Experimental and kinetic modeling investigation on pyrolysis and combustion of *n*-butane and *i*-butane at various pressures

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ABSTRACT

Butane is the smallest alkane with normal and branched isomers. To obtain insight into the effects of fuel structure and pressure on its intermediate-to-high temperature combustion chemistry, flow reactor pyrolysis and laminar burning velocities of the butane isomers were investigated at various pressures. In the pyrolysis experiments, species profiles were measured as function of the heating temperature at 0.04, 0.2 and 1 atm using synchrotron vacuum ultraviolet photoionization mass spectrometry. Laminar burning velocities of both *n*-butane/air and *i*-butane/air mixtures were measured at 298 K and 1–10 atm using spherically expanding flames. It was observed that both the pyrolysis and combustion behaviors of the butane isomers were influenced by the fuel structures. A detailed kinetic model of butane isomers was developed and validated against the new experimental data. Both rate of production analysis and sensitivity analysis were performed to give insight into the chemistry of butane pyrolysis and combustion. In the flow reactor pyrolysis, the weaker primary-tertiary C–C bond than the primary-secondary and secondary-secondary C–C bonds leads to lower initial decomposition temperatures of *i*-butane than *n*-butane. Under both pyrolysis and combustion conditions, the reaction pathways towards C_2 and C_3 species pool are emphasized for the decomposition of *n*-butane and *i*-butane, respectively. The more abundant production of C_3 precursors explains the higher concentrations of benzene in the *i*-butane pyrolysis, while the higher laminar burning velocities of *n*-butane/air mixtures at all investigated pressures are mainly attributed to the easy production of H atom from *n*-butane decomposition and the dominance of the reactive C_2 chemistry. Moreover, the *i*-butane/air flames exhibit stronger pressure dependence than the *n*-butane/air flames. The model was further validated against a wide range of experimental data in the literature, including ignition delay times and species profiles in flow reactor pyrolysis and oxidation, shock tube pyrolysis and oxidation, jet-stirred reactor oxidation and laminar premixed flames.

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1. Introduction

Alkanes constitute an important component family in transportation fuels [1,2], playing a critical role in determining their combustion characteristics such as ignition, flashback, engine knock and combustion instabilities [3]. Among them, butane is the smallest alkane with both normal and branched isomers, and is a major component of liquefied petroleum gas [4,5] and a minor component of natural gas [6] and syngas [7]. The butane isomers, i.e. *n*-butane and *i*-butane, consist of primary, secondary and tertiary carbon atoms and consequently three different types of C–C bonds. Thus they are widely used as prototype fuels for understanding the combustion chemistry of large alkanes [8–10].

Extensive experimental investigations have been conducted on *n*-butane and *i*-butane combustion, leading to the determination of global combustion parameters such as ignition delay times [5,8–17] and laminar burning velocities [18–30], as well as speciation in flow reactor pyrolysis [31,32] and oxidation [33], high-pressure shock tube pyrolysis and oxidation [34–36], jet-stirred reactor (JSR) oxidation [37–39] and rich premixed flames [40–

42]. Specifically, Dagaut et al. [37,39] investigated the JSR oxidation studies of the butane isomers at 1 atm, 1000–1450 K and equivalence ratios of 0.5, 1.0 and 1.5 using gas chromatography (GC). Oehlschlaeger et al. [43] measured the time history of the methyl radical concentration in the shock tube pyrolysis of *n*-butane/Ar and *i*-butane/Ar using laser absorption spectroscopy at 0.2–8.8 atm and 1297–1601 K, and determined the rate constants of the C−C bond dissociation reactions. Oßwald et al. [41] studied rich ($\phi = 1.71$) laminar premixed flames of *n*-butane and *i*-butane at 40 mbar using electron-impact ionization mass spectrometry (EIMS) and synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). Zhang et al. [32] identified the pyrolysis products of the butane isomers at a very low pressure (3 Torr) and 823–1823 K using SVUV-PIMS at the National Synchrotron Radiation Laboratory (NSRL), but without providing any concentration information. Ogura et al. [5] measured the ignition delay times of different ratios for *n*-butane/*i*-butane mixtures diluted in Ar behind reflected shock waves at 1.9–2.4 atm, 1200–1600 K, and equivalence ratio of 0.72. Healy et al. [9,10] measured the ignition delay times of *n*-butane and *i*-butane at various equivalence ratios (0.3, 0.5, 1, and 2) in a shock tube and a rapid compression machine, extending the range of pressures up to 30 atm and temperatures down to 690 K. Laminar burning velocities of *n*-butane/air and *i*-butane/air mixtures were measured at 298 K and 1 atm by several groups [18,24,26], while Farrell et al. [44] measured the values for the butane isomers at 450 K and 304 kPa. Marshall et al. [45] calculated the laminar burning velocities of *n*-butane at 1–15 atm from the pressure record in a constant volume combustion vessel. While these studies provide valuable validation data for the development of kinetic models of butane isomers [9,10,42,46], further investigations on the pyrolysis and combustion of butane isomers are still desired. Specifically, it is noted that the pyrolysis of butane isomers was performed with limited speciation information, while large discrepancies in the laminar burning velocities of butane isomers exist between the high-pressure results of Farrell et al. [44] and Marshall et al. [45], which leads to the need of more high-pressure measurements [45].

