines [5–7]. Decalin occurs in two isomers, *cis* and *trans*, in which the *trans* isomer has a lower cetane number, is energetically more stable, and has a lower boiling point. Thermal stability experiments have also shown that *cis*-decalin will isomerize to *trans*-decalin under supercritical conditions [8]. In the study of Mueller et al. [9], *trans*-decalin has been chosen as a surrogate component to represent dicycloparaffins in transportation fuels. Based on the abovementioned characteristics, the experimental and theoretical investigations of *trans*-decalin combustion kinetics are of fundamental and practical importance.

Previous chemical kinetic studies on decalin have primarily focused on pyrolysis experiments, and most of which were based on mixture of *cis* and *trans* decalin with certain mass and volume fractions [10–23]. Those past pyrolysis works have been conducted over a wide range of pressures from below atmosphere to 100 atm, along with a temperature range up to 1450 K. As a result, major products of decalin pyrolysis for different conditions have been identified. Compared with pyrolysis, fewer studies in the literature have focused on the oxidation of decalin [5,21,22,24–27]. Nixon et al. [24] investigated the ignition delay times of *cis* + *trans* decalin mixture in a shock tube under high temperatures of 1060–1290 K, low pressures of 0.6–1.5 atm, and equivalence ratios of 0.1 and 0.2

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diluted by Argon. Agosta [25] studied the oxidation of *cis* + *trans* decalin in a pressurized flow reactor for surrogate selection of JP-8 fuel. The experiments of [25] were conducted at equivalence ratios of ϕ = 0.3 and 0.4 at 8 atm, with negative temperature coefficient (NTC) behavior being observed in terms of carbon monoxide production. Subsequently, Oehlschlaeger et al. [21] studied the high-temperature (993–1305 K) ignition of *cis* + *trans* decalin/air mixtures in a shock tube at equivalence ratios of 0.5 and 1.0, with pressures ranging from 9.3 to 15.2 atm and from 34.6 to 48 atm. Heyne et al. [5] measured the ignition delay time and derived cetane number of decalin in an ignition quality tester. In addition, Zhu et al. [22] measured ignition delays for *cis* + *trans* decalin/air mixtures in a shock tube over temperatures of 769–1202 K, pressures of 11.7–51.2 atm, and equivalence ratios of 0.5, 1.0, and 2.0. NTC behavior of *cis* + *trans* decalin was observed at temperatures below 920 K for the first time [22]. While those studies appear to have covered a wide range of temperatures and pressures, investigations focused on the oxidation of neat *trans*-decalin are meager, especially at low-to-intermediate temperatures (e.g., < 900 K) and elevated pressures. Therefore, the first objective of the current work is to extend the fundamental experiment database of *trans*-decalin to include conditions at low-to-intermediate temperatures and elevated pressures by undertaking rapid compression machine experiments. In addition to the effects of temperature, pressure, and fuel loading on autoignition of *trans*-decalin, the effect of oxygen concentration is also investigated due to its importance in engine performance and emissions with exhaust gas recirculation [28].

The chemical kinetic modeling study of Ranzi [29] was, to our knowledge, the first published kinetic model describing the oxidation of decalin. Dagaut et al. [30] added several reaction paths to the model of Ranzi [29], and Zhu et al. [22] then explored some improvements on the model of Dagaut et al. [30] to have a better prediction on their experimental shock tube data. However, in these chemical kinetic models of [22,29,30] the low temperature chemistry was treated in a reduced manner with global reactions. Hence, the second objective of this study is to present an updated chemical kinetic model that has a fully-detailed treatment of the low-to-intermediate temperature oxidation chemistry of *trans*-decalin.

2. Experimental specifications

The rapid compression machine (RCM) used in this study consists of a pneumatic cylinder, a hydraulic cylinder, and a reaction chamber, in which the reactant gases are compressed by a creviced piston arrangement during each experimental run. First, the creviced piston in the reaction chamber is retracted from top dead center to bottom dead center. It is held in place by pressurized oil in the hydraulic cylinder. When the solenoid valve is triggered, the pressure in the hydraulic chamber is released and the creviced piston moves forward, driven by the high-pressure air tank and the pneumatic piston inside the pneumatic cylinder. The creviced piston is then decelerated and stopped by a stopping ring and groove mechanism. A dynamic pressure transducer is equipped on the reaction chamber for dynamic pressure measurements during experiment. The compression ratio of this RCM can be varied by changing the length of stroke or/and the clearance volume. More details about the RCM design and operation can be found in [31,32].

