Laminar flame speeds, counterflow ignition, and kinetic modeling of the butene isomers

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Abstract

Laminar flame speeds and ignition temperatures of nonpremixed counterflow were measured experimentally for the butene isomers at normal and elevated pressures. Results show that the flame speed increases in the order of isobutene, trans-2-butene, and 1-butene. Furthermore, isobutene has the highest ignition temperature, while those of trans-2-butene and cis-2-butene are quite similar to each other and are slightly higher than that of 1-butene. These results indicate that the reactivities of the butene isomers increase in the order of isobutene, 2-butene, and 1-butene. Furthermore, the critical reaction paths for butene isomer oxidation during ignition were analyzed by sensitivity analysis and a new kinetic model was developed with updated rate coefficients from *ab initio* calculation and kinetic theories. Simulations with the present kinetic model agree well with the measured laminar flame speeds, counterflow ignition temperatures as well as recent laminar flame speciation and ignition delay times for all butene isomers.
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Keywords: Butene; Isomeric effects; Laminar flame speed; Counterflow ignition; Kinetic model

1. Introduction

The isomeric structure of a fuel can fundamentally affect its combustion chemistry and consequently the nature of its practical applications. For example, the research octane numbers of the heptane isomers vary from 0 for *n*-heptane to 112 for 2,2,3-trimethylbutane [1]. Furthermore, since the mass diffusivities of the isomers are close to each other, chemical effects, which are usually coupled to diffusional effects, can be easily isolated and revealed.

Butene (C_4H_8), being the smallest alkene with isomeric structures, is a common component in many practical fuels. Compared with the larger alkenes, it has the essential features of the double bond variation with the smallest number of isomers, and its four isomers are all gaseous at room temperature and moderate pressures. Experimental studies have been performed on various aspects

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of butene combustion, including pyrolysis, oxidation, diffusion flames, and premixed flames [2–12], although few were specifically concerned with the effects of isomeric fuel structures. In addition, while kinetic models have been developed for the combustion process of specific butene isomers [2,6–8,11,13], only a few have been reported for all the butene isomers. This is possibly due to the paucity of experimental studies of isomeric effects at identical conditions. Among these studies, Zhang et al. [11] developed a model to describe the pyrolysis of butene isomers between 900 and 1900 K under low pressures, in which relevant kinetic data for the thermal decomposition of butene isomers was proposed and recently adopted in the kinetic model of isomeric butanol by Cai et al. [14]. Most recently, Schenk et al. [12] developed a high temperature kinetic model for butene isomers based on the validation against the low pressure laminar premixed flames which, however, did not include some reactions essential to the ignition process in the low- to intermediate-temperature range. Furthermore, in order to construct reliable kinetic models for isomeric butenes, it is necessary to provide extensive targets from well-defined experiments to quantify the kinetic parameters from multiple dimensions and in broader temperature/pressure/equivalence ratio ranges.

In view of the above considerations, we have performed experimental determination of the laminar flame speeds and nonpremixed counterflow ignition temperatures of butene isomers at normal and elevated pressures of 2, 5 and 10 atm, with the experimental conditions kept functionally identical so as to reveal the isomeric effects on the combustion chemistry. These experimental data were further simulated with the high temperature kinetic model of $H_2/CO/C_1–C_4$ compounds developed by Wang et al. [15] (hereafter referred to as USC Mech II), by incorporating recent thermodynamic, kinetic, and transport updates relevant to the oxidation of hydrogen, carbon monoxide, and $C_1–C_4$ hydrocarbons. The model prediction, however, exhibited substantial differences with the present experimental results. It is identified later that several reaction pathways with crucial impact on ignition were not adequately described in Refs. [12,15], particularly the allylic H-abstraction by the OH radical with isomeric butenes, the OH radical induced oxidation reactions of butenes and reactions between butenyl radicals and HO_2/O_2, etc. In this work, such reaction paths are systematically considered with their kinetic rates evaluated from the literature. With these effects incorporated in the current model, improved agreement with the experimental data is achieved.

In the following we shall sequentially present the experimental specifications, the development of the butene mechanism, the experimental results as well as the comparison with the present model prediction.

2. Experimental specifications

A combustion bomb with a novel double-chamber design to allow for high- and constant-pressure experimentation [16] was used to determine the laminar flame speeds from spark-ignited, outwardly-propagating spherical flames. Details of the apparatus, its operation procedure and constraints such as the ignition transient and chamber confinement effects, as well as the need to use a nonlinear regression analysis to eliminate stretch effects, are given in Refs. [16,17]. The uncertainties of the equivalence ratio, ϕ, and the measured laminar flame speed were estimated to be $\pm2\%$ and ±2 cm/s, respectively.

The ignition temperatures of the butene isomers were measured by using a nonpremixed counterflow apparatus and procedure, discussed in Ref. [18]. The ignition temperature was corrected for radiative and convective heat transfer, with an estimated maximum uncertainty of ±30 K, which constitutes the *systematic* error of the experimental data. The qualitative trend of the data, however, is influenced mainly by the *relative* error, which denotes the repeatability of our experimental data and ranges within ±2–5 K. The velocity field corresponding to the incipient ignition state was measured by a two-component Laser Doppler Velocimetry system with frequency shifting, with the axial velocity gradient on the air side of the stagnation surface yielding the relevant strain rate.

3. Preliminary comparison and modeling assessment

Simulation of the freely-propagating spherical flame was performed using the Sandia Premix code [19], with enough grid refinement over a domain of 15 cm. Simulation of the nonpremixed counterflow ignition was performed using the flame continuation method of Nishioka et al. [20] based on the stagnation flow code of Smooke et al. [21], with detailed chemistry [22] and transport [23]. The computation determines the steady-state solution for different hot boundary temperatures assuming potential flow, yielding the ignition–extinction S-curve [24,25] with the ignition temperature identified as that of the hot boundary temperature at the lower turning point of the primary S-curve.

Upon simulation of the experiments using the USC Mech II, substantial differences were found between the calculated and experimental results for the ignition temperatures of all the isomers as well as the flame speeds of 2-butene, which lumps cis-2-butene and trans-2-butene in the model. Specifically, Fig. 1 shows that the model over-predicts the ignition temperatures by about 65–100 K at 1–2 atm, and that the predicted trend