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Full Length Article

Ab initio calculation and kinetic modeling study of diethyl ether ignition with application toward a skeletal mechanism for CI engine modeling

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ABSTRACT

Quantum chemistry and rate constants of reactions such as H-abstraction of diethyl ether (DEE) by H, OH, HO_2, O and CH_3 radicals as well as DEE and DEE radicals decomposition and isomerization were carried out through high-level ab initio and RRKM master equation computations. A comparison was made between some of the calculated rate constants and literature data. A detailed kinetic mechanism for DEE ignition contains 341 species and 1867 reactions was developed mainly based on the theoretical calculation and literature data and it was then further compared with the literature measurements along with three other existing DEE models, the Yasunaga model, the Sakai model and the Tran model. Compared with the other three models, the current model can give reasonable predictions on the validated ignition data over a wider temperature range. Based on the current model, a skeletal mechanism which contains 49 species and 192 reactions was developed by using a Jacobian-aided DRGEP approach, followed with a TSA method. The skeletal mechanism can precisely represent the detailed mechanism under a wide range of compression engine related conditions for DEE ignition. Finally, reaction pathway analysis and sensitivity analysis was conducted using the current model to gain an in-depth comprehension on DEE ignition at different temperatures.

1. Introduction

Engine researchers are trying hard to study engine emission and performance of diesel blend with some oxygenated fuels such as alcohols, acetates, esters, and ethers because the oxygenates are proved to decrease particulate matter (PM) emissions and increase thermal efficiency in the diesel engine [1–6]. Diethyl ether (DEE) is a promising oxygenated fuel which can be cheaply produced through the dehydration of ethanol. Research showed that the addition of DEE to diesel, liquefied petroleum gas (LPG) and biodiesel etc. in engines can effectively reduce engine soot particulate emission [7–9]. In addition, DEE can be used to support cold-start in diesel and gasoline engines [10] because it has a high cetane number of 125. In fact, DEE even has been regarded as a potential diesel engine alternative fuel [11].

Apart from the engine studies, fundamental combustion investigations are also very necessary since they are beneficial for engine researchers to effectively organize the combustion process of DEE or DEE/fuel blends in the engine and decrease the pollutant discharge. We conducted a high temperature ignition chemistry study by using a shock tube facility [12]. Werler et al. [13] also measured the ignition delay times of DEE over a wide range of conditions in the shock tube and rapid compression machine. Liu et al. [14] carried out a comparison study of the oxidation characteristic, thermal stability and product formation of totally five ethers including DEE by using an accelerating rate calorimeter under low temperature. Hashimoto et al. [15] performed an extinction limit measurement on non-premixed flames in a counterflow burner for DEE flames. Chemical kinetic model is extremely important in fundamental combustion study as we can obtain many important parameters during the combustion process of the fuel by using an accurate chemical model through computer simulations, instead of complicated and expensive experiments. Up to now, there are totally three models available for DEE combustion. Yasunaga et al. [16] conducted a DEE pyrolysis and oxidation experiment behind reflected shock waves at pressures from 1 to 4 atm and temperatures from 900 to1900 K, and they constructed a chemical kinetic model for DEE based on the measurements. The model was mainly constructed using estimated reaction rate constants. Tran et al. [17] measured flame speeds at elevated pressure and species distributions in low-pressure flames and proposed a kinetic model mainly focused on high-temperature combustion chemistry of DEE. In their model, the rate constants of H-abstraction reactions of DEE by H radical as well as high pressure limit rates of DEE radicals decomposition and isomerization reactions were

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carried out at CBS-QB3 level. The model gives pretty good predictions on the ignition delay times at high temperature. Sakai et al. [18] calculated unimolecular reactions of the ethoxyethylperoxy (ROO) radicals, which are very important in DEE low temperature chemistry at CBS-QB3 and CASPT2 level of theory using conventional transition state theory (CTST) and variational transition state theory (VTST). In their latter study [19], they further calculated high pressure limit rates of unimolecular reactions of the DEE radicals and estimated rate constants of DEE H-abstraction reactions and OOQOOH unimolecular reactions. Based on these calculations and estimations, they developed a DEE model which can give good performance on DEE ignition under engine-relevant temperature range. However, neither of the rate constants of important H-abstraction reactions by HO_2, O, and CH_3 radicals was calculated in these studies, nor the pressure dependencies for the DEE radical decomposition reactions were considered. On the other hand, since the comprehensive detailed chemical mechanism covers a wide range of conditions, it is prohibitively expensive for large-scale 3-dimensional simulations in terms of CPU time and memory. Simultaneously, the stiffness resulted from wide range of time scales among species in the detailed mechanism must be considered as well. Hence, it is imperative to reduce the size of the detailed mechanisms while maintaining adequate species and reactions to sufficiently reproduce physical phenomena such as ignition delay time and laminar flame speeds at engine related temperatures and pressures [20]. However, up to now, no relative study on simplified DEE models has been reported at all.

