

Experimental and numerical study of the ignition delay times of primary reference fuels containing diethyl ether

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1 Introduction

Research on ignition and combustion of diethyl ether (DEE) has gained significant interest due to the promising properties of DEE as alternative fuel [1, 2] and as ignition enhancer. It can also help to reduce soot formation. DEE is typically produced from ethanol by catalytic dehydrogenation [3] and is therefore of interest as a biomass-derived fuel component. In addition, DEE is used as a model fuel to test safety-relevant ignition processes caused by hot surfaces. It has a surprisingly high cetane number of 125 when compared with alkanes with the same molecular size (e.g., 22 for butane and 30 for pentane). Therefore, understanding the ignition chemistry of DEE is of high practical interest. There are many investigations dealing with diethyl ether. Di Tommaso et al. [4] studied reactions relevant to autoxidation of DEE using computational methods. Recently, the effects of blending DEE to Diesel fuel on the combustion behavior were studied in a direct-injection Diesel engine [5]. Interestingly, DEE was found to increase the ignition delay times, despite its high cetane number. Laminar burning velocities of DEE/air mixtures were measured at various equivalence ratios, initial temperatures, and pressures in a spherical bomb by schlieren photography [6, 7]. Inomata et al. [8] studied the ignition delay times of DEE in air. They found that the mixture is extremely reactive and observed a monotonic decrease of the ignition delay time with increasing temperature. Clothier et al. [9] investigated the effect of DEE on Diesel fuel and concluded that DEE inhibits the ignition of Diesel fuel and thus decreases the cetane number of Diesel fuel. The increased ignition delay times were attributed to the interaction of DEE with some aromatics in Diesel fuel [10].

Griffiths and Inomata [11] studied oscillatory cool flames of DEE between 430 and 590 K experimentally and numerically. They associated the low-temperature reactivity of DEE with hydroperoxide formation. Yasunaga et al. [12] studied the pyrolysis and the oxidation of DEE at 900–1900 K and 1–4 bar behind reflected shock waves. They monitored the decay of DEE, ignition onset, and OH induction times, respectively, using time-resolved infrared absorption at 3.39 μm , time-resolved emission at 431 nm and absorption at 306.7 nm, respectively. A kinetics model was assembled and tested against the experimental data. Good agreement between experiment and simulation was found at 1–3.5 bar and at equivalence ratios ϕ of 0.5, 1, and 2. Werler et al. [13] extended the temperature range for igni-

tion delay time measurements down to 550 K using a shock tube and a rapid compression machine. Recently, Sakai et al. [14] determined the (high-pressure limiting) rate coefficients of the unimolecular reactions of 1-ethoxyethylperoxy ($\text{C}_2\text{H}_5\text{OCH}(\text{OO})\text{CH}_3$, p-RO₂) and 2-ethoxyethylperoxy ($\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OO}$, s-RO₂) radicals using transition-state theory based on quantum-chemical calculations. Different reactions paths including intramolecular hydrogen shift to hydroperoxyalkyl (QOOH) radicals, concerted HO₂ elimination and back dissociation to $\text{R} + \text{O}_2$ for RO₂, as well as unimolecular decomposition of QOOH radicals were considered. In a new study Sakai et al. [15] determined the potential energy surfaces for the unimolecular reactions of OOQOOH isomers and 1- and 2-ethoxyethyl radicals with a CBSQB3 composite method. The reaction rates of OOQOOH isomers were determined. Based on these results and the results obtained on our earlier study [16], a detailed chemical kinetics model with low-temperature oxidation chemistry was developed and validated against measured IDTs. This model considerably improves the prediction of the ignition delay times of DEE.

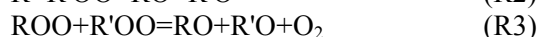
The goal of the present study is to check the performance of this model based on new experimental data of ignition delay times of blends of reference fuels (PRF95: 95% *iso*-octane and 5% *n*-heptane, representative for gasoline) and diethyl ether with 10 and 30 Vol.% DEE relative to PRF95 at high pressure (10 and 40 bar) and intermediate temperature (650–1250 K).

