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journal homepage: www.elsevier.com/locate/combustflameIntermediate species measurement during *iso*-butanol auto-ignitionWeiqi Ji^a, Peng Zhang^a, Tanjin He^b, Zhi Wang^b, Ling Tao^c, Xin He^{a,b,*}, Chung K. Law^{a,d}^a Center for Combustion Energy, Tsinghua University, Beijing 100084, China^b State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, China^c National Renewable Energy Laboratory, Golden, CO 80401, USA^d Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA

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ABSTRACT

This work presents the time histories of intermediate species during the auto-ignition of *iso*-butanol at high pressure and intermediate temperature conditions obtained using a rapid compression machine and recently developed fast sampling system. *iso*-butanol ignition delays were acquired for *iso*-butanol/O₂ mixture with an inert/O₂ ratio of 7.26, equivalence ratio of 0.4, in the temperature range of 840–950 K and at pressure of 25 bar. Fast sampling and gas chromatography were used to acquire and quantify the intermediate species during the ignition delay of the same mixture at $P = 25.3$ bar and $T = 905$ K. The ignition delay times and quantitative measurements of the mole fraction time histories of methane, ethene, propene, *iso*-butene, *iso*-butyraldehyde, *iso*-butanol, and carbon monoxide were compared with predictions from the detailed mechanisms developed by Sarathy et al., Merchant et al., and Cai et al. It is shown that while the Sarathy mechanism well predicts the overall ignition delay time, it overpredicts ethene by a factor of 6–10, underpredicts *iso*-butene by a factor of 2, and overpredicts *iso*-butyraldehyde by a factor of 2.

Reaction path and sensitivity analyses were carried out to identify the reactions responsible for the observed inadequacy. The rates of *iso*-butanol hydrogen atom abstraction by OH radical and the beta-scission reactions of hydroxybutyl radicals were updated based on recently published quantum calculation results. Significant improvements were achieved in predicting ignition delay at high pressures (25 and 30 bar) and the species concentrations of ethene and *iso*-butene. However, the updated mechanism still overpredicts *iso*-butyraldehyde concentrations. Also, the updated mechanism degrades the prediction in ignition delay at lower pressure (15 bar) compared to the original mechanism developed by Sarathy et al.

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1. Introduction

In recent years, the bio-butanol isomers including *n*-butanol, 2-butanol and *iso*-butanol have received extensive attention as the next generation biofuel [1]. This work focuses on *iso*-butanol because it is used as a blending component in petroleum fuels [2], while its oxidation mechanism is also a building block in developing the combustion kinetics of the larger alcohols.

Previous experiments on *iso*-butanol have been performed in flames [3–7], jet stirred reactors (JSR) [8], and shock tubes [9–15], providing kinetics targets for the development of *iso*-butanol kinetics mechanisms [8–10, 16–19]. Experiments have also been performed in rapid compression machines, although the acquired ignition delay times [20] exhibited significant discrepancies with model

predictions, especially at high pressure (30 bar) and low to intermediate temperature (754–857 K) conditions. Furthermore, intermediate species measurements were shown to be sensitive for evaluating the performance of *iso*-butanol kinetic mechanisms [8,12,19,21,22]. Specifically, from shock tube experiments Yasunaga et al. [12] measured the species concentration profiles during pyrolysis at pressures of 1.2–2.2 atm and temperatures of 1000–1500 K using gas chromatography (GC), while Stranic et al. [21] measured the species time histories of hydroxide (OH), water (H₂O), carbon monoxide (CO), and methane (CH₄) using UV and IR laser absorption during pyrolysis at pressure of 1.7 atm and temperatures of 1400–1520 K. These speciation studies provided insight into the high temperature reaction network for *iso*-butanol pyrolysis, especially the subset of reactions involving fuel decomposition [21]. Furthermore, Welz et al. [22] detected both transient and stable species profiles at 550 K and 750 K at low pressures (4–5.1 Torr) using multiplexed time-resolved synchrotron photoionization mass spectrometry, and Togbé et al. [8] investigated the *iso*-butanol oxidation in a JSR over the temperature range of 770–1250 K at 10 atm and with equivalence ratios of 0.5–4.0. These speciation studies provided insight into the low temperature

* Corresponding author at: Center for Combustion Energy and State Key Laboratory of Automotive Safety and Energy, Room 112, Automobile Research Institute, Tsinghua University, Beijing 100084, China. Fax: +86 10 62798267.

E-mail address: hexin1976@tsinghua.edu.cn, hexin.tsinghua@gmail.com (X. He).