In this study, quantum chemistry and rate constant calculations for the DEE high temperature sub-model, including H-abstraction reactions of diethyl ether (DEE) by H, OH, HO_2, O and CH_3 radicals as well as DEE and DEE radicals decomposition and isomerization reactions were carried out systematically through high-level ab initio and RRKM master equation computations. The pressure dependent effect of unimolecular reactions was considered. A detailed chemical kinetic model with 341 species and 1867 reactions for DEE ignition was obtained by assembling the current calculation and literature data together, and it can give reasonable prediction on DEE ignition from low to high temperatures. Moreover, a 49-species and 192-reaction DEE skeletal mechanism is reduced from the newly developed 341-species detailed mechanism under the target conditions of compression ignition (CI) engines.

2. Computational methods

2.1. Ab initio rate constant calculation

The quantum chemistry was calculated through the Gaussian 09 software package [21] in current study. High-accuracy ab initio and RRKM master equation calculations were carried out to determine the calculated rate constants. In detail, for all the reactions calculated, the geometries and vibrational frequencies of the reactants, transition states, and products were performed at MP2/6-311G(d,p) [22] level. The harmonic frequencies were scaled by a factor of 0.9496 as recommended by Merrick et al. [23]. The single-point energies were further refined at G3 level [24], based on the MP2/6-311G(d,p) geometries. The final G3 energies are based on a series of single-point energy calculations at the MP2, MP4, and QCI levels of theory, with different basis sets. H-abstractions from DEE by OH and HO_2 radicals proceed through pre- and post-reaction van der Waals complexes, thus these reactant complex (RC) and product complex (PC) were also computed by the aforementioned methods. An intrinsic reaction coordinate (IRC) calculation [25] was performed to each transition state to verify its connection between the designated reactant (or reactant complex) and product (or product complex). The calculated geometries and vibrational frequencies of the reactants, reactant complexes, transition states, product complexes and products are provided in Supplementary material.

The rate constants of the calculated reactions were computed by the ChemRate software [26], on the basis of the molecular geometries, frequencies and energies obtained from the abovementioned quantum calculations. The rate constants of all the reactions were calculated according to TST within the temperature range of 500–2500 K. The RRKM/Master Equation method was applied to determine the pressure dependencies for the decomposition reactions and isomerization reaction. The pressure range covers from 0.1 to 100 atm.

To calculate the pressure dependent rate constants, Lennard-Jones (L-J) parameters σ and ε were employed to evaluate the interaction between the bath gas and the reactants. Argon was used as the bath gas collider with the L-J parameters of $\sigma = 3.465$ Angstrom and $\varepsilon/k_B = 113.5$ K [27]. For other reactants in the decomposition reactions, the L-J parameters σ and ε were calculated using the following empirical equations [28]:

$$\sigma = 2.44(T_c/P_c)^{1/3} \tag{1}$$

$$\varepsilon/k_B = 0.77T_c \tag{2}$$

where k_B, P_c and T_c respectively are the Boltzmann constant, the critical pressure and the critical temperature. P_c and T_c were estimated using the Constantinou and Gani method [29]. An exponential-down model ($\langle\Delta E_{down}\rangle = 150(T/300)^{0.85}\ cm^{-1}$), which was adopted by various literatures [30–32], was used in the collision energy transfer in this study.

It is confirmed that treating low-frequency internal rotations as harmonic oscillator or free rotors can lead to pronounced errors in the partition function calculation. Thus, the low-frequency torsional modes were treated as one-dimensional (1-D) hindered internal rotors according to the Pitzer method [33]. The hindrance barrier of each internal rotation between the heavy atoms (i.e. C atom or O atom) for stable species was computed at the MP2/6-311G(d,p) level by performing a relaxed energy scan of the dihedral angle with an interval of 10°. For each transition state, the energy scan was calculated by freezing the atoms involved in the reaction coordinate.

Tunneling correction was considered using the Eckart formalism [34] in Chemrate, in which the barrier width L was calculated according to Eqs. (3) and (4) [35].

$$\frac{L}{2\pi} = \sqrt{-\frac{2}{F^*}}\left[\frac{1}{\sqrt{E_1}} + \frac{1}{\sqrt{E_{-1}}}\right]^{-1} \tag{3}$$

$$v^* = \frac{1}{2\pi}\sqrt{\frac{-F^*}{m}} \tag{4}$$

Here, E_1 and E_{-1} represent for the forward and reverse barrier heights at 0 K, respectively. v^* is the transition state's imaginary frequency and F^* stands for the second derivative of the potential energy function calculated at its maximum (force constant). m is the reduced mass of H.

2.2. Chemical mechanism reduction

The skeletal reduction is conducted with two stages. First, a directed relation graph with error propagation (DRGEP) based method [36] is applied as the first-cut reduction. A pairwise relation defined by Jacobian matrix elements is applied for a pair of species by calculating a semi-normalized sensitivity coefficient. Chen and Chen [36] show that the Jacobian pairwise relation can improve the searched species list with a more accurate ranking such that a smaller size of skeletal mechanism can be obtained for a fixed worst case error. For the graph