In this work, the flow reactor pyrolysis of *n*-butane and *i*-butane were studied at 0.04, 0.2 and 1 atm over the temperature range of 840–1350 K by using SVUV-PIMS to help understand the different pyrolysis behaviors between the butane isomers. The laminar burning velocities were measured from spherically expanding flames at 298 K and 1–10 atm to provide new data for exploring the high-pressure combustion characteristics of the butane isomers. A kinetic model for the butane isomers was developed and validated comprehensively against the experimental data obtained in this work, as well as the literature data from intermediate to high temperatures including species profiles and global combustion parameters. Kinetic analysis including the rate of production (ROP) analysis and sensitivity analysis has also been conducted to provide insight into the combustion chemistry influenced by the fuel structure, pressure and equivalence ratio.

2. Experimental methods

2.1. Flow reactor pyrolysis

The flow reactor pyrolysis experiment was performed at NSRL, University of Science and Technology of China (USTC). Detailed descriptions of the synchrotron VUV beamline (BL03U) are given in Ref. [47]. The schematic diagram of the pyrolysis reactor is shown in Fig. 1(a). Compared with our previous pyrolysis reactor [48–51], heating length in this reactor was extended from 150 mm to 224 mm and the density of the heating wire was doubled in region A (the first quarter heating length) and region C (the last eighth heating length). Consequently a broader high-temperature

region can be obtained at the temperature profile along the reactor centerline, as shown in Fig. 1(b). During the pyrolysis experiment, the gas flow rates of fuel (*n*-butane or *i*-butane, 99.9%) and diluent gas (argon, 99.999%) were controlled at 20 and 980 standard cubic centimeters per minute (SCCM) by mass flow controllers. According to Shrestha et al. [31], the heat of reaction in such diluted pyrolysis systems is weak and was found to have only very small influence on the centerline temperature profiles ($\leq$5 K). This very small variation was also considered in the uncertainties of the measured temperatures. The fuel/Ar mixtures were then fed into a flow tube which is made of α-alumina to reduce wall catalytic effects [52,53]. Previous study [54] has shown that α-alumina is almost 1000 times less active than reforming grade γ-alumina under the same surface area, while its surface area of unit mass is an order of magnitude smaller than reforming grade γ-alumina. A small inner diameter (i.d.) of 7.0 mm of the flow tube was selected to ensure strong radial diffusion effects, reduce radial concentration gradients and achieve adequately homogeneous reaction circumstances [55–57]. The pyrolysis species were sampled at 5 mm downstream from the outlet by a quartz nozzle. The formed molecular beam was ionized by the synchrotron VUV light after entering the photoionization chamber through a nickel skimmer, followed by detection by a home-made reflected time-of-flight mass spectrometer (RTOF-MS). A series of pressures (0.04, 0.2 and 1 atm) were investigated in this work. Using the same strategy as that of Skjøth-Rasmussen et al. [59], the centerline temperature profiles of the flow tube were measured under non-reacting conditions (i.e., 1000 SCCM flow rate of argon) after experiment by an S-type thermocouple, which is not shown in Fig. 1(a). The measured centerline temperature profiles were identified as the maximum values (T_{max}) [51,58] and the relationships between the mole fractions of species measured at the outlet of the flow tube and T_{max} are provided as experimental data. The uncertainty was estimated to be within $\pm$30 K. The data evaluation method can be found in previous work [50], and the photoionization cross sections (PICSs) are available in the online database [60]. Mole fraction uncertainties were estimated to be 10%, 25% and a factor of 2 for the major species, intermediates with known PICSs and those with estimated PICSs, respectively.

2.2. Laminar burning velocity

Detailed descriptions of the laminar burning velocity apparatus at Shanghai Jiao Tong University (abbr. SJTU apparatus) are given in [61]. Briefly, the constant-volume, single-chamber apparatus consists of a 2.77 L cylindrical combustion vessel (150 mm i.d., 152 mm length), a 9.06 L premixing vessel, a sample inlet system, an ignition coil and a schlieren system. Mixtures of synthetic air (21% O_2 and 79% N_2) and fuel (*n*-butane or *i*-butane) were prepared using the partial pressure method in the premixing vessel. After mixing by a magnetic stirrer, the combustible gas was fed into the combustion vessel and ignited by two tungsten electrodes. Thus, a spherically expanding flame was formed and the schlieren system with a high speed camera was used to record the flame propagating process. The camera was running at 10,000 frames per seconds (fps), with a resolution of 480×480 pixels, such that the spatial resolution of the camera corresponded to around 0.15 mm/pixel.

Descriptions of the constant-pressure, dual-chamber cylindrical combustion vessel at Princeton University (abbr. PU apparatus) are given in Ref. [62]. Briefly, the dual-chamber vessel consists of an inner chamber (82.55 mm i.d., 127 mm length) and an outer chamber, with the wall of the inner chamber consisting of a series of holes that could be mechanically opened and closed so as to control the initial separation of the gases between the two chambers. The inner chamber was initially filled with the test combustible mixture, while the outer chamber with nitrogen to match