# An extensive experimental and modeling study of 1-butene oxidation

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## ABSTRACT

In this study, a series of ignition delay time (IDT) experiments of 1-butene were performed in a high-pressure shock tube (HPST) and in a rapid compression machine (RCM) under conditions of relevance to practical combustors. This is the first 1-butene IDT data taken at engine relevant conditions, and the combination of HPST and RCM results greatly expands the range of data available for the oxidation of 1-butene to higher pressures (10–50 atm), lower temperatures (670–1350 K) and to a wide range of equivalence ratios (0.5–2.0).

A comprehensive chemical kinetic mechanism to describe the combustion of 1-butene has simultaneously been applied. It has been validated using the IDT data measured here in addition to a large variety of literature data: IDTs, speciation data from jet-stirred reactor (JSR), premixed flame, and flow reactor, and laminar flame speed data. Important reactions have been identified via flux and sensitivity analyses including: (a) H-atom abstraction from 1-butene by hydroxyl radicals and molecular oxygen from different carbon sites; (b) addition reactions, including hydrogen atom and hydroxyl radical addition to 1-butene; (c) allylic radical chemistry, including the addition reactions with methyl radical, hydroperoxy radical and self-recombination; (d) vinylic radical chemistry, including the addition reaction with molecular oxygen; (e) alcohol radical chemistry, including the Waddington type propagating reaction pathways and alkyl radical low-temperature branching chemical pathways.

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## 1. Introduction

Alkenes are important intermediates formed during the combustion of larger hydrocarbons and alcohols. Moreover, liquefied petroleum gas (LPG) produced during oil refining contains a significant quantity of alkenes, particularly propene and butenes [1], with gasoline fuel containing butenes, pentenes, and hexenes in various amounts. Butene is the shortest alkene with structural isomers including, isobutene, 1-butene, cis-2-butene, and trans-2-butene. 1-butene is the smallest unsaturated hydrocarbon having a secondary allylic carbon group and a primary carbon group which exhibit both alkane- and alkene-type chemistry.

There have been some high-temperature and low-pressure experimental and kinetic modeling studies of 1-butene consumption, including pyrolysis and oxidation. The types of reactors and conditions studied are shown in Table 1.

Most recently, Zhao et al. [9] developed a high temperature kinetic model for the four butene isomers (1-, trans-2-, cis-2-, and isobutene) validated using laminar flame speeds and non-premixed

counter-flow ignition temperatures at pressures of 2, 5, and 10 atm. Furthermore, the critical reaction paths for butene isomer oxidation during the induction period for ignition, particularly the allylic H-atom abstractions by ȮH radical, were systematically updated with rate coefficients from *ab-initio* calculations and kinetic theory.

Schenk et al. [7] studied premixed, low-pressure (40 mbar), flat, argon-diluted (25%) flames of three of the butene isomers (1-, trans-2-, and isobutene) under fuel-rich ($\varphi = 1.7$) conditions. This was the first detailed flame study of the butene isomers performed under fuel-rich conditions. The isomer-specific species information and the quantitative mole fraction profiles of more than 30 stable and radical species were measured using a newly developed analytical combination of high-resolution in-situ molecular-beam mass spectrometry (MBMS) and *in-situ* gas chromatography (GC), and it was used to validate and improve the subset of $C_4$ kinetics in a general hydrocarbon oxidation mechanism based on the work of Hoyermann et al. [10].

Zhang et al. [6] measured product and intermediate concentrations during the pyrolysis of 1-, 2-, and isobutene using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) with the molecular-beam sampling technique in the temperature range 900–1900 K at a pressure of 3 Torr. Based on the experimental results, a kinetic model consisting of 76 species and

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**Table 1**
List of experimental literature data for 1-butene pyrolysis and oxidation.

| No. | Reactor | $\varphi$ | Diluent (%) | $T$ (K) | $p$ (atm) | References |
|---|---|---|---|---|---|---|
| 1 | Shock tube | 0.5, 1.0, 2.0 | 87.0–96.0 (Ar) | 1000–1700 | 1.2, 4.0, 16.0 | Pan et al. [2] |
| 2 | Shock tube | 0.5, 1.0, 2.0 | 87.0–96.0 (Ar) | 1200–1670 | 6.6–8.9 | Heyberger et al. [3] |
| 3 | Combustion vessel | 0.7–1.4 | 75.31–77.11 | – | 1 | Fenard et al. [4] |
| 4 | Jet-stirred reactor | 0.25, 0.5, 1.0, 2.0 | 97.5–99.6 | 900–1440 | 1 | Fenard et al. [4] |
| 5 | Jet-stirred reactor | 0.15, 1.0, 4.0 | 90.0–93.85 | 900–1200 | 1.0–10.0 | Chakir et al. [5] |
| 6 | Flow reactor | $\infty$ | 96.0 (Ar) | 900–1900 | 0.004–0.016 | Zhang et al. [6] |
| 7 | Flame burner | 1.7 | 25.0 (Ar) | 2204 | 0.04 | Schenk et al. [7] |
| 8 | Counterflow | 0.7–1.7 | 74.6–77.1 | 2329 | 1.0, 2.0, 5.0, 10 | Davis et al. [8] |
| 9 | Counterflow | – | – | 1000–1300 | 1.0–5.0 | Zhao et al. [9] |

232 reactions was also developed to simulate the measured species mole fractions.

