Combustion and Flame 161 (2014) 3003–3013

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

An experimental and modeling study of 2-methyl-1-butanol oxidation in a jet-stirred reactor

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ARTICLE INFO

Article history:
Received 19 March 2014
Received in revised form 28 May 2014
Accepted 5 June 2014
Available online 3 July 2014

Keywords:
Jet-stirred reactor
2-Methyl-1-butanol
Oxidation
Chemical kinetics

ABSTRACT

In an effort to understand the oxidation chemistry of new generation biofuels, oxidation of a pentanol isomer (2-methyl-1-butanol) was investigated experimentally in a jet-stirred reactor (JSR) at a pressure of 10 atm, equivalence ratios of 0.5, 1, 2 and 4 and in a temperature range of 700–1200 K. Concentration profiles of the stable species were measured using GC and FTIR. A detailed chemical kinetic mechanism including oxidation of various hydrocarbon and oxygenated fuels was extended to include the oxidation chemistry of 2-methyl-1-butanol, the resulting mechanism was used to simulate the present experiments. In addition to the present data, recent experimental data such as ignition delay times measured in a shock tube and laminar flame speeds were also simulated with this mechanism and satisfactory results were obtained. Reaction path and sensitivity analyses were performed in order to interpret the results.

1. Introduction

Given the ongoing worldwide energy demand and non-sustainable character of fossil fuels, biofuels have recently been given a lot of interest. Among these, bio-ethanol dominates over 90% of the total biofuel production and is currently being used as a first generation biofuel despite its low energy density (21 kJ/mL) compared to gasoline, and its hygroscopic character. Recently larger alcohols have been the focus of many studies due to their higher energy density and better solubility in gasoline. Although many experimental studies now exist on alcohols up to C_4, fewer studies are available for larger ($C \geqslant 5$) alcohols. As far as the C_6 alcohols are concerned, Togbé et al. studied *n*-hexanol oxidation in a jet stirred reactor and a spherical bomb [1], Heufer and co-workers measured ignition delay times of *n*-hexanol at high pressures in a shock tube and a rapid compression machine [2]. Among the pentanol isomers, *iso*-pentanol is the most widely studied one; its oxidation has been investigated in a jet stirred reactor at an operating pressure of 5–10 atm and various equivalence ratios [3,4], in laminar flames [4,5] as well as in shock tubes and a rapid compression machine for ignition delay times [4,6,7]. Similarly, experimental kinetic studies exist on the *n*- isomer; Togbé et al. [8] studied *n*-pentanol oxidation in a jet stirred reactor and in laminar flames, Tang et al. [6] and Heufer et al. [2] studied auto-ignition of this biofuel behind reflected shocks.

The present study focuses on a mono-methylated isomer of pentanol; 2-methyl-1-butanol (2-MB). Atsumi et al. [9] studied non-fermentative pathways to synthesize larger alcohols (than ethanol) including 2-MB, from glucose, which is a renewable source. To the best of our knowledge, the only kinetic studies available on 2-MB combustion focus on global reactivity. Li and co-workers [10] recently reported laminar flame speed measurements of this alcohol in a spherically propagating flame at unburned mixture temperatures of 393, 433 and 473 K and pressures of 1, 2.5, 5 and 7.5 bar, they found that flame speeds of 2-MB were higher than *iso*-octane and lower than ethanol. Tang and co-workers measured ignition delay times of 2-MB behind reflected shock waves at 1 and 2.6 atm and over a temperature range of 1100–1500 K, along with *n*- and *iso*-pentanol [6], they also developed a kinetic mechanism in order to represent their results and concluded that further improvements would be needed. They observed that 2-MB reactivity was between the latter two. As far as 2-MB is concerned, no speciation data is reported so far.

This study aims to provide new kinetic data through a detailed product analysis of 2-MB oxidation in a jet stirred reactor. Four dilute mixtures with equivalence ratios from 0.5 to 4.0 were investigated at 10 atm at a residence time of $\tau = 0.7$ s between 700 and

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http://dx.doi.org/10.1016/j.combustflame.2014.06.004

1200 K. A chemical kinetic mechanism is used to represent the present data as well as the available literature data discussed above.

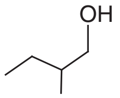
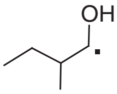
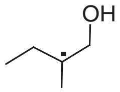
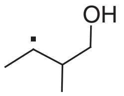
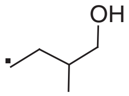
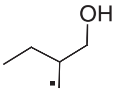
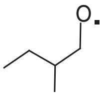
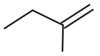
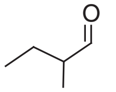
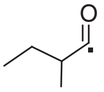
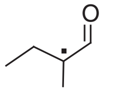
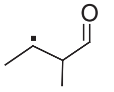
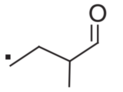
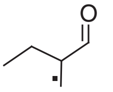
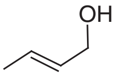
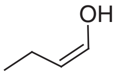
2. Experimental

