



Full Length Article

Exploration of the pyrolysis chemistry of 1,1-diethoxybutane: A flow reactor and kinetic modeling study



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ABSTRACT

1,1-Diethoxybutane is a promising next-generation biofuel and this work reports the first study for its pyrolysis chemistry. Pyrolysis of 1,1-diethoxybutane was investigated in a flow reactor at 0.04 and 1 atm using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). A series of oxygenated and hydrocarbon products, including several radicals, were detected and their mole fractions were evaluated. A detailed kinetic model of 1,1-diethoxybutane, including 253 species and 1577 reactions, was developed and validated against the present experimental data. Modeling analyses including the rate of production analysis and sensitivity analysis were performed to reveal the crucial consumption pathways of 1,1-diethoxybutane, as well as the formation and consumption pathways of intermediates and products. The H-abstraction reactions of 1,1-diethoxybutane play a key role in fuel consumption. The intra-molecular elimination reactions and unimolecular C–C or C–O dissociation reactions of 1,1-diethoxybutane make minor contributions to fuel consumption. The sensitivity analysis also shows that the fuel consumption reactions have large sensitivities to 1,1-diethoxybutane. Further β -C–C and β -C–O scission reactions closely connect the consumption of six fuel radicals and the formation of most oxygenated products. The observation of high mole fractions of C₁–C₄ acids and aldehydes demonstrates the structural features of 1,1-diethoxybutane. Besides, several hydrocarbon products, such as C₂–C₄ alkenes, benzene and its precursors, were detected, some of which, such as propene, are also produced from the consumption reactions of fuel radicals. Besides, hydrocarbon products can also be produced from the combination reactions of small species, such as the combination reactions of C₃ species to produce benzene and the combination reaction of allyl and methyl to produce 1-butene. The low benzene production ability of 1,1-diethoxybutane implies its low sooting tendency compared with fossil-derived transportation fuels.

1. Introduction

In recent years, the increasing demand of energy supply, limited reserves of fossil fuels and great pollutant emissions from fossil fuel combustion have motivated the utilization of environment friendly and sustainable biofuels, such as alcohols, ethers and esters [1,2]. Ethers have been widely regarded as alternative transportation fuels due to many advantages, such as high cetane numbers and oxygenated molecular structures, which can achieve low pollutant emissions [3,4]. As an ether, 1,1-diethoxybutane (C₈H₁₈O₂) has a favorable cetane number (~96), which is close to dibutyl ether (~95) and higher than dimethyl ether (~57), and a low heat value around 34 MJ/kg [5]. 1,1-Diethoxybutane can be obtained indirectly from the fermentation of lignocellulosic biomass, mainly through the reaction of ethanol (4C₂H₅OH=C₈H₁₈O₂+2H₂O+H₂) [5]. Besides, under acidic

conditions, the synthesis of 1,1-diethoxybutane can be performed by the acetalization reaction of ethanol and *n*-butanal [6–9]. The potential yield of 1,1-diethoxybutane from biomass is considered to be close to that of *n*-butanol and much higher than that of dibutyl ether [5].

Due to the abovementioned advantages as potential alternative transportation fuels, the combustion chemistry of ethers with four and more carbon atoms has attracted increasing concerns [3,4,10–12]. It is recognized that the structural features of ethers, e.g. the number of oxygen atoms and the different types of carbon atoms, play crucial roles in determining the radical pools and product distributions [3,4]. However, most investigations were focused on ethers with one oxygen atom, including straight ethers such as dibutyl ether [3,10,12] and diethyl ether [4,13] and branched ethers like tert-butyl ethyl ether [14,15]. Only few studies were performed on ethers with two or more oxygen atoms, such as dimethoxy methane (CH₃OCH₂OCH₃) [16,17]

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and polyoxymethylene dimethyl ethers (e.g. $\text{CH}_3\text{O}(\text{CH}_2\text{O})_2\text{CH}_3$) [16]. To our knowledge, there is no previous investigation on the combustion chemistry of 1,1-diethoxybutane.

This work reports the first investigation on the combustion chemistry of 1,1-diethoxybutane. The pyrolysis of 1,1-diethoxybutane was investigated in a flow reactor at low and atmospheric pressures (0.04 and 1 atm). Synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) was used to detect the pyrolysis products, especially radicals and isomers. Their mole fractions were evaluated as a function of temperature. Besides, a detailed kinetic model of 1,1-diethoxybutane combustion was developed, which consists of 253 species and 1577 reactions. The model can reasonably reproduce the experimental results. The modeling analyses including the rate of production (ROP) analysis and sensitivity analysis were performed to help understand the chemistry in 1,1-diethoxybutane pyrolysis, such as the primary decomposition pathways of 1,1-diethoxybutane and the formation and consumption pathways of pyrolysis products.

2. Experimental section

The experiments were performed at the National Synchrotron Radiation Laboratory (NSRL), Hefei, China. Detailed descriptions of the beamline have been reported elsewhere [18,19]. The pyrolysis apparatus consists of three parts [20–22], i.e. a pyrolysis chamber, a differentially pumped molecular-beam sampling system and a photoionization chamber with a home-made reflectron time-of-flight mass spectrometer (RTOF-MS). An electrically heated α -alumina flow reactor with an inner diameter of 7.0 mm and a length of 220 mm was mounted inside the pyrolysis chamber. In this work, the experiments were performed at 0.04 and 1 atm. During the experiments, the gas mixture of 1,1-diethoxybutane (1% in mole) and argon with a total flow rate of 1000 standard cubic centimeters per minute (SCCM) was fed into the flow reactor. The pyrolysis species were sampled by a quartz nozzle downstream from the reactor outlet and then formed a molecular beam. After passing through a nickel skimmer, the molecular beam entered the ionization region where the species were ionized by the synchrotron VUV light. The formed ions were recorded by the RTOF-MS.

