Chemical kinetic study of a novel lignocellulosic biofuel: Di-n-butyl ether oxidation in a laminar flow reactor and flames

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A B S T R A C T

The combustion characteristics of promising alternative fuels have been studied extensively in the recent years. Nevertheless, the pyrolysis and oxidation kinetics for many oxygenated fuels are not well characterized compared to those of hydrocarbons. In the present investigation, the first chemical kinetic study of a long-chain linear symmetric ether, di-n-butyl ether (DBE), is presented and a detailed reaction model is developed. DBE has been identified recently as a candidate biofuel produced from lignocellulosic biomass. The model includes both high temperature and low temperature reaction pathways with reaction rates generated using appropriate rate rules. In addition, experimental studies on fundamental combustion characteristics, such as ignition delay times and laminar flame speeds have been performed. A laminar flow reactor was used to determine the ignition delay times of lean and stoichiometric DBE/air mixtures. The laminar flame speeds of DBE/air mixtures were measured in the stagnation flame configuration for a wide rage of equivalence ratios at atmospheric pressure and an unburned reactant temperature of 373 K. All experimental data were modeled using the present kinetic model. The agreement between measured and computed results is satisfactory, and the model was used to elucidate the oxidation pathways of DBE. The dissociation of keto-hydroperoxides, leading to radical chain branching was found to dominate the ignition of DBE in the low temperature regime. The results of the present numerical and experimental study of the oxidation of di-n-butyl ether provide a good basis for further investigation of long chain linear and branched ethers.

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1. Introduction

Limited fossil fuel reserves, increasing petroleum fuel prices, and the adverse environmental impacts of combustion generated pollutants have motivated research in the recent years related to the utilization of alternative fuels in practical combustion devices. In the transportation sector [1–4], ethers are widely regarded as alternative fuels and/or fuel blending components for compression-ignition engines. Compared with diesel fuels, their high cetane number (CN) and oxygenated molecular structure could result in improved fuel efficiency and reduced pollutant emissions from internal combustion engines. Furthermore, the potential of ether production from lignocellulosic biomass is a significant advantage [5], as that route has no direct competition with food

production. Therefore, ethers are generally considered as important next-generation biofuels [6].

Industrially, ethers can be obtained by dehydration of alcohols [5]. From lignocellulosic biomass, ethanol is produced by hexose fermentation. While ethanol can be converted directly into diethyl ether (DEE) by dehydration, it can dehydrogenate also into acetaldehyde, followed by aldol condensation into crotonaldehyde and subsequent hydrogenation into n-butanol. Through the further dehydration of n-butanol, di-n-butyl ether (DBE) can be obtained [5]. An alternative method for production of DBE is demonstrated by using dry n-butanol derived from fermentation broth [7].

Up to now, combustion research has focused mainly on short chain ethers. For the thoroughly studied dimethyl ether (DME), fundamental investigations on combustion characteristics [8–15], kinetic modeling [13,16,17] as well as practical applications in combustion engines [18,19] can be found in the literature. Recently, Yasunaga et al. [20] studied the pyrolysis and oxidation of diethyl ether (DEE) behind reflected shock waves, presented ignition and species data, and constructed a chemical kinetic model

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to predict the data. The model was later advanced to include the combustion chemistry of branched ethers, ethyl methyl ether (EME), methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE) [21]. From the standpoint of quantum chemistry, Di Tommaso et al. [22] conducted Density Functional Theory (DFT) calculations of auto-oxidation reactions of DEE and revealed that the typical competing chain branching and termination pathways found in *n*-alkane oxidation are also dominant in DEE oxidation.

DBE has been identified recently as a candidate biofuel produced from lignocellulosic biomass [5]. Its particularly high cetane number of 100 [3] indicates shorter ignition delay times than those of diesel fuels, which results in a relatively longer combustion process and thus less unburned fuel in compression-ignition engines. Its boiling temperature of 142.4 °C permits facile vaporization of the fuel after injection while minimizing tank evaporation losses. More importantly, high molecular weight fuels are generally attractive as alternative fuels, because their volumetric energy content is comparable to that of petroleum fuels (~36 MJ/L) and they can be applied in conventional compression-ignition engines without the need for extensive engine modifications. While the volumetric energy content of DME is about half that of petroleum fuels [23], the calculated volumetric energy density of DBE and DEE are 31.6 and 26.9 MJ/L, respectively. However, limited combustion studies are reported in the literature for DBE. Beatrice et al. [3] tested DBE as pure fuel in diesel engines and observed a strong decrease of soot emission in exhausts, as expected. Heuser et al. [4] studied DBE as an ignition enhancing blending component for 2-methyltetrahydrofuran (2-MTHF) in single-cylinder diesel engine experiments and found that the addition of DBE to 2-MTHF increases the fuel ignitability, while decreasing the combustion noise level. In addition, CO, unburned hydrocarbons (HC), and soot emissions are reduced notably in comparison to conventional diesel fuel combustion.

