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A comprehensive experimental and modeling study of isobutene oxidation

Chong-Wen Zhou^a, Yang Li^a, Eoin O'Connor^a, Kieran P. Somers^a, Sébastien Thion^b, Charles Keesee^b, Olivier Mathieu^b, Eric L. Petersen^b, Trent A. DeVerter^c, Matthew A. Oehlschlaeger^c, Goutham Kukkadapu^d, Chih-Jen Sung^d, Majed Alrefae^e, Fathi Khaled^e, Aamir Farooq^e, Patricia Dirrenberger^f, Pierre-Alexandre Glaude^f, Frédérique Battin-Leclerc^f, Jeffrey Santner^{g,1}, Yiguang Ju^g, Timothy Held^{g,2}, Francis M. Haas^g, Frederick L. Dryer^g, Henry J. Curran^{a,*}

^a Combustion Chemistry Centre, National University of Ireland, Galway, Ireland

^b Department of Mechanical Engineering, Texas A&M University, College Station, TX, United States

^c Department of Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY, United States

^d Department of Mechanical Engineering, University of Connecticut, CT, United States

^e Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

^f Laboratoire Réactions et Génie des Procédés, CNRS-Université de Lorraine, Nancy, France

^g Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, United States

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ABSTRACT

Isobutene is an important intermediate in the pyrolysis and oxidation of higher-order branched alkanes, and it is also a component of commercial gasolines. To better understand its combustion characteristics, a series of ignition delay time (IDT) and laminar flame speed (LFS) measurements have been performed. In addition, flow reactor speciation data recorded for the pyrolysis and oxidation of isobutene is also reported. Predictions of an updated kinetic model described herein are compared with each of these data sets, as well as with existing jet-stirred reactor (JSR) species measurements.

IDTs of isobutene oxidation were measured in four different shock tubes and in two rapid compression machines (RCMs) under conditions of relevance to practical combustors. The combination of shock tube and RCM data greatly expands the range of available validation data for isobutene oxidation models to pressures of 50 atm and temperatures in the range 666–1715 K. Isobutene flame speeds were measured experimentally at 1 atm and at unburned gas temperatures of 298–398 K over a wide range of equivalence ratios. For the flame speed results, there was good agreement between different facilities and the current model in the fuel-rich region. Ab initio chemical kinetics calculations were carried out to calculate rate constants for important reactions such as H-atom abstraction by hydroxyl and hydroperoxyl radicals and the decomposition of 2-methylallyl radicals.

A comprehensive chemical kinetic mechanism has been developed to describe the combustion of isobutene and is validated by comparison to the presently considered experimental measurements. Important reactions, highlighted via flux and sensitivity analyses, include: (a) hydrogen atom abstraction from isobutene by hydroxyl and hydroperoxyl radicals, and molecular oxygen; (b) radical–radical recombination reactions, including 2-methylallyl radical self-recombination, the recombination of 2-methylallyl radicals with hydroperoxyl radicals; and the recombination of 2-methylallyl radicals with methyl radicals; (c) addition reactions, including hydrogen atom and hydroxyl radical addition to isobutene; and (d) 2-methylallyl radical decomposition reactions. The current mechanism accurately predicts the IDT and LFS measurements presented in this study, as well as the JSR and flow reactor speciation data already available in the literature.

* Corresponding author. Fax: +353 91525700.

E-mail address: henry.curran@nuigalway.ie (H.J. Curran).

¹ Current address: Argonne National Laboratory, Lemont, IL, United States.

² Current address: Echogen Power Systems 405 South High Street, Akron, OH, United States.

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The differences in low-temperature chemistry between alkanes and alkenes are also highlighted in this work. In normal alkanes, the fuel radical \dot{R} adds to molecular oxygen forming alkylperoxy ($\dot{R}O_2$) radicals followed by isomerization and chain branching reactions which promote low-temperature fuel reactivity. However, in alkenes, because of the relatively shallow well (~ 20 kcal mol $^{-1}$) for $\dot{R}O_2$ formation compared to ~ 35 kcal mol $^{-1}$ in alkanes, the $\dot{R} + O_2 \rightleftharpoons \dot{R}O_2$ equilibrium lies more to the left favoring $\dot{R} + O_2$ rather than $\dot{R}O_2$ radical stabilization. Based on this work, and related studies of allylic systems, it is apparent that reactivity for alkene components at very low temperatures (< 800 K) emanates from hydroxyl radical addition followed by addition of molecular oxygen to radical. At intermediate temperatures (800–1300 K), alkene reactivity is controlled by hydrogen abstraction by molecular oxygen and the reactions between resonantly stabilized radicals and hydroperoxy radicals which results in chain branching. At higher temperatures (> 1300 K), the reactivity is mainly governed by the competition between hydrogen abstractions by molecular oxygen and $\dot{O}H$ radicals.

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1. Introduction

Isobutene, one of the butene isomers, is a known component of transportation fuels, as well as being an important intermediate in the pyrolysis and oxidation of higher-order branched hydrocarbons such as isooctane. The pyrolysis and oxidation of methyl and ethyl *tertiary*-butyl ethers, used worldwide as octane enhancers, also produces a significant amount of isobutene. Therefore, kinetic modeling of the combustion of commercial fuels requires a reliable computational tool that can predict the pyrolysis and oxidation behaviors of isobutene and similar compounds (1- and 2-butene). Serving as an archetypal alkene fuel, isobutene is also a precursor for soot formation. Following H-atom abstraction from isobutene, a resonantly stabilized 2-methylallyl radical is formed. Allylic species are implicated in the formation of aromatic and subsequent polyaromatic hydrocarbon species [1]; therefore, understanding the oxidation chemistry of isobutene is important in helping mitigate pollutant formation.

