

Experimental and Kinetic Study on Ignition Delay Times of Diethyl Ether

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ABSTRACT

Ignition delay times of Diethyl Ether (DEE) were measured behind reflected shock waves for the temperatures from 1050 to 1600 K, pressures of 1.2, 4 and 16 atm and equivalence ratios of 0.5 and 1.0. Result shows that the ignition delay times increase with the increase of the equivalence ratio and the decrease of the pressure. The only literature DEE mechanism (Yasunaga et al. model) was employed to simulate the experimental data and result shows that the model gives reasonable prediction on lean mixtures, while the prediction on stoichiometric mixtures is slightly higher. Sensitivity analysis was conducted to pick out the key reactions in the process of DEE ignition at high and low pressures, respectively. Reaction pathway analysis shows that the consumption of DEE is dominated by the H-abstraction reactions. Through linear analysis, a correlation for the DEE ignition data was obtained. Using this correlation, the measured DEE data were compared to the literature correlations of DME and n-butane, for they have the similar molecular structure. Result shows that DEE has the strongest overall reactivity among the three fuels, while that of DME and n-butane are comparable. Sensitivity analysis and radical pool analysis were conducted to gain a further understanding of the ignition process of the three fuels.

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INTRODUCTION

Finding clean and renewable alternative vehicle fuels is becoming more and more urgent due to the excessive consumption of petroleum and the serious pollution in atmosphere. Among the alternative fuels researched as promising diesel substitutes, dimethyl ether (DME) has been extensively researched [1, 2, 3, 4, 5, 6, 7, 8, 9]. Having a similar molecular structure, diethyl ether (DEE) has some analogous attractive properties to DME for application in diesel engines [10]. DEE can be easily produced by a dehydration reaction from two ethanol molecules. Moreover, DEE also has some extra advantages compared to DME, such as higher cetane number and higher energy density. While DME is a gaseous fuel at normal temperatures and pressures, DEE is in liquid form which poses less problems for fuel delivery infrastructure and current vehicle technology. Thus it is a promising alternative to diesel fuel which has gained extensive attention recently [11].

Up to now, research on DME have been widely reported, however, studies on DEE are relative few. While most of the available studies focused on the potential of DEE as a supplementary blending component with biodiesel, diesel or LPG etc. in engines [12, 13, 14, 15], few of them concentrated on the combustion and ignition characteristics of DEE. Using a cylindrical-type bomb, Di et al. [16] measured the unstretched laminar flame velocities and Markstein lengths for DEE-air mixtures at different temperatures, pressures and equivalence ratios. Zhang et al. [17] investigated the effect of diluent gas (nitrogen) on combustion characteristics of DEE-air mixtures. Yasunaga et al. [18] conducted DEE oxidation and pyrolysis

experiments in shock tube facilities at limited conditions. They constructed a detailed chemical reaction mechanism for DEE to describe its oxidation and pyrolysis kinetics.

Ignition delay times directly influence the performance of the combustion processes and emissions in many combustion devices and they are a fundamental parameter in engine and combustion simulations. Moreover, they are essential parameters in developing and validating a chemical kinetic model. Until now, only limited studies measured the ignition delay times of DEE over a narrow range of conditions with a shock tube. Thus, accurate ignition data under wide conditions are necessary. In current study, ignition delay times at temperatures from 1050 to 1600 K, pressures from 1.2 to 16 atm and equivalence ratios of 0.5 and 1.0 are provided. Simulations were conducted using the DEE model developed by Yasunaga et al. [18]. Reaction pathway analysis and sensitivity analysis were made to gain a further insight into the ignition process. In addition, comparison between DEE and another two fuels with similar structures, namely DME and n-butane are presented.