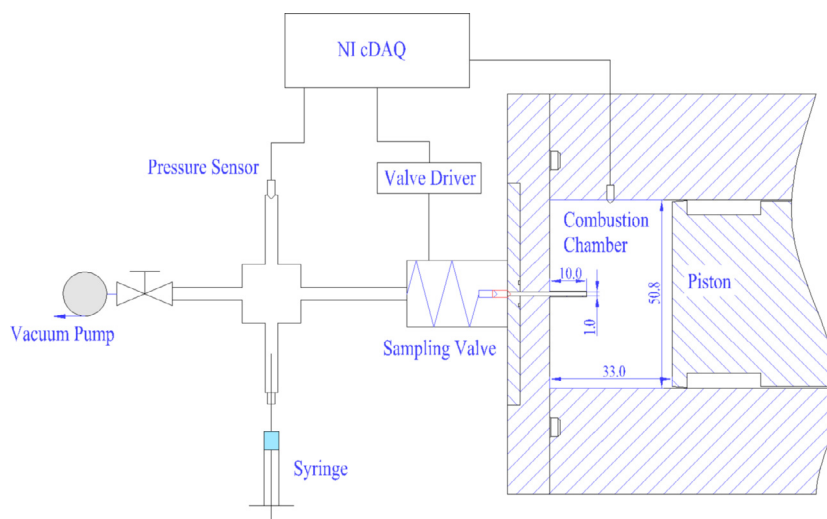


Fig. 1. The schematic of the fast sampling system.

reaction network for *iso*-butanol oxidation, especially the pathways involving oxygen addition to fuel radicals [22].

No speciation studies have been reported at high pressures and low to intermediate temperatures. Weber and Sung [20] commented that none of the existing models can predict the ignition delays at high pressure (30 bar) and low to intermediate temperature (754–857 K) well, and highlighted the importance of the peroxy chemistry in the low temperature pathways of *iso*-butanol oxidation based on sensitivity analysis of the ignition delay time using the Sarathy mechanism [17]. Without intermediate species information, the competing ratios between β -scission reactions and fuel propagation into the low temperature chain branching pathway of oxygen addition to fuel radicals were not investigated directly.

Recognizing the substantial deficiency of the *iso*-butanol chemistry, especially at intermediate temperature and high-pressure conditions, we have experimentally determined the time histories of the intermediate species of CH_4 , ethene (C_2H_4), propene (C_3H_6), *iso*-butene (*i*- C_4H_8), *iso*-butyraldehyde (*i*- $\text{C}_3\text{H}_7\text{CHO}$), CO, carbon dioxide (CO_2) and *iso*-butanol (*i*- $\text{C}_4\text{H}_9\text{OH}$) during the auto-ignition of *iso*-butanol. Furthermore, the production pathways of the measured species were analyzed, species sensitivities to relevant chemical reactions based on the Sarathy mechanism [17] were discussed. The reaction rates of the key reactions, including *iso*-butanol hydrogen atom abstraction by OH radical and the beta-scission reactions of hydroxybutyl radicals, were updated based on recently published quantum calculation results. These then led to a substantially improved version of the Sarathy mechanism [17] to better predict *iso*-butanol auto-ignition. Details of this comprehensive investigation are presented herein.

2. Experimental method

2.1. The rapid compression machine

All experiments were performed using the Tsinghua University Rapid Compression Machine (TU-RCM). A detailed description of the TU-RCM can be found in Di et al. [23]. The mixture in the test section can be compressed to high pressure and high temperature within 25–30 ms. The compression ratio can be controlled by adjusting the length of the test section, and thus achieving different end-of-compression (EOC) gas temperature and pressure. A creviced piston design effectively captures the cooler gas in the boundary layer that is scraped from the chamber wall during compression, thus reducing its mixing with the hot gas in the center of the test section. The test

section was instrumented with a piezoelectric pressure transducer (KISTLER6125C) combined with a charge amplifier (KISTLER 5018A) for pressure measurements.

In this study, the compression and test sections of the rapid compression machine, the fast sampling valve, the sampling chamber, the mixing tank, and all tubing were heated to about 60 °C.

2.2. Test mixtures

The test mixture was prepared in a stainless steel mixing tank at room temperature and then maintained at 60 °C. The mixture composition was determined using the partial pressures of the mixture components. Ultra-high purity grade nitrogen ($\text{N}_2 > 99.999\%$), argon ($\text{Ar} > 99.999\%$), oxygen ($\text{O}_2 > 99.995\%$), and *iso*-butanol ($> 99.5\%$, Sigma-Aldrich) were used. *iso*-butanol partial pressure was controlled below 60% of the saturated vapor pressure at room temperature to prevent condensation. All experiments were conducted at fuel-to-oxygen equivalence ratio of 0.4 with dilution ratio of 7.26, which was selected to avoid high pressure rise during ignition that could cause potential leakage through the sampling valve.

2.3. Fast sampling system

A fast sampling system was developed for intermediate species sampling and quantification. When conducting sampling experiments, a small amount of mixture was withdrawn from the core region of the combustion chamber during the ignition delay period. Only one fast sampling was performed for each ignition experiment. Then the sample was analyzed using gas chromatography (GC) for the species concentrations. By conducting a series of fast sampling experiments at different times during the ignition delay targeting at the same end of compression (EOC) condition, the time-histories of the intermediates were obtained.

The fast sampling system, shown in Fig. 1, mainly consists of a sampling probe, a fast-acting solenoid valve (Parker Series 9), a vacuum pump and a sample tank ($\sim 5.4 \pm 0.1$ mL). The sample tank was equipped with a piezoresistive pressure transducer (KISTLER 4045A5) with an amplifier (KISTLER 4618 A0) and a septum port for gas extraction. Figure 1 shows the cross section view of the combustion chamber along with the sampling probe when the piston is stopped after compression. The clearance height of the test section is 33 mm. The sampling probe, mounted at the center of the end wall, is made of stainless steel with 1 mm in inner diameter. The opening of the sampling probe is located on the chamber center line and

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