2 Experimental

The high-pressure shock-tube facility used for measuring ignition delay times is described in detail in Refs. [17, 18]. The shock tube has a constant inner diameter of 90 mm with lengths of the driver and driven sections of 6.4 and 6.1 m, respectively. Allowable peak pressures are 500 bar and the test times up to 15 ms can be achieved by driver-gas tailoring. All experiments were conducted behind the reflected shock between 650 and 1250 K at pressures of 10 ± 1.5 and 40 ± 1.5 bar and at two equivalence ratios ($\phi = 0.5$ and 1). Mixtures of PRF95/DEE with ratios of 100/0, 90/10 and 70/30 by volume were selected. PRF95 (95% *iso*-octane and 5% *n*-heptane) was chosen as reference fuel. The mixtures were prepared manometrically in a mixing vessel and stirred for one hour before use to ensure homogeneity. The temperature T_5 and pressure p_5 behind the reflected shock waves were computed from the incident shock velocity, with an estimated temperature uncertainty of <15 K. Bandpass-filtered (431 ± 5 nm) emission from CH* chemiluminescence was monitored through a window in the sidewall (15 mm from the end flange) with a Hamamatsu 1P21 photomultiplier tube. Ignition delay times were defined as the interval between the rise in pressure due to the arrival of the shock wave at the measurement port and the extrapolation of the steepest increase in CH* chemiluminescence to its zero level on the time axis [19].

3 Modeling

In this work a detailed kinetics model for DEE and PRF is assembled. The initial kinetics model for DEE was taken from Sakai et al. [15]. This model was developed and validated against ignition delay times measured by using a shock tube and RCM covering a wide range of conditions (1–40 bar, 500–1300 K). The sub-mechanism of PRF combined to DEE mechanism was taken from the recent study of Cai and Pitsch [20]. The following cross reactions between DEE and PRF were also included in the mechanism.



R1 is the H-atom abstraction reaction from a fuel molecule by R'OO radicals, and its rate constant is assumed as the same value with the H-atom abstraction reaction of CH₃O₂ or HO₂ radical. R2 is the O-

atom abstraction reaction from R'OO by a R radical, and its rate constant is taken from the typical value of alkane oxidation [21]. R3 is the reaction between ROO radicals, and their rate constants are taken from the typical value of alkane oxidation [21]. The resulting detailed kinetics model for PRF/DEE consists of 525 species and 2692 reactions. All simulations were performed under constant pressure with considering predefined measured pressure profiles and by accounting for thermochemical data to refer the rate of reversible reactions.

4 Results and discussions

The current mechanism was validated against the ignition delay times measured by using a shock tube. The comparison between experiments and simulations are shown in figure 1 for PRF95, figure 2 for PRF95 doped with 10% of DEE, and figure 3 for PRF 95 doped with 30% of DEE. To take into account the slight temporal variations in temperature after the arrival of the reflected shock wave due to facility effects [4], the simulations was performed with the assumption of 5%/ms pressure increase up to 2.8 ms and constant pressure after 2.8 ms as a result of driver-gas tailoring after the reflected shock wave reaches the contact surface. Ignition was defined by the time of maximum reaction rate for the production of CH*. The present model reproduces well the ignition delay times of PRF95 at 720–1200 K and 40bar. The model also well produces the ignition delay times for the mixture of PRF95/DEE. Figure 4 shows the influence of DEE addition to PRF95. The present mechanism well captures the behavior of DEE addition to PRF95 although the model predicts too long ignition delay times compared to the experiments at temperatures below 800 K.