Detailed methods of temperature measurements along the centerline of flow reactor were described elsewhere [21]. The measured temperature profiles can be found in the [Supplementary materials](#). The uncertainty of measured temperatures is estimated to be within ± 30 K. The methods of species identification and mole fraction evaluation have been reported elsewhere [22,23]. The uncertainties of evaluated mole fractions are estimated to be within $\pm 10\%$ for major species, within $\pm 25\%$ for intermediates with known photoionization cross sections (PICSSs), and a factor of 2 for those with estimated PICSSs. The PICSSs are available in the online database [24].

3. Kinetic modeling

A detailed kinetic model of 1,1-diethoxybutane was developed in this work. Fig. 1 shows the molecular structure of 1,1-diethoxybutane. There is no previous theoretical calculation or experimental measurement for the decomposition reactions of 1,1-diethoxybutane and its radicals. Thus, the primary decomposition pathways of 1,1-

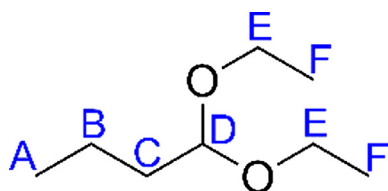


Fig. 1. The molecular structure of 1,1-diethoxybutane with six carbon sites labelled from A to F.

diethoxybutane were mainly referred to those of other ethers [3,4,25] because all of them have the typical C–O–C structure. The primary decomposition pathways of 1,1-diethoxybutane in the present model include the unimolecular C–C (or C–O) bond dissociation reactions, intra-molecular alcohol elimination reactions and H-abstraction reactions. For example, the rate constants of intra-molecular alcohol elimination reactions of 1,1-diethoxybutane in the present model were referred to similar reactions of diethyl ether whose pressure-dependent rate constants were reported by Yasunaga et al. [25].

Considering the structure of 1,1-diethoxybutane, the H-abstraction reactions of 1,1-diethoxybutane can occur at six carbon sites to produce six fuel radicals. As demonstrated in the previous work of ethers [3] and *n*-alkanes [20,26–28], the isomerization reactions and β -scission reactions are the most important reactions for the fuel radicals [3,20,26–28]. Thus, the isomerization and β -scission reactions are considered for the fuel radicals ($\text{C}_6\text{H}_{17}\text{O}_2$) in the present model, which were mainly referred to those of alkyls [27,28] and oxygenated radicals [4]. For example, the rate constants of the isomerization reactions via 1,4-, 1,5- and 1,6-H shift in the present model were referred to the pressure-dependent rate constants of alkyls calculated by Tsang et al. [27,28]. The sub-mechanism of C_0 – C_4 species was mainly taken from previous models [20,29]. Thermodynamic data of most species were mainly taken from previous models [20,29] and the database of Goos et al. [30]. For some new species involved in the fuel sub-mechanism, the thermodynamic data were calculated in this work using the THERGAS software [31]. The reaction mechanism and thermodynamic data are available in the [Supplementary materials](#). A detailed list of the species discussed in this work is presented in [Table S1](#) of the [Supplementary materials](#). Furthermore, the simulation work was performed using the Plug Flow Reactor module in the Chemkin-Pro software [32]. A detailed description of the simulation method can be found in our previous work [33].

4. Results and discussion

Dozens of pyrolysis species were identified in this work, including the fuel, oxygenated products, hydrocarbon products and several radicals. Their experimental and simulated mole fraction profiles are shown in the following figures. The ROP analysis and sensitivity analysis were performed at 0.04 atm, 1065 K and 1 atm, 925 K, which both correspond to about 40% conversion of the fuel.

4.1. Consumption pathways of 1,1-diethoxybutane

Fig. 2a presents the experimental and simulated mole fraction profiles of 1,1-diethoxybutane. 1,1-Diethoxybutane is consumed by three types of reactions, i.e. the unimolecular C–C and C–O bond dissociation reactions, two intramolecular elimination reactions, and the H-abstraction reactions. The bond dissociation reactions of the fuel to produce two radicals serve as chain initiation reactions in pyrolysis. There are six unimolecular C–C or C–O bond dissociation reactions of 1,1-diethoxybutane ((R1)–(R6)), as shown in Fig. 3. Benefitting from the utilization of SVUV-PIMS, methyl radical (CH_3) involved in these reactions was detected, as shown in Fig. 2(c). The produced oxygenated radicals from ((R1)–(R6)) contributes to the formation of oxygenated species. For example, (R6) can produce 3,3-diethoxy propyl radical ($\text{C}_2\text{H}_5\text{OC}_3\text{H}_5\text{OC}_2\text{H}_5$), whose isomerization reaction produces $\text{SC}_2\text{H}_4\text{OC}_3\text{H}_6\text{OC}_2\text{H}_5$ radical. Two steps β -C–O scission reactions of $\text{SC}_2\text{H}_4\text{OC}_3\text{H}_6\text{OC}_2\text{H}_5$ radical can produce propanal ($\text{C}_2\text{H}_5\text{CHO}$) (Fig. 2(d)). The unimolecular decomposition reactions have small contributions to the consumption of 1,1-diethoxybutane based on the ROP analysis, which is similar to the situation in the jet stirred reactor (JSR) pyrolysis of diethyl ether [34]. In contrast, the sensitivity analysis of 1,1-diethoxybutane (Fig. 4) indicates that (R3) is among the top sensitive reactions, which can be explained by its role as a chain initiation reaction.

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