



Impact of branched structures on cycloalkane ignition in a motored engine: Detailed product and conformational analyses



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ABSTRACT

The ignition process of ethylcyclohexane (ECH) and its two isomers, 1,3-dimethylcyclohexane (13DMCH) and 1,2-dimethylcyclohexane (12DMCH) was investigated in a modified CFR engine. The experiment was conducted with intake air temperature of 155 °C, equivalence ratio of 0.5 and engine speed of 600 rpm. The engine compression ratio (CR) was gradually increased in a stepwise manner until autoignition occurred. It was found that ECH exhibited a significantly higher oxidation reactivity compared to its two isomers. The autoignition criterion was based on CO emissions and the apparent heat release rates. Ethylcyclohexane (ECH) indicated noticeable two stage ignition behavior, while less significant heat release occurred for the two isomers at comparable conditions. The mole fractions of unreacted fuel and stable intermediate species over a wide range of compression ratios were analyzed by GC-MS and GC-FID. Most of the species indicated constant rates of formation and the trends of relative yield to unreacted fuel are well in agreement with the oxidation reactivity in the low temperature regime. The major intermediate species are revealed as a group of conjugate olefins, which possess the same molecular structure as the original fuel compound except for the presence of a double carbon bond. Conjugate olefins were mostly formed through (1,4) H-shift isomerization during the low temperature oxidation of alkylcyclohexanes. Conformation analysis explains the reactivity differences in the three isomers as well as the fractions of intermediate species. The hydrogen availability located in alkyl substituents plays an important role in determining oxidation reactivity, requiring less activation energy for abstraction through the (1,5) H-shift isomerization. This reactivity difference contributes to building up the major intermediate species observed during oxidation of each test fuel. 12DMCH, whose ignition reactivity is the lowest, less favors β -scission of C–C backbone of cyclic ring, thereby resulting in lower concentrations of small olefins and higher concentrations of conjugate olefins and large oxygenated species in the low temperature regime, prior to autoignition.

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1. Introduction

In response to the increasing demand for diesel fuel in the United States, recent studies have considered cycloalkanes due to their abundance in many of the “unconventional oil” sources such as oil sands, oil shale and coal derived liquids. Furthermore, cycloalkanes can constitute 40 wt% of commercial diesel and 20 wt% of commercial jet fuels [1–4]. Despite the significance of cycloalkanes, there remains a lack of fundamental understanding of the

combustion chemistry of cycloalkanes. Recently, a few studies have focused on the low temperature chemistry of cycloalkanes, which is of great importance for the application of cycloalkanes in next generation engine designs that employ low temperature combustion strategies.

The characteristics of oxidation and autoignition behavior of cycloalkanes are different from those of the acyclic alkanes. For example, observations of ignition delay in rapid compression machines (RCM) indicate that the oxidation reactivity of cyclohexane in the low temperature regime is significantly less than that of n-hexane [5], consistent with the lower cetane number of cyclohexane than n-hexane. For low temperature oxidation of cyclohexane,

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the degenerate chain branching is a main factor that determines the oxidation reactivity and represents the intermolecular (1,5) H-shift of fuel peroxy radical ($\text{ROO}\cdot \rightarrow \cdot\text{QOOH}$). Although this isomerization reaction is similar mechanistically to aliphatic alkanes such as n-heptane [6] or isooctane [7], gas-phase cycloalkane oxidation possesses its own kinetic features that cannot be extrapolated from the rate constants of analogous acyclic alkanes with corrections for the ring. In two recent kinetic modeling studies of methylcycloalkane [8] and cyclohexane [9], Pitz et al. and Buda et al. reached the conclusion that the cyclic ring plays an important role in determining the activation energy barriers for these isomerization reactions. In addition, Yang et al. found that (1,4) H-shift can concurrently occur to form conjugate olefins, i.e., olefins with the same molecular structure as the original fuel compound except for the presence of a double carbon bond, with elimination of HO_2 during the (1,5) H-shift reaction indicated above. This competition in those two cases during low temperature oxidation of cycloalkanes results in the tradeoff relationship between low temperature reactivity and formation of conjugate olefins [10].