Fenard et al. [4] conducted experiments for the oxidation of 1- and cis-2-butene in a jet-stirred reactor and in a combustion vessel. The concentration profiles of stable species were measured in the temperature range 900–1440 K, at atmospheric pressure, for different equivalence ratios ($0.25 \leq \varphi \leq 2$). Laminar burning velocities were determined at $p = 1$ atm, at unburned gas temperatures in the range of 300–450 K, and at equivalence ratios in the range 0.8–1.4. A chemical kinetic mechanism based on a previously proposed scheme for the oxidation of hydrocarbons was also used to reproduce their experimental data (201 species involved in 1787 reactions).

Pan et al. [2] measured IDTs of 1-butene oxidation at pressures of 1.2, 4.0, and 16.0 atm, in the temperature range 1000–1700 K, and at equivalence ratios of 0.5, 1.0, and 2.0 in 87–96% argon diluent. Three widely used models, NUIG AramcoMech1.3 [11], USC Mech 2.0 [12] and the LLNL C4 [13] model were used to simulate the measured ignition delay times. It was found that none of the models could satisfactorily reproduce the experimental data, especially at lower temperatures.

Chakir et al. [5] measured the concentrations of molecular species produced from the oxidation of 1-butene in a jet-stirred reactor in the temperature range 900–1200 K, at pressures extending from 1 to 10 atm, for a wide range of fuel–oxygen equivalence ratios (0.15–4.0). A chemical kinetic reaction mechanism developed previously [14, 15] was used to simulate the experimental data.

Heyberger et al. [3] automatically generated a kinetic model for 1-butene using EXGAS, and it was used to simulate two sets of experimental results: species measurements in a jet-stirred reactor between 900 and 1200 K [5], and IDT measurements in a ST at temperatures in the range 1200–1670 K, at pressures from 6.6 to 8.9 atm, equivalence ratios from 0.5 to 2.0, using argon as bath gas.

There is still a lack of experimental data for 1-butene oxidation available in the literature at engine relevant, high-pressure, and low-temperature conditions. In addition, based on previous work on propene [16, 17], isobutene [18], and 2-butene [19], a comprehensive kinetic model for 1-butene oxidation will extend our understanding on alkene combustion chemistry.

In view of the above considerations, we have measured ignition delay times in a high-pressure shock tube (HPST) and in a rapid compression machine (RCM) at low temperatures (600–1000 K) and high pressures (>10 atm), which are of direct relevance to gasoline, diesel, and low-temperature combustion (LTC) engine technologies. In this work a comprehensive chemical kinetic mechanism to describe 1-butene oxidation has been developed, including detailed low-, intermediate- and high-temperature reaction pathways specific to unsaturated fuel chemistry. The model has been validated against a wide range of ignition delay time measurements from this work, the speciation and flame speed results from jet-stirred reactor, flow reactor, flame in the literature.

**Table 2**
Percentage molar composition of 1-butene mixtures.

| | Fuel | $O_2$ | Diluent | $\varphi$ | $p$ (atm) |
|---|---|---|---|---|---|
| 1-butene | 1.72 | 20.64 | 77.64 | 0.5 | 10, 30, 50 |
| | 3.38 | 20.29 | 76.33 | 1.0 | 10, 30, 50 |
| | 6.54 | 19.63 | 73.83 | 2.0 | 10, 30, 50 |

## 2. Experimental methods

IDT measurements for 1-butene were performed in a HPST and in an RCM located at NUI Galway (NUIG). Table 2 provides the detailed experimental conditions investigated in the present study. All fuels were acquired from Sigma Aldrich at 99.5% purity. Oxygen, nitrogen, argon and carbon dioxide were acquired from BOC Ireland at high purity ($\geq$99.5%).

### 2.1. NUIG HPST

The HPST at NUIG was used to measure IDT for 1-butene at intermediate to high temperatures ($\sim$900–1300 K) at 10, 30, and 50 atm. The tube has an inner diameter of 63.5 mm, a 3 m driver section, a 5.7 m driven section, and a 3 cm double diaphragm section that is located between the driver and driven sections. Two pre-scored aluminum diaphragms are placed in the double-diaphragm section, and used to initiate the incident shock wave.

As to the diagnostic system, six PCB 113B24 pressure transducers are mounted in the sidewall of tube at known positions. The shock velocity at the end-wall is calculated by linearly extrapolating the five velocities to the end-wall. A Kistler 603B pressure transducer is mounted in the end-wall to measure the pressure versus time history behind the reflected shock wave. The IDT is defined as the interval between the rise in pressure due to the arrival of the shock wave at the end-wall and the rapid rise in pressure due to the ignition event, as shown in Fig. 1.

Post-shock conditions were determined using the normal shock relations as employed by Gaseq [20] utilizing measurements of incident shock velocity, initial temperature and pressure, and the thermodynamic properties of the shock-heated fuel/oxidizer mixtures. More detailed information can be found in a previous paper [21].

As to the uncertainty quantification of IDT measurements in our HPST, it has been reported by Petersen et al. [22] that the uncertainty of the reflected shock temperature is mainly attributable to the uncertainty of the incident shock velocity, which is determined by the uncertainties in the precise positions of the pressure transduces and the shock pass time recorded by the signal relayed to the oscilloscope from the pressure transducers. We have adopted a standard rt-sum-squares (RSS) method used by Petersen et al.