EXPERIMENTAL SETUP AND NUMERICAL APPROACH

The ignition delay data were measured in a shock tube facility which has been described in details previously [19,20]. This shock tube with an internal diameter of 11.5 cm consists of a 2 m long driver section and a 7.3 m long driven section. The two parts are separated by double PET (polyester terephthalate) diaphragms. Before experiment, the driven section is evacuated by a Nan Guang vacuum system to pressure below 1 Pa. Helium and nitrogen mixtures with high purity

were used as driver gas. Purities of DEE, oxygen and argon are higher than 99.5%, 99.999% and 99.999%, respectively. The mole fraction of DEE in the reactant mixtures was fixed at 1% as shown in Table 1. DEE/O₂/Ar mixtures were prepared in a 128 L stainless steel tank and allowed to diffuse for at least 12 h to ensure sufficient mixing. Selected by a narrow filter centered at 430 ± 10 nm, the OH* chemiluminescence was detected by a photomultiplier (Hamamatsu, CR131) located at the end wall. End wall shock velocity was determined by linear extrapolation using four fast-response piezoelectric pressure transducers (PCB 113B26) with three time interval counters (Fluke PM6690) located along the driven section at fixed intervals. The temperatures behind reflected shock wave were calculated by Gaseq [21], a chemical equilibrium software.

Table1. Composition of Fuel Mixtures (in mole fraction)

ϕ	DEE (%)	O ₂ (%)	Ar (%)
0.5	1	12	87
1	1	6	93

The definition of ignition delay time is the time interval between the arrival of incident shock wave at the end wall and the extrapolation of the steepest rise of OH*chemiluminescence to the zero baseline, as shown in Figure 1.

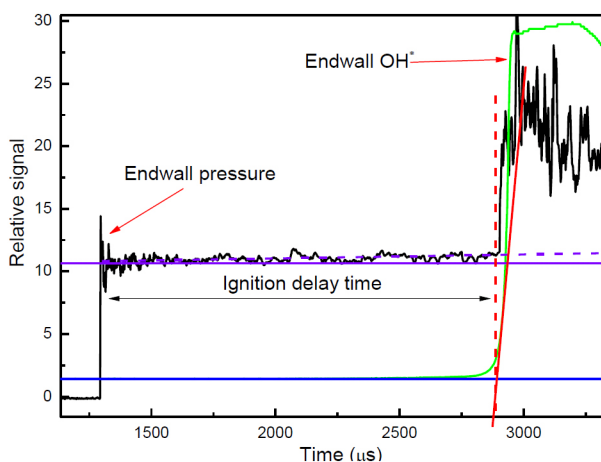


Figure 1. Definition of ignition delay times.

The Senkin [22] code in Chemkin II program [23] was used to simulate the experimental data. All models were assumed to be adiabatic and zero-dimensional. 4%/ms in pressure rise was considered in all simulations due to the interaction between reflected shock wave and boundary layer.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Ignition delay time measurements and correlation

A correlation of ignition delay times as a function of pressure, equivalence ratio and temperature for all tested mixtures was obtained through the regression analysis as following,

$$\tau = 8.28 \times 10^{-4} p^{-0.61} \phi^{0.61} \exp(145.76 / RT) \quad (1)$$

Where τ is the ignition delay times in microsecond, p is the pressure in atmosphere, $R = 8.314 \times 10^{-3}$ KJ/(mol.K) is the universal gas constant and T is the temperature in Kelvin. Eq.1 is only applicable to the temperature range of 1050-1600 K, pressure range of 1.2-16 atm, equivalence ratio range of 0.5-1.0 and fuel mole fraction of 1% for the experimental conditions of this study.

Figure 2 illustrates the measured data and correlated values. Generally, the measured data agree fairly well with the fitting curves. The ignition delay times increase with a decrease in pressure, which is consistent with the negative exponent of pressure in Eq.1. Moreover, from the positive exponent of equivalence ratio, we can infer that the ignition delay times increase when equivalence ratio increases.