The jet stirred reactor experimental setup used here has been described earlier [8,11]. The reactor consists of a 4 cm diameter fused silica sphere (42 cm^3) equipped with four nozzles of 1 mm i.d. Prior to the injectors, the reactants were diluted with nitrogen (<100 ppm H_2O, <50 ppm O_2, <1000 ppm Ar, <5 ppm H_2 from Air Liquide) and mixed. A high degree of dilution (0.1–0.15% mol. of fuel) was used, reducing temperature gradients and heat release in the JSR. The reactants were high-purity oxygen (99.995% pure form Air Liquide) and high-purity 2-methyl-1-butanol (>99% pure from Aldrich, CAS 137-32-6). The reactants were preheated before injection to minimize temperature gradients inside the reactor. A Shimadzu HPLC pump (LC10 AD VP) with an on-line degasser (Shimadzu DGU-20 A3) was used to deliver the fuel to an in-house atomizer-vaporizer assembly maintained at 200 °C. Good thermal homogeneity along the vertical axis of the reactor (gradients of ca. 1 K/cm) was observed during the experiments by thermocouple measurements (0.1 mm Pt–Pt/Rh-10%, located inside a thin-wall fused silica tube). The reacting mixtures were sampled using a movable fused silica low-pressure sonic probe. The samples were sent to analyzers via a Teflon heated line maintained at 200 °C. Analyses were performed online using a FTIR spectrometer (10 m path length, resolution of 0.5 cm^{-1}, 200 mBar in the cell) and offline after collection and storage in 1 L Pyrex bulbs [12]. Off-line analyses were performed using gas chromatographs (GC) equipped with capillary columns (0.32 mm i.d.: DB-624 and CP-Al_2O_3–KCl, and 0.53 mm i.d.: Carboplot-P7), a TCD (thermal conductivity detector), and an FID (flame ionization detector). Two GC–MS (Varian quadrupole V1200) operating with electron ionization (70 eV) were used for product identification.

The experiments were performed at steady state, at a constant mean residence time, τ, of 0.7 s and a constant pressure of 10 atm, with the reactants continually flowing in the reactor while the temperature of the gas inside the reactor was increased stepwise. A good repeatability of the measurements and a reasonably good carbon balance (typically 100 ± 10%) were obtained in these experiments. Hydrogen and oxygen balances were also checked and found to be within ±10% for most of the experimental points except for a few ones where they reach 12–15%.

Experimental uncertainties can be summarized as follows: uncertainty related to temperature measurements is expected to be less than 10 K, and that related to residence time it is less than 5%, inlet uncertainty is less than 5% for the reactants and that of the measured species is determined as <10% for concentrations higher

Table 1
Structures and enthalpies of formation of some selected species (kcal mol^{-1}, at 298 K) in 2-MB oxidation.

 Butoh2m $\Delta_f H° = -71.88$	 Butoh2m-1 $\Delta_f H° = -28.98$	 Butoh2m-2 $\Delta_f H° = -28.38$	 Butoh2m-3 $\Delta_f H° = -25.28$	 Butoh2m-4 $\Delta_f H° = -23.08$	 Butoh2m-5 $\Delta_f H° = -23.78$	 Buto2m $\Delta_f H° = -20.58$	 But2m1d $\Delta_f H° = -8.68$
 Butal2m $\Delta_f H° = -55.45$	 Butal2m-a $\Delta_f H° = -20.85$	 Butal2m-t $\Delta_f H° = -18.35$	 Butal2m-s $\Delta_f H° = -8.45$	 Butal2m-4 $\Delta_f H° = -6.65$	 Butal2m-5 $\Delta_f H° = -6.65$	 Butoh2d $\Delta_f H° = -37.36$	 Butoh1d $\Delta_f H° = -42.23$

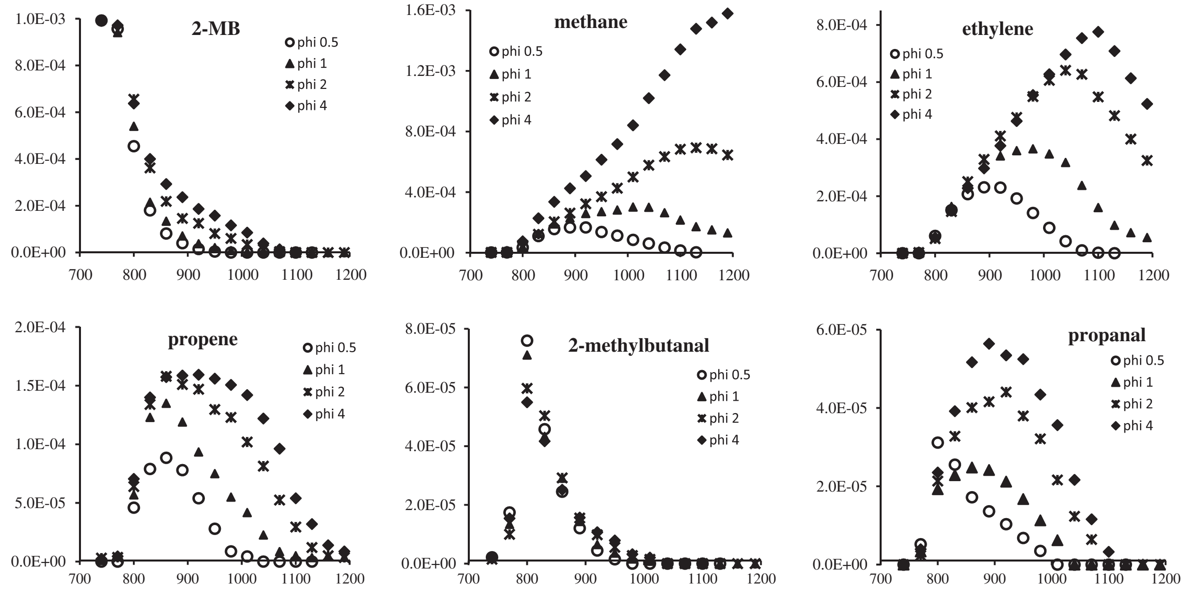


Fig. 1. Experimental mole fraction profiles of some main oxidation products of 2-MB as a function of temperature ($\varphi = 4$ profiles are normalized to an initial fuel concentration of 1000 ppm).