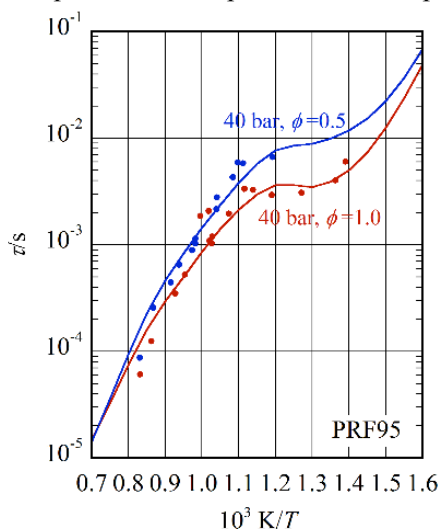


Fig. 1: Ignition delay times τ of PRF95/air at equivalence ratio ϕ of 0.5 and 1.0 and pressure of 40 bar. The symbols are experiments measured behind reflected shock waves and the lines are simulations with the detailed kinetics model developed in this work

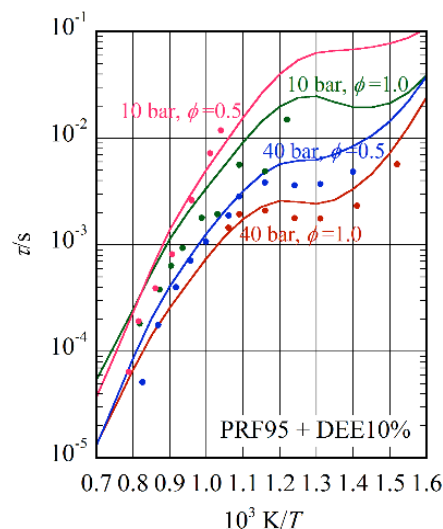


Fig. 2: Ignition delay times τ of PRF95/air doped with 10 vol% of diethylether in the liquid phase at a total equivalence ratio ϕ of 0.5 and 1.0 and pressures of 10 and 40 bar. The symbols are data measured behind reflected shock waves and the lines are simulations with the detailed kinetics model developed in this work.

To identify the key reaction responsible for the reaction progress of PRF95/DEE mixture, we performed a reaction path and sensitivity analysis for pure PRF95, PRF95 doped with 10 and 30 Vol.% of DEE, and pure DEE at an initial temperature of 666 and 909 K, a pressure of 40 bar, and an equivalence ratio of 1.0. Table 1 shows the main elementary reactions that produce OH radicals at the point of 10 K temperature increase from the initial condition. At 666 K, the low-temperature oxidation mechanism of both *iso*-octane (R8 – R11) and DEE (R4 – R7) contribute to the production of OH rad-

icals. Even addition of small amounts of DEE, for example PRF95 + DEE 10 Vol.%, the reactions derived from DEE oxidation cover 28.3% of the OH production path. This is because the rate of H-atom abstraction reactions of DEE is much faster than that of *iso*-octane. Thus even 10 Vol.% addition of DEE changes the ignition delay times of PRF95 considerably. Sensitivity analysis also shows that the DEE oxidation controls the temperature increase of the reaction system. At 909 K, the low temperature oxidation reactions of DEE (R12 and R13) still contribute to the OH production, although there is no reaction that originates from the low-temperature oxidation of *iso*-octane. Figure 4 shows also that at 909 K DEE already cross the negative-temperature coefficient region whereas *iso*-octane still undergoes the high-temperature oxidation mechanism at this temperature.

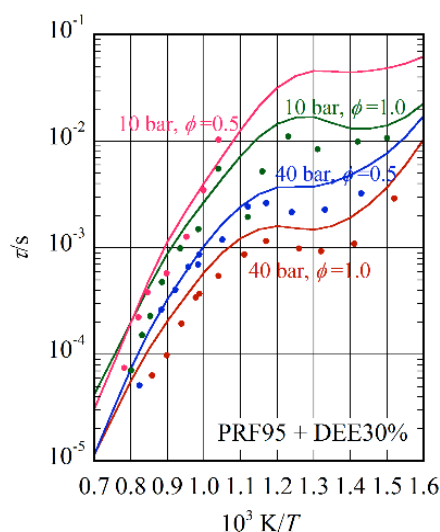


Fig. 3: Ignition delay times τ of PRF95/air doped with 30 vol% of diethylether in the liquid phase at total equivalence ratio ϕ of 0.5 and 1.0 and pressures of 10 and 40 bar. The symbols are data measured behind reflected shock waves and the lines are simulations with the detailed kinetics model developed in this work.

