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Shock tube measurements and kinetic modeling study on autoignition characteristics of cyclohexanone



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ABSTRACT

Cyclohexanone was identified as an attractive second-generation biofuel that can be used as an alternative fuel or blending component, thereby reducing greenhouse gas and particulate emissions from internal combustion engines. This paper investigates auto-ignition characteristics of cyclohexanone/O2/Ar mixtures behind reflected shock waves. Ignition delay time measurements cover the temperature range of 1255-1646 K, with pressures near 2.5, 5, and 10 atm, argon/oxygen dilution ratios of 23.9, 48.9 and 98.9, and equivalence ratios of 0.5, 1.0, and 2.0. Five kinds of mixtures were prepared to determine the effects of pressure, equivalence ratio and dilution ratio on the reactivity over the entire temperature range. An ignition delay correlation, $\tau = 6.87 \times 10^{-6} P^{-0.52} \Phi^{0.70} D^{0.66} \exp(45.59/RT)$ (μ s), has been developed for cyclohexanone, including dependencies on pressure, equivalence ratio and dilution ratio. Experimental data have been compared to the kinetic modeling predictions of Serinyel et al. [Proc. Combust. Inst. 35 (2015) 507–514]. In general, the predictions overestimate the experimental data by 30–50%. With several reaction rate constants of selected small radical reactions updated, the predictions by modified mechanism present satisfactory agreement with the measured ignition delay data. Also, simulations based on the original model and modified model were compared to species concentrations measured in a jet-stirred reactor at 10 atm from the literature. Reaction pathway and sensitivity analyses were performed to identify the fuel consumption paths and key reactions during the ignition process of cyclohexanone. To our knowledge, the auto-ignition measurement of gas-phase cyclohexanone presented here are the first measurement for this compound.

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1. Introduction

The wide use of petroleum-based fuels in transportation and industry has caused serious environmental pollution and global warming through the emission of large amount of carbon dioxide. Moreover, with the shortage of fossil fuels, energy security has attracted increasing attention. To reduce the use of conventional fossil fuels, biofuels have attracted considerable attention as one of promising alternative fuels. Biofuels can be produced from biomass, and have clean combustion characteristic and low sulfur content, thus their use can help to reduce greenhouse gas emissions [1,2].

Ketones are potential candidates for biofuels produced through lignocellulosic biomass conversion, as well as through other approaches [3], and their combustion characteristics receive much more attention nowadays [4,5]. Especially, cyclohexanone, a rep-

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resentative six-carbon cyclic molecule with a ketone functional group (the molecule structure is shown in Table 1), has been identified as a promising second-generation biofuel [6,7]. However, its combustion characteristics are not well-known up to date. To the best of authors' knowledge, the early studies on cyclohexanone were focus on photochemical decomposition of cyclic ketones performed by Saltmarsh et al. [8] and Bamford et al. [9] in 1930s. Subsequently, Mayo et al. [10] used a flow system to investigate the thermal fragmentation of cyclohexanone at 1050 °C. They observed seven kinds of decomposition products and found methyl vinyl ketone was the major product among other stable species. Recently, investigations on cyclohexanone mainly focus on the soot variation of fuels blending cyclohexanone. Klein-Douwel et al. [6] employed a heavy-duty diesel engine to investigate soot production of cyclohexanone/Fischer-Tropsch synthetic fuel mixtures, and they found the additive cyclohexanone can efficiently reduce soot emissions. Boot et al. [7] investigated the sooting tendency of three oxygenates (tripropylene glycol methyl ether, dibutyl maleate, and cyclohexanone) in a DAF heavy-duty direct-injection diesel engine. The results shown that the cyclic oxygenate cyclohexanone

 Table 1

 Cyclohexanone structure and bond dissociation energies (BDEs) [11].

Structure	Bond	BDE(kcal mol ⁻¹)
2 3 4 4 4 4 4 4 4 4 4 4	$\begin{array}{c} C_{1}-C_{2} \\ C_{2}-C_{3} \\ C_{4}-C_{5} \\ C_{2}-H \\ C_{3}-H \\ C_{4}-H \end{array}$	81.4 84.8 90.5 91.5 98.3 99.1

contributes to lower particle emission compared to the linear oxygenate dibutyl maleate and branched oxygenate tripropylene glycol methyl ether.

