A laminar flame study on di-*n*-butyl ether as a potential biofuel candidate

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ABSTRACT

The combustion chemistry of di-*n*-butyl ether (DBE, $C_8H_{18}O$), conceivable as a potential biofuel candidate, was studied here for the first time under flame conditions with examining a detailed species dataset. Two flames, *i.e.,* a fuel-rich ($\phi = 1.5$) and a fuel-lean ($\phi = 0.8$) one, were analyzed at the same pressure (4 kPa), argon dilution (50%), and cold-gas velocity (60 cm s^{-1}) by molecular-beam mass spectrometry (MBMS) using electron ionization (EI). About 50 species including reactants, diluent, combustion-related intermediates, and products, were detected with a special interest in fuel-specific intermediates, harmful species as well as important soot precursors. *n*-Butanal was detected in high concentration and identified as an important fuel-specific intermediate in the DBE flames, while cyclic soot precursors (*e.g.,* 1,3-cyclopentadiene, benzene, toluene) were detected with low mole fractions (∼10 ppm). The present experimental data were compared to simulations by the kinetic model of Cai et al. [Combust. Flame 161 (2014)] and the very recent model of Thion et al. [Combust. Flame 185 (2017)], with the dual purpose to support the data interpretation and to examine the performance of these models also in comparison to each other. Note that species in the range of C_5 to C_7 (known as important soot precursors) that are not yet addressed in either of the models have been well detected and are presented in the present work.

For further insight into the combustion chemistry of DBE, its fuel-rich flame was also compared to those of successively smaller ethers, namely dimethyl ether (DME) and diethyl ether (DEE). This comparison showed a strong effect of the aliphatic side chains of ethers on the formation of intermediate species. Not unexpectedly, increasing the length of side chains enhances the formation tendency of larger unsaturated hydrocarbons. However, the contribution of highly toxic carbonyl compounds, namely formaldehyde and acetaldehyde, was found to be much lower upon the use of DBE as a fuel than for DME and DEE, respectively. Similarly, DBE was also compared to its half-structurally similar fuels, *i.e., n*-butane and *n*-butanol. This comparison generally indicates that the distribution of hydrocarbon species (except for C_4H_8) in DBE flames is quite similar to those in *n*-butane and *n*-butanol flames, whereas the formation of oxygenated species is very different for the three fuels.

1. Introduction

Di-*n*-butyl ether (DBE, $C_8H_{18}O$), a long-chain linear symmetric ether, has been recently suggested as a promising next-generation biofuel. This fuel could be produced *via* the dehydration of *n*-butanol which is accessible from lignocellulosic biomass [1,2]. DBE has attractive properties for compression ignition engines, such as a high cetane number (∼100) and high energy density (∼38 MJ/kg versus ∼28 MJ/kg for dimethyl ether) [1,3–6]. The addition of DBE to diesel has been shown to decrease the soot emissions of diesel engines [3–6]. Compared to diesel fuel and to its structural isomer 1-octanol, DBE shows lower CO and hydrocarbon (HC) emissions [6] from a single-cylinder engine. Moreover, DBE in blends with 2-methyltetrahydrofuran has been proposed as a promising biofuel mixture for diesel engines [7]. Also, the addition of DBE into diesel or biodiesel fuel is found to improve the spray atomization performance effectively [8–10].

While the combustion chemistry of short-chain ethers, including dimethyl ether (DME) and diethyl ether (DEE), has been investigated quite extensively in different configurations such as premixed flames [11–15], flow reactors [16], jet-stirred reactors [17–19], and shock tubes [20–22], experimental studies addressing DBE

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as a fuel still remain very scarce. A few investigations determined ignition delay times of DBE [23,24]. Cai et al. [23] measured the laminar flame speed of DBE in air in a stagnation-flame configuration at atmospheric pressure with an unburned reactant temperature of 373 K for a range of equivalence ratios ϕ of 0.7-1.5. These authors [23] also used a laminar flow reactor to investigate the ignition delay time of lean and stoichiometric DBE/air mixtures in the low-temperature range of 485-525 K at atmospheric pressure, and noted a high reactivity for this fuel. Guan et al. [24] measured the ignition delay time of DBE in a shock tube for pressures of 1.2-4 bar, temperatures of 1100-1570 K, and equivalence ratios of 0.5-1.5, and pointed out that DBE shows a higher overall reactivity than DME and DEE. Recently, Thion et al. [25] investigated the oxidation of DBE for lean, stoichiometric, and fuel-rich mixtures in a jet-stirred reactor at temperatures ranging from 470 K to 1250 K and pressures of 1 and 10 atm, respectively.

