A quantum chemical and kinetics modeling study on the autoignition mechanism of diethyl ether

Yasuyuki Sakai [a,*], Jürgen Herzler [b], Marc Werler [c], Christof Schulz [b], Mustapha Fikri [b]

[a] *Graduate School of Engineering, University of Fukui, 3-9-1 Bunkyo, 910-8507 Fukui, Japan*
[b] *Institute for Combustion and Gas Dynamics – Reactive Fluids, University of Duisburg-Essen, 47048 Duisburg, Germany*
[c] *Institute of Technical Thermodynamics, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany*

Abstract

A detailed chemical kinetics model has been developed to elucidate the auto-ignition behavior of diethyl ether (DEE) under conditions relevant for internal combustion engines. The present model is composed of a C_0–C_4 base module from literature and a DEE module. For the low-temperature oxidation mechanism, the reactions of ROO and QOOH radicals were studied previously with a quantum-chemical and transition state theory approach by Sakai et al. (2015). In the present study, the potential energy surfaces for the unimolecular reactions of OOQOOH isomers and 1- and 2-ethoxyethyl radicals were determined with a CBSQB3 composite method. In the presence of an OOH group, the reaction barrier of the hydrogen shift from the β site (terminal carbon atom) decreases as it does in alkane oxidation but there is no effect on the hydrogen shift from the α site (next to the ether oxygen atom). Therefore, the reaction barriers of OOQOOH isomers have the same trend as the corresponding ROO radical and rate constants for the reactions of OOQOOH isomers were determined. The constructed model was validated against the recent data of ignition delay times provided in literature by Werler et al. (2015). The agreement is good over the temperature range 500–1300 K and pressure range 1–40 bar, although, open questions remain regarding the non-consensus at 900–1150 K and 40 bar. Reaction-path and sensitivity analyses attribute the importance of the reactivity at the α site to the decrease of the C H bond dissociation energy due to the ether oxygen atom.
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Keywords: Ignition delay; Diethyl ether; Detailed chemical kinetics mechanism; CBSQB3; Transition-state theory

1. Introduction

Diethyl ether (DEE) has an exceptionally high cetane number compared to conventional gasoline and Diesel fuel components. To utilize this property for optimizing fuel blends for internal combustion (IC) engines, detailed knowledge on the chemical kinetics of DEE oxidation, especially under engine-relevant temperatures and pressures, is required. The pyrolysis and oxidation of DEE have been studied in shock tubes [1]. A detailed chemical kinetics model was proposed and validated

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* Corresponding author. Tel.: +81-776-27-9836.
E-mail address: y_sakai@u-fukui.ac.jp (Y. Sakai).

against these measurements. This model can reproduce the measured species data and ignition delay times (IDTs) over the temperature range 900–1900 K at pressures of 1 and 3.5 bar. Recently, IDTs of DEE were measured in a shock tube at 900–1300 K and pressures of 10, 20, and 40 bar, and in a rapid compression machine (RCM) at 500–1060 K and 2.5–13 bar [2]. In this work, reaction-path and sensitivity analyses were performed using the Yasunaga model [1]. It was shown that the H-atom abstractions from both, the α site (carbon atom next to the ether oxygen atom) and the β site (terminal carbon atom) in DEE by the HO_2 has the highest sensitivity to IDTs measured by shock-tube experiments, and that the increase of the pre-exponential factor of these reactions by a factor of 5 was necessary to yield good agreement between measurements and simulations. Zhang et al. also measured IDTs of DEE behind reflected shock waves at 1050–1600 K and pressures of 1.2, 4, and 16 bar [3]. They analyzed the ignition mechanism by using a reaction-path and sensitivity analysis with the Yasunaga mechanism [2] and showed that the unimolecular decomposition reactions of DEE and the H-atom abstraction from the β site in DEE by H atoms both have high sensitivity with respect to ignition delay times. However, these analyses [2,3] focused on $T > 900$ K only, where the low-temperature oxidation mechanism has a minor role only. Thus, the low-temperature oxidation mechanism of DEE remains unresolved.

Our earlier theoretical study reported the potential energy surfaces and high-pressure rate constants of 1- and 2-ethoxyethylperoxy radicals, which are important intermediates in the low-temperature oxidation of DEE [4]. In the present study, the potential energy surfaces of all OOQOOH isomers, identified in the submechanism of DEE oxidations, were determined from quantum-chemical calculations. Based on potential energy surfaces obtained in this and in our earlier study, a detailed chemical kinetics model with low-temperature oxidation chemistry was developed and validated against measured IDTs.

2. Model development

The chemical kinetics mechanism developed here is composed of a C_0–C_4 base mechanism from Burke et al. [5,6] that is expanded by a new DEE module. The C_0–C_4 base model includes the reaction mechanism and thermodynamic properties for the oxidation of H_2, syngas, C_1–C_3 hydrocarbons, and oxygenates such as ethanol and dimethyl ether (DME), and also includes the *CH reaction mechanism which is used to define IDTs. The model [5,6] was shown to reproduce IDTs, laminar flame speeds, and species concentrations over a wide range of conditions including those typical for IC engines. The mechanism neglects species larger

than C_5 and their reactions. The DEE module includes reactions and thermodynamic properties of the species relevant for DEE oxidation which are not already included in the C_0–C_4 base module. The mechanism contains 341 species and 1867 reactions including 69 species and 219 reactions in the DEE module. The methodology of the development of the DEE module is described in Sections 2.1–2.6, especially for the reactions that are sensitive to autoignition.

2.1. Hydrogen-atom abstraction reaction from DEE

H-atom abstraction from the α and the β site in DEE produce 1- and 2-ethoxyethyl radicals, respectively. The rate constants of H-atom abstraction with O_2, H, OH, O, CH_3, C_2H_5, C_2H_3, CH_3O_2, RO_2 ($C_2H_5O_2$, CH_3CO_3, O_2CHO), and RO (CH_3O, C_2H_5O) were taken from the reaction-rate rules with the automatic model-generation software, KUCRS developed by Miyoshi [7]. The reaction-rate rules are based on the work for iso-octane oxidation [9] for the β site and on the work for butanol isomers [10] for the α site. The rate constants of H-atom abstraction by HO_2 for both sites were taken from Mendes et al. [11], and additional data for H-atom abstraction from the α site was taken from literature for O_2 [12], H, and OH [13]. To well reproduce the measured IDTs, the rate constant of H-atom abstraction from the α site was decreased by a factor of 2 for OH and increased by a factor of 2 for HO_2; and this rate constant for HO_2 was applied to CH_3O_2 and RO_2. In the present model, the rate constants in the DEE module are given reversible. The backward rate constants are calculated from thermo data, thus the modifications of forward rate constants mentioned above and also hereafter have no effect on equilibria.

2.2. Unimolecular reactions of ROO and QOOH isomers

1- and 2-ethoxyethyl radicals react with O_2 and produce 1-(sROO) and 2-ethoxyethylperoxy (pROO) radicals, respectively (Fig. 1). The rate constants for the unimolecular reactions of pROO and sROO, their isomerization products, and QOOH were taken from Ref. [4]. To well reproduce the measured IDTs, the rate constants for the O_2 dissociation reactions of pROO and sROO were increased by a factor of 2.

2.3. Unimolecular reactions of OOQOOH isomers

There are six OOQOOH isomers in the DEE module as shown in Fig. 1. To estimate the reaction mechanism of OOQOOH isomers, quantum chemical calculations were performed using Gaussian09 [14]. The optimized structures, frequencies,