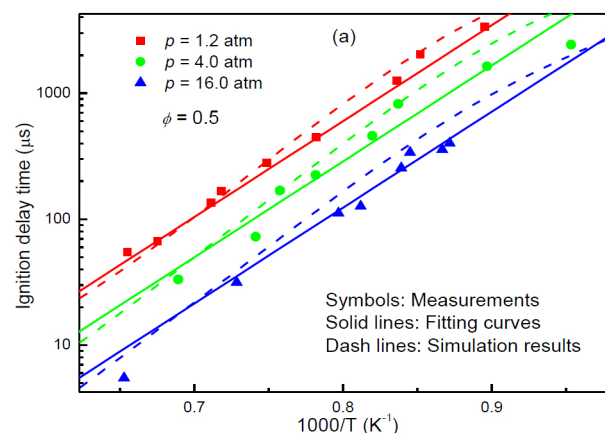


Figure 2 (a). Measured and fitted ignition delay times of lean DEE/O₂/Ar mixtures (Symbols: Measurements, Solid lines: Fitting curves, Dash lines: Simulation results).

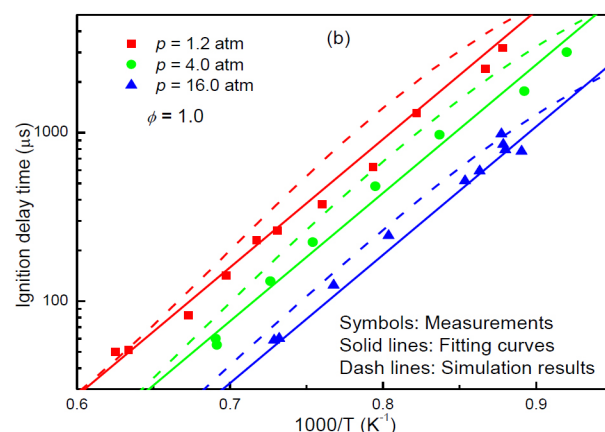


Figure 2 (b). Measured and fitted ignition delay times of stoichiometric DEE/O₂/Ar mixtures (Symbols: Measurements, Solid lines: Fitting curves, Dash lines: Simulation results).

Chemical Kinetic Analysis

Simulation Results

Up to now, the only available chemical kinetic model for DEE is the one developed by Yasunaga et al. [18]. Based on their shock tube ignition and pyrolysis data, a model comprising 148 species and 751 reactions was constructed. Although the model generally gives good prediction of the measurements on which they were based, further validation is still necessary. In this section, the simulation results presented by the Yasunaga et al. model are compared to current ignition data, to verify the predictive ability of the model. From Figure 2 (a), it can be seen that the model gives fairly good prediction on the lean mixture at three pressures investigated. However, for the stoichiometric mixture, as shown in Figure 2 (b), the simulation results are slightly higher, especially at lower pressure. In general, the model gives reasonable prediction on the measurements.

Sensitivity Analysis

Sensitivity analysis was conducted to find out the most influential reactions during ignition process. The normalized sensitivity coefficient (S) is defined as:

$$S = \frac{\tau(2k_i) - \tau(0.5k_i)}{1.5\tau(k_i)} \quad (2)$$

where τ is the ignition delay time and k_i is the reaction rate of the i^{th} reaction in the model. Negative S indicates a promoting effect on the overall reactivity and a decrease in the ignition delay time and vice versa.

Figure 3 presents the top 18 sensitive reactions at the temperature of 1200 K, equivalence ratio of 0.5, fuel mole fraction of 1% and pressures of 1.2 and 16 atm. It is found that the small molecular reactions $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ and $\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}$ present a much larger negative sensitivity than the other reactions at a pressure of 1.2 atm, thus they exhibit the largest promoting effect on ignition. At high pressure, the two reactions also promote the ignition, but their sensitivity coefficients are relatively small. As reactions $\text{HO}_2 + \text{O} = \text{H}_2\text{O} + \text{O}_2$ and $\text{CH}_3 + \text{HO}_2 = \text{CH}_4 + \text{O}_2$ consume reactive radicals and produce stable molecules, they exhibit a significant inhibiting effect on the overall reaction at both high and low pressures. Beside these small molecule reactions, some fuel specific reactions also influence the ignition progress greatly. The molecule decomposition reaction, i.e. $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 (+\text{M}) = \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{O}$, has a large negative sensitivity coefficient and it exhibits the largest promoting effect among all the fuel specific reactions. Consuming the reactive H radical and forming a stable H_2 molecule instead, reaction $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{H} = \text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{S} + \text{H}_2$ strongly decreases the overall reactivity. Other H abstraction reactions, such as $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{HO}_2 = \text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{P} + \text{H}_2\text{O}_2$, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{HO}_2 = \text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{S} + \text{H}_2\text{O}_2$ and $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{CH}_3\text{O}_2 = \text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{S} + \text{CH}_3\text{O}_2\text{H}$, show the negative coefficients and their promoting effects are more remarkable at 16 atm.