The rate parameters for the reactions of OH radical with DBE were investigated by Mellouki et al. [24] at temperatures and pressures relevant to atmospheric oxidation chemistry. In addition, Marrouni et al. [25] carried out density functional theory (DFT) calculations for linear symmetrical monoethers spanning from DME to DBE. The authors reported that rate constants of H-atom abstraction by molecular O_2 are similar for different types of C–H sites. On the other hand, no attempt has been made to determine experimentally the fundamental combustion properties of DBE, e.g. ignition delay times. This has made it challenging to develop the theoretical reaction mechanism, as no experimental data from the literature were available for model validation. At present, computational fluid dynamics (CFD) simulations coupled with detailed chemistry are often performed in research and in engine design to provide insights into fuel combustion in complex combustion devices [26–28]. Despite the combined uncertainties of CFD modeling and chemistry, detailed kinetic models provide higher chemical fidelity in numerical studies compared to models represented by global reactions and empirical equations. However, for DBE, this is presently impossible, since a kinetic model is currently unavailable.

The main goal of this study was to investigate systematically the combustion characteristics of DBE, for the first time. Fundamental combustion properties, such as ignition delay times and laminar flame speeds were determined experimentally. A detailed kinetic model coupled with thermodynamic and transport data was developed based on reaction classes and rate constant rules, and the model was validated against the present data. Both low- and high-temperature kinetic schemes were included in the model. Particular emphasis was placed on low-temperature ignition, which is of great interest to compression-ignition and low temperature combustion (LTC) engines. The kinetic model proposed here was employed to elucidate the oxidation pathways of DBE at rele-

vant conditions. Comparisons of its combustion characteristics with those of *n*-alkanes, alcohols, and short chain ethers were also performed to illustrate the effect of the ether functional group.

The presentation is organized as follows. First, the development of the kinetic model for DBE oxidation is presented. Next, the experimental facilities are described. Then, numerical simulations using the proposed model are presented and compared with the data. Finally, the reaction pathways of DBE oxidation at relevant conditions are illustrated and sensitivity analyses of elementary reactions are performed to provide insights into DBE oxidation chemistry.

2. Kinetic model development

DBE contains an oxygen molecule bound within two normal butyl chains, thus bringing about different associated rate constants, product channels, and higher ignition propensity compared to alkanes, alcohols, and short di-alkyl ethers. This section describes the formulation of a chemical kinetic model for DBE using current understanding of combustion chemistry for a wide variety of structurally similar molecules, such as alcohols, esters, other di-alkyl-ethers (e.g., dimethyl ether, diethyl ether, etc.), and *n*-alkanes.

2.1. Naming of species

To illustrate the naming of the species for the model, DBE is denoted as $C_4H_9OC_4H_9$ in the model (see Fig. 1 for its molecular structure). The carbon chain is labeled numerically (i.e., 1, 2, 3) starting with the location of the carbon bonded to the oxygen. In DBE, the location of a double bond is identified by a hyphen followed by the number of the second carbon in the double bond. Additional notations are provided to denote radical sites in the molecule, where the carbon sites are labeled alphabetically (i.e., a, b, c) starting with the location of the carbon bonded to the oxygen. In this way, the DBE radical at the alpha site (i.e., carbon bonded to the oxygen site) is denoted by $C_4H_9OC_4H_8$-a.

2.2. General model features

The proposed DBE kinetic model includes both low-temperature and high-temperature kinetics. The DBE model was added to the *n*-butanol model developed recently by Sarathy et al. [29]. The thermodynamic data for DBE and related radicals were calculated using the THERM program of Ritter and Bozzelli [30]. Transport properties for molecules in the high temperature mechanism were determined using the methods described previously in Refs. [31,32], which was developed originally by Tee et al. [33] and Wang and Frenklach [34]. The entire model consists of 426 species and 2335 reactions. 301 species among 1830 reactions are found in the high temperature part. These input files for numerical simulation are available as supplementary material.

The present kinetic model is based on the hierarchical nature of combustion mechanisms (e.g. [32,35,36]). The validation simulations were conducted in CHEMKIN PRO [37] or in FlameMaster [38] using the appropriate reactor modules. A few rare instances required minor modifications to the solver convergence criteria (i.e., absolute tolerance), and in such cases it was ensured that the solution was well converged and accurate.
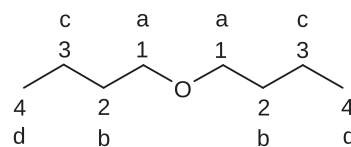

Fig. 1. Structure of di-n-butyl ether ($C_4H_9OC_4H_9$).