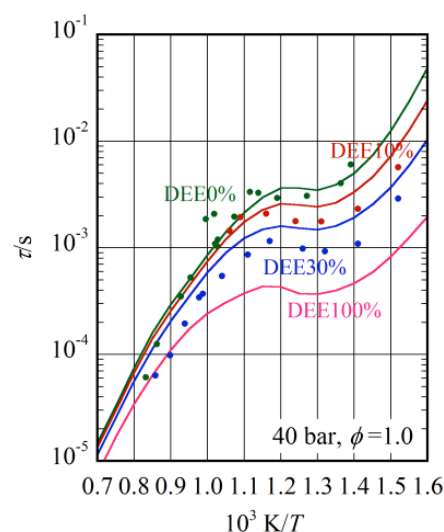


Fig. 4: Effect of addition of diethyl ether to PRF95/air on the ignition delay times at total equivalence ratio ϕ of 1.0 and pressures of 40 bar. The symbols are data measured behind reflected shock waves and the lines are simulations with the detailed kinetics model developed in this work.

Table 1: Key reactions that produce OH radical and their respective contributions ^a.

Reactions	DEE	PRF95+DEE30%	PRF95+DEE10%	PRF95
Initial temperature 666 K				
(R4) $C_4H_8ObOOHc \rightleftharpoons 2CH_3CHO + OH$	13.4	6.9	3.0	0.0
(R5) $C_4H_8ObOOHcOO \rightleftharpoons bCOC_3H_7OcOOH + OH$	59.6	32.8	14.4	0.0
(R6) $bCOC_3H_7OcOOH \rightleftharpoons OH + bCOC_3H_7OcO$	10.5	15.4	9.3	0.0
(R7) $bC_4H_7OacOOH \rightleftharpoons C_4H_8OcOOHcyOab + OH$	5.6	3.8	1.6	0.0
(R8) $BC_8H_{16}OOHXAO_2 \Rightarrow IC_8KETBA + OH$	0.0	10.5	19.6	27.4
(R9) $BC_8H_{16}OOHXDO_2 \Rightarrow IC_8KETBD + OH$	0.0	7.0	13.1	18.2
(R10) $IC_8KETBA \Rightarrow CH_2O + IC_3H_7COC_3H_6XT + OH$	0.0	3.1	8.5	13.5
(R11) $IC_8KETBD \Rightarrow CH_2O + TC_4H_9COC_2H_4S + OH$	0.0	2.1	5.7	9.0
initial temperature 909 K				
(R12) $C_4H_8OaOOHc \rightleftharpoons C_4H_8OcyOac + OH$	9.8	4.3	1.7	0.0
(R13) $C_4H_8ObOOHc \rightleftharpoons 2CH_3CHO + OH$	27.3	12.8	5.3	0.0
(R14) $C_3H_5O_2H \rightleftharpoons C_2H_5O + OH$	21.5	6.7	1.6	0.2
(R15) $H_2O_2(+M) \rightleftharpoons 2OH(+M)$	0.6	3.5	5.2	5.4
(R16) $CH_3 + HO_2 \rightleftharpoons CH_3O + OH$	3.7	6.7	8.0	9.0
(R17) $CH_3O_2H \rightleftharpoons CH_3O + OH$	14.0	31.8	37.1	39.8

^a Contributions are the ratio of OH radical production at the point of 10 K increase from initial temperature. The initial conditions are pressure of 40 bar and equivalence ratio of 1.0.

4 Conclusions

Ignition delay times of lean and stoichiometric mixtures of the primary reference fuel PRF95 doped with DEE (10 and 30 Vol.%) were measured between 650 and 1250 K at pressures of 10 and 40 bar. The experiments show that DEE drastically increases the reactivity of the base fuel. The model for gasoline surrogates of Cai and Pitsch [20] was embedded in a new DEE mechanism [15], in which important low-temperature species such as QOOH and O₂QOOH were considered. The prediction of the measured ignition delay time data was very good.

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