The previous experimental studies of oxidation of alicyclic compounds have focused mostly on cyclohexane (CH) [9,11,12] and methylcyclohexane (MCH) [13]. Detailed intermediate and final product analyses for the oxidation of representative cyclic-based fuels including CH, MCH, methylcyclopentane (MCP), tetralin and decalin have been studied in low and intermediate temperature regimes in a motored engine [14,15]. Yang et al. reported that the methyl substituent enhances low temperature reactivity of CH, as confirmed by conformational analysis and quantum calculations using an *ab initio* method [10,16]. Few studies focused on the effect of the presence or the length of alkyl chains on branched cycloalkanes, nor on the effect of the location of the methyl substituents. Ethylcyclohexane was examined in an experimental and modeling study of laminar flame speed in a counter flow configuration and compared with mono-alkylated cyclohexane and cyclohexane. This study found that a mono-alkylated group leads reaction intermediates that lower rates of flame propagation for butyl, propyl, ethyl and methylcyclohexane relative to cyclohexane [17]. The ignition delay for methyl and ethylcyclohexane was measured in a shock tube at conditions of relevance to practical combustion devices in order to investigate the influence of the length of the alkyl side chain on the ignition of alkylcyclohexanes [18]. The very recent study of Husson et al. investigated detailed intermediate products during low and intermediate oxidation of ethylcyclohexane in a jet-stirred reactor [19]. In another study, pyrolysis of ethylcyclohexane was performed near supercritical conditions in a batch reactor [20], providing product analysis and proposed reaction pathways.

Recognizing a considerable effect of the length of alkyl substituent in alicyclic compounds on low temperature reactivity, this work considers the effect of a methyl substituent and its location within the chemical structure on ignition behavior. The test fuels are ethylcyclohexane, 1,3-dimethylcyclohexane and 1,2-dimethylcyclohexane. To our knowledge, no previous oxidation studies comparing ethylcyclohexane, 1,3- and 1,2-dimethylcyclohexane have been reported. However, Do et al. investigated the ring opening reactions of 1,2- and 1,3-dimethylcyclohexane over Ir catalysts [21]. One noticeable conclusion from this study is that the presence of a methyl substituent in the reactant molecule has a positive impact on the ring opening of substituted C–C bonds. The C–C bonds between methyl substituents are opened preferentially compared with other C–C bonds, which explains why the position of the methyl substituents on a cycloalkane influences the ignition behavior of branched cycloalkanes.

The main goal of the current study is to examine the low temperature reactivity of substituted cycloalkanes through determination of the critical compression ratios (CCR) of three test fuels.

Furthermore, this study includes observations of major intermediate species from oxidation of each of the test fuels and proposed reaction pathways during low- and intermediate-temperature regimes. Lastly, conformation analysis of three different isomers demonstrates how the alkyl substituents can affect their low temperature oxidation reactivity. These results provide new information on the impact of alkyl substituents on ignition behavior during low temperature combustion in a motored engine environment.

2. Experimental conditions

2.1. Engine setup

A modified CFR octane rating engine was used to perform a series of studies on the ignition behavior, and ignited fuel oxidation chemistry of various promising alternative fuels and fuel surrogates [14,15,22–25]. This engine has variable CR ranging from 4:1 to 15:1 and a modified fueling system, described in detail elsewhere [14,15,22–25]. The original carbureted intake fueling system used for octane rating was replaced with a gasoline direct injection (GDI) system, located 1.4 meters above the engine intake valve, allowing for premixing of fuel and air. The intake manifold of the engine includes an electric heater which can heat the intake air and fuel mixture to as high as 260 °C. The intake temperature used in the present study is 155 °C for all the test fuels and all test conditions. The intake heating and mixing system allows the fuel to be fully mixed and vaporized before entering the engine as a pre-mixed homogeneous mixture. The liquid fuel was pressurized using helium gas and was injected at a pressure of 700 psi and a frequency of 10 Hz. The engine is naturally aspirated and the intake pressure constant at atmospheric pressure. The ASTM knock meter originally used for octane rating was substituted with a piezoelectric pressure transducer (Kistler 6052B). In-cylinder pressure data were measured at a resolution of 0.1 Crank Angle (CA) using a shaft encoder and recorded in a custom Labview data acquisition system. Bulk in-cylinder temperature and apparent heat release were calculated from the in-cylinder pressure traces by using a zero-dimensional single zone model established by Heywood [26]. The residual gas fraction was estimated by the method reported by Fox et al. [27]. Steady-state engine operation data was monitored and recorded every 10 s through a custom Labview data acquisition system. The CFR engine specifications are shown in Table 1.

2.2. Test fuels

In the present study, ethylcyclohexane (ECH) and two isomers, 1,3-dimethylcyclohexane (13DMCH) and 1,2-dimethylcyclohexane (12DMCH), were used so as to observe the impact of alkyl

Table 1
CFR engine specifications.

Number of cylinders	1
Bore (cm)	8.26
Stroke (cm)	11.43
Connection rod (cm)	25.4
Swept volume (cm^3)	611.7
Compression ratio	4–15.7
Number of overhead valve	2
Engine speed (rpm)	600
Intake valve open (degrees after TDC)	10
Intake valve closes (degrees after BDC)	34
Exhaust valve open (degrees before BDC)	40
Exhaust valve closes (degrees after TDC)	15

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