The *trans*-decalin/oxidizer mixture is prepared in a stainless steel mixing tank. A magnetic stirrer is placed at the center of the tank bottom to provide a mixing mechanism. A rupture disc is used as a safety measure against accidental overpressure within the tank. For the current study, the mixture is prepared at room temperature, with *trans*-decalin (liquid fuel) injected directly inside the mixing tank using a glass syringe, followed by oxygen and nitrogen filled into the tank on a barometric measure in the desired O_2:N_2 molar proportion. Recognizing that the gas heating effect can occur during the tank filling process as the line enthalpy is converted to tank internal energy, we always ensure filling each gas to the target pressure while the tank temperature is within ± 1.5 °C of the room temperature. High purity of fuel and gases are used for this study, including *trans*-decalin (> 98%) from TCI America and O_2 (> 99.99%) and N_2 (> 99.99%) from Airgas. The mixing tank, the manifold, and the reaction chamber, all equipped with heating tapes, are heated to the desired preheat temperature (373–393 K for this study) for 2–3 h before starting the experiments to ensure complete vaporization of *trans*-decalin and a homogeneous mixture. It is also noted that when preparing the mixture, we ensure that the partial pressure of *trans*-decalin is less than half of its saturated pressure at a given preheat temperature. In order to monitor the wall temperature uniformity of the reaction chamber, three thermocouples are used and evenly distributed along the outside wall of the reaction chamber. The scatter of the three thermocouples is typically less than ± 3 K from the set preheat temperature.

Table 1
Test conditions of *trans*-decalin experiments.

ϕ	Oxidizer	$X_{decalin}$ (%)	X_{O_2} (%)	X_{N_2} (%)	P_C (bar)
1.0	N_2 diluted	0.72	10.43	88.85	25
0.5	air	0.72	20.86	78.42	10, 15, 25
1.0	air	1.43	20.71	77.86	10, 15
2.0	air	2.82	20.42	76.76	10

Figure 1(a) shows a representative pressure trace at $P_C = 15$ bar, $T_C = 689$ K, and ϕ = 0.5 in air, demonstrating the definitions of ignition delay times used in this study. Here, P_C and T_C are the pressure and temperature at the end of compression (EOC), respectively. The EOC point was regarded as the starting point of ignition delay time, which is set as $t = 0$ ms. In Fig. 1(a), τ_1 indicates the first-stage ignition delay time and τ indicates the total ignition delay time, with both of them being identified based on the respective local maximum of the time derivative of the pressure trace. The non-reactive pressure trace of the same experimental condition has also been shown in Fig. 1(a) as a reference. For each reactive set of P_C and T_C, the corresponding non-reactive pressure trace is measured by replacing oxygen with nitrogen to characterize the heat loss effect on the ignition process and to verify that no heat release has occurred during the compression stroke. Four to five consecutive runs were taken for each experimental condition to ensure data repeatability, which can be seen in Fig. 1(b). The typical scatter was found to be less than 15% of the reported ignition delay value, which is closest to the mean of the consecutive runs.

The compressed temperature (T_C) is deduced from the measured pressure trace by using the assumption of “adiabatic core hypothesis” [33]. Under this hypothesis, it is assumed that the heat loss from the core volume of the reaction chamber only occurs in a thin boundary layer near the wall, and the central core region is adiabatic by modeling the heat loss as an effective reduction in the compression ratio [34,35]. Thus, the compressed temperature can be calculated by:

$$\ln\left(\frac{P_C}{P_0}\right) = \int_{T_0}^{T_C} \frac{\gamma}{T(\gamma - 1)} dT,$$

where P_0 is the initial pressure, T_0 is the initial temperature, and γ is the temperature-dependent specific heat ratio.

The test conditions investigated in the current study are summarized in Table 1, where X_i represents the mole percentage of species i in the reactant mixture. The compressed pressures and