Moreover, understanding the combustion chemistry of the butene isomers is a prerequisite for a comprehensive description of the chemistry of C1–C4 hydrocarbon and oxygenated fuels. For the development and validation of combustion models, it is thus crucial to improve our knowledge of detailed C4 combustion chemistry. Building a comprehensive kinetic model for isobutene is also an extension of our work on propene [2,3].

Several research groups have investigated isobutene pyrolysis and oxidation in shock tubes [4–10], a turbulent flow reactor [11], a jet-stirred reactor [12] and in premixed laminar flames [13–15]. Yasunaga et al. [9] investigated the pyrolysis and oxidation of isobutene behind reflected shock waves over a temperature range of 1000–1800 K, measuring the product distribution using infrared laser absorption spectroscopy and gas-chromatography. The authors reported species profiles for CH_4 (methane), C_2H_6 (ethane), C_2H_2 (acetylene), C_3H_4 -p (propyne), C_3H_4 -a (allene), C_3H_6 (propene), 1,3- C_4H_6 (1,3-butadiene) and C_6H_6 (benzene).

Bauge et al. [4] measured ignition delay times of isobutene/oxygen mixture containing 74.45–98.5% argon diluent between 3 ms and 760 ms in the temperature range of 1230–1930 K, over the pressure range of 9.5–10.5 atm and covering the equivalence ratio of 1.0 to 3.0. They also measured speciation data in a continuous-flow stirred-tank reactor at 1 atm in the temperature range 833–913 K. Curran [10] measured ignition delay times for isobutene/oxygen mixtures containing 80.8–98.8% argon diluent in the temperature range 1200–1980 K, at pressures in the range 2.2–4.5 atm, and over the equivalence ratio range of 0.1–4.0.

Dias and Vandoooren [13] studied a lean, premixed isobutene/hydrogen/oxygen/argon flame ($\phi = 0.225$) using molecular beam mass spectrometry at low pressure (40 mbar). They reported the following detected species: H_2 , $\dot{C}H_3$, \dot{O} , $\dot{O}H$, $\dot{H}O_2$, H_2O , C_2H_2 (acetylene), CO , C_2H_4 (ethylene), CH_2O (formaldehyde),

O_2 , Ar, C_3H_6 (propene), CO_2 , CH_3CHO (acetaldehyde), 1,3- C_4H_6 (1,3-butadiene), iC_4H_8 (isobutene), C_3H_6O (acetone), C_4H_6O (1-propen-1-one, 2-methyl) and tautomers of isobutanal (C_4H_8O , prop-1-en-1-ol).

There have been several kinetic mechanisms published in the literature that can be used to simulate isobutene combustion [12,14–16]. Dagaout and co-workers [12] studied the oxidation of isobutene in a jet-stirred reactor at high temperature (~ 800 –1230 K) and at 1, 5 and 10 atm. Measured species profiles were reported as a function of temperature. Molecular species concentration profiles of O_2 , H_2 , CO , CO_2 , CH_2O , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_4 (allene and propyne), C_3H_6 , acetone, acrolein, methacrolein, 1- C_4H_8 , iC_4H_8 , 1,3- C_4H_6 , 1-butyne, 2-methyl-1-butene, 2-methyl-2-butene, and benzene were obtained by probe sampling and gas chromatograph (GC) analysis. They also presented a chemical kinetic reaction mechanism capable of reproducing their speciation results. Zhang et al. [16] developed a model to describe the pyrolysis of the butene isomers in the temperature range 900–1900 K at low pressures (~ 7.5 –12.5 Torr), in which kinetic data for the thermal decomposition of butene isomers was measured and recently adopted in the kinetic model of isomeric butanols by Cai et al. [17]. Schenk et al. [14] developed a high-temperature kinetic model for the butene isomers based on a validation against low-pressure laminar premixed flames. However this study did not include some reactions essential to the ignition process in the low- to intermediate-temperature range. Most recently, Law and co-workers [15] reported laminar flame speeds and ignition temperatures for non-premixed counter-flow flames at normal and elevated pressures. Their mechanism was built on previous studies by Zhang et al. [16] and Cai et al. [17] and included additional rate constants for the reactions of isobutene with \dot{H} and \dot{O} atoms and $\dot{O}H$, $\dot{H}O_2$ and $\dot{C}H_3$ radicals.

In view of the above considerations, we can see that there is a lack of experimental data available in the literature for isobutene at low temperatures (600–1000 K) and at high pressures (> 10 atm), which are conditions of direct relevance with respect to gasoline, diesel, and low-temperature combustion (LTC) engine technologies.

2. Experimental methods

Table 1 compares the experimental conditions investigated as part of this study to those of studies found in the literature. Ignition delay times for isobutene oxidation were measured in four different shock tube facilities and two rapid compression machines (RCMs) shown below. Laminar flame speeds for isobutene were measured at the Université de Lorraine (LRPG). Spherical flame speed measurements were also recorded at Princeton University (PU) and Texas A&M University (TAMU). All experimental data are provided in the appended Supplementary material.

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