The theoretical works concerning cyclohexanone chemical kinetic mechanism also are scarce. Until recently, Zaras et al. [11] reported a theoretical kinetic investigation for the unimolecular thermal decomposition pathways of cyclohexanone by using DFT/ab initio methods, and they obtained six different decomposition pathways and calculated rate constants for these pathways in the temperature range of 800-2000 K. Then, in order to improve the knowledge of the kinetics of cyclohexanone combustion, as a follow-up work of Zaras et al. [11], Serinyel et al. [12] employed a jet stirred reactor to measure concentration profiles of reactants, stable intermediates and products for the oxidation of cyclohexanone at 10 atm and temperatures ranging from 530 to 1220 K, and proposed a kinetic reaction mechanism for describing oxidation of cyclohexanone. However, this mechanism over-predicts the product concentrations at some conditions, indicating that a further modification on the mechanism is needed.

Cyclohexanone is an important biofuel, but the comprehension on its combustion process is still limited. The purpose of this study is to get a better understanding of its combustion characteristics through a new experimental study and to improve the relative kinetic mechanism based on the measured data. In this paper, a comprehensive experimental dataset for cyclohexanone oxidation was provided over a wide range of temperatures, pressures, and equivalence ratios. Modifications to Serinyel et al. [12] mechanism were performed, and reaction rate constants of some key reactions have been modified to better predict the measured ignition delay data. To our knowledge, this experimental study is the first to measure ignition delay times of gas-phase cyclohexanone/oxygen/argon mixtures.

2. Experimental methods

2.1. Shock tube setup

Auto-ignition experiments reported in this work were carried out in a heated stainless steel shock tube, using the reflected wave technique. The shock tube is comprised of a 6 m driver section and a 5 m driven section (inner diameter of both is 10 cm), which are separated by a 3 cm diaphragm section. A double-diaphragm bursting mechanism that utilizes different thicknesses of polycarbonate diaphragms is employed to reach various nominal reflected shock pressures. Further details of this facility were provided in previous publications [13,14].

Pressure time-histories were monitored by four piezoelectric pressure transducers (PCB 113B, with rise times of less than $1.0\,\mu$ s) mounted on the last 56.4 cm of the driven section, and time intervals between the adjacent transducers were recorded through a digitizing oscilloscope (Tektronix DPO5054) to obtain incident shock wave velocity. The shock wave speed at the end wall was determined by linearly extrapolating the three measured incident





Fig. 2. Typical heated shock tube inner temperature profiles for the heated driven section.

shock wave speeds to the end wall. Typical incident shock wave attenuation rates ranged from 0.5 to 2%/m in present work; an example of the obtained incident shock wave velocity profile is demonstrated in Fig. 1. Reflected shock conditions (pressure P_5 and temperature T_5) can be determined through the one-dimensional normal shock relations using the measured initial temperature (T_1) and pressure (P_1) in the driven section, the measured incident shock wave velocity and the thermodynamic properties of the reactant mixtures. Additionally, the light emission during the combustion process was captured using a quartz optical fiber located at the same cross section as the last pressure transducer being 15 mm away from the shock tube end wall. A grating monochromator (Zolix Omni- λ 3009) coupled with a photomultiplier tube was set to 431 nm to detect the CH* chemiluminescence from $A^2 \Delta - X^2 \Pi$ transition.

A heating system was designed and installed on the driven section to ensure no condensation of the fuel occurred. The driven section was wrapped with heating wires and uniformly heated to 393 K during experimentation to prevent condensation of cyclohexanone. The heaters are controlled by six zone controllers to ensure a homogeneous temperature distribution along the tube length with a maximum deviation of ± 3 K, and the temperature is monitored by a thermometer digital output coupled with sensors. The measured initial temperature profiles of the driven section (T_1) are shown in Fig. 2. Helium was used as the driver gas with purity of 99.99%.

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