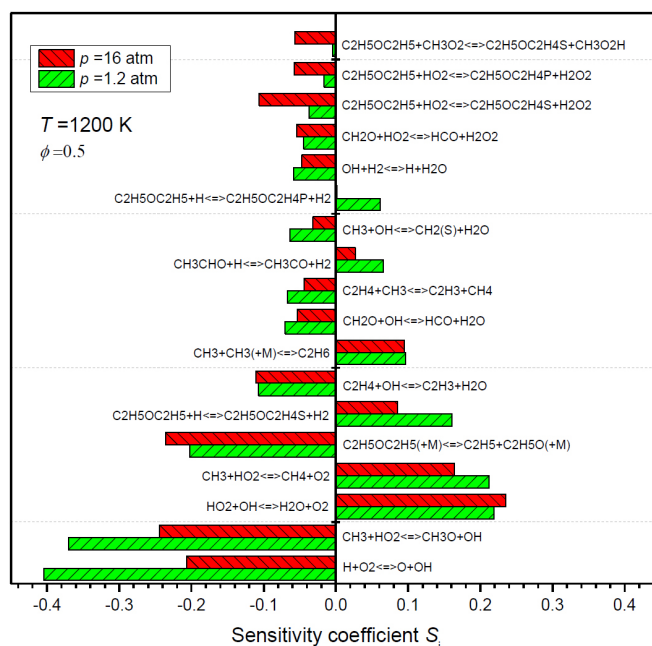


Figure 3. Normalized sensitivity of the ignition delay time for lean mixture at high and low pressures.

Reaction Pathway Analysis

Figure 4 gives the reaction pathways at the same conditions as that of the sensitive analysis. It can be seen that at both conditions, the reactant is dominantly consumed through H-abstraction reactions. At both pressures, the H abstraction from the α -carbon site has the largest branching ratio. About half of the fuel is consumed through this path at 1.2 atm and when the pressure increases to 16 atm, the branching ratio reaches to 62.0%. The product, $\text{C}_2\text{H}_5\text{OCHCH}_3$, then exclusively breaks through the β C-O bond and forms an ethyl radical and an acetaldehyde molecule. The branching ratio of the H abstraction reaction from the β -carbon site is relatively small because of the large bond dissociation energy (BDE) of DEE at the β carbon. $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2$, which is generated through this pathway, then mainly degenerate through breaking the β C-O bond and forming ethylene molecule and ethoxylated radical. Generally, H abstractions contribute to 67.2% and 79.9% fuel consumption at 1.2 atm and 16 atm, respectively and most of the fuels are attacked by H, OH, O and HO_2 radicals. Although the ignition process is dominated by the H abstractions, the unimolecular decomposition of DEE is still important, especially at 1.2 atm as it accounts for about 1/3 fuel consumption. DEE mainly decompose through two routes and their products are ethyl radical + ethoxylated radical and ethylene + ethanol, respectively.

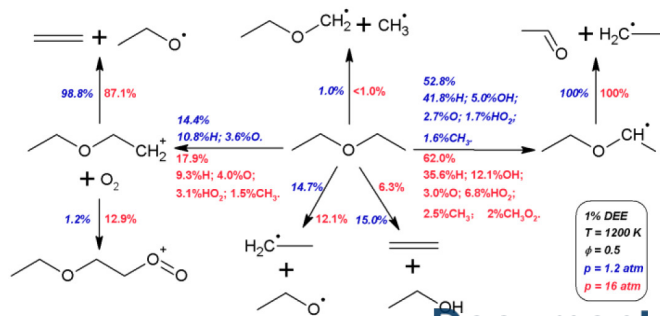


Figure 4. Reaction pathway analysis for lean mixture at high and low pressures at 20% fuel consumption