Besides experimental investigations, the combustion of DBE was also studied numerically. Cai et al. [23] developed a first kinetic model covering low- and high-temperature reaction pathways of DBE with the kinetic data of the primary reaction subset, for which the rate parameters were mainly determined using rate rules presented recently in [26] or by analogy to structurally similar alkanes and alcohols. This model was tested against the data of ignition delay time and premixed laminar flame speeds of their study, and a satisfactory agreement between experiments and predictions was observed. After the release of the Cai et al. model [23], Rashidi et al. [27] performed theoretical calculations for the rate coefficients of several reactions of DBE, *e.g.,* unimolecular decomposition, H-abstraction by hydrogen atoms, and isomerization as well as β-scission reactions of some of the resulting radicals, using the CBS-QB3 and G4 composite methods in conjunction with conventional transition state theory. These authors [27] found that the calculated rates of several reaction classes differ markedly from those obtained for similar reactions of alcohols or alkanes, indicating that analogies to alkanes and alcohols are, in some cases, inappropriate means of estimating the reaction rates of ethers. More recently, a kinetic model covering low- and high-temperature reaction pathways of DBE has been developed by Thion et al. [25]. The submechanism of DBE in their model is based on previous work of Cai et al. [23] to which modifications were made based on analogies with butanol and computations. The thermodynamic data for the fuel and the respective fuel radicals resulted from theoretical calculations performed with the G3B3 compound method. We therefore consider it useful to test the performance of both models and analyze potential differences in the prediction quality. For such a stringent examination, quantitative intermediate species profiles measured in flames will be appreciated, especially when considering the prediction of pollutant emissions. Since DBE is suggested to be of potential use in diesel engines, data carried out from flame experiments could be useful to elucidate the fuel-specific reaction pathways when full development of ignition and high temperatures are reached.

To the best of our knowledge, quantitative sets of species profiles in premixed DBE flames are not yet available, and the flame chemistry of this fuel has not fully been understood. We have thus studied the combustion chemistry of DBE by quantifying key species formed in low-pressure laminar premixed flames using electron ionization (EI) molecular-beam mass spectrometry (MBMS). The experimental data obtained in the present study have been analyzed and compared with the predictions by the models of Cai et al. [23] and Thion et al. [25]. Furthermore, a comparison of the combustion behavior and the potential of pollutant formation between DBE, short-chain ethers (DME and DEE), and its half-structurally similar fuels (*n*-butane and *n*-butanol) has been performed with the aim of an improved understanding of the flame chemistry of DBE.

2. Experiments and modeling

2.1. Flame conditions

Two laminar premixed flames of di-*n*–butyl ether ($\phi = 1.5$ and $\phi = 0.8$), *i.e.,* DBE/oxygen/argon, were stabilized on a home-built flat sintered bronze burner (diameter $d = 65$ mm) and investigated at identical pressure (4 kPa), argon dilution (50%), and cold-gas velocity (60 cm s^{-1} at 333 K and 4 kPa). The conditions for all flames are presented in Table 1.

Gas flows of argon and oxygen were established with calibrated mass-flow controllers. Since DBE is a liquid fuel at room temperature, its flow was metered with a syringe pump and the fuel was evaporated at 460 K with a home-built evaporation system. To monitor the inlet conditions of the premixed gas composition, the burner surrounding was cooled with water at a constant temperature of 333 K.

2.2. EI-MBMS experiment

A detailed description of the EI-MBMS system available in Bielefeld can be found elsewhere [28,29]. Here the flame is probed by a quartz cone (~400 μm orifice, 25° angle) which is mounted on a water-cooled holder. Due to the pressure difference of the burner chamber (4 kPa) and the first-stage pumping chamber (10^{-5} kPa), a molecular beam is formed that quenches the reactions in the gas sample. The molecular beam is then directed through a home-made copper skimmer to the ion source of the mass spectrometer. The connection of the two stage Wiley-McLaren ion source with a reflectron time-of-flight detection unit provides a mass resolution of $m/\Delta m$ ~4000 and therefore enables the determination of C/H/O species and their respective elemental composition. Undesired fragmentation processes were reduced as much as possible by the use of soft ionization energies in the region of 11-13 eV for intermediates, whereas ionization energies of 16 and 17 eV served for major species quantification. The resulting energy- and position-dependent raw ion signals of the respective species were then integrated by fitting with Gaussian functions. Further signal processing involved the correction for fragment ions initially related to the fuel itself, as well as from intermediate species by measuring respective fragment spectra from independent cold-gas energy scans and subtracting the individual fragment contributions. Finally, corrections were performed for isotopic contributions from ^{13}C- and ^{18}O- containing species.

2.3. Species quantification

The EI-MBMS data evaluation followed the routines reported in detail before [29]. A second order polynom was used to connect the recorded flight time of a species to their exact mass. The integrated signal S_i is related to the mole fraction x_i as shown in Eq. (1).

$$S_i = x_i \cdot c \cdot SW \cdot D_i \cdot \varphi \cdot FKT(h) \cdot \int \sigma_i(\tau) \cdot f(E - \tau)\mathrm{d}\tau \qquad (1)$$

Here, c is an instrument factor, SW the number of sweeps, D_i the mass discrimination factor and φ the number of ionizing electrons. Note that according to previous measurements by Schenk et al. [28], the mass discrimination factors were set to unity for all species except for hydrogen that was calibrated *via* an internal calibration strategy [28]. The term $FKT(h)$ describes a temperature and position-dependent sampling function. $\sigma_i(\tau)$ is the electron ionization cross section for a respective species i at the energy E, and $f(E-\tau)$ reflects the energy distribution of electrons with τ being the integration variable over the selected energy range. If the respective species signal S_i is compared to a reference signal S_R of the