

# Ignition delay times of primary reference fuels doped with diethyl ether at high pressure and intermediate temperatures

Mustapha Fikri<sup>a</sup>, Jürgen Herzler<sup>a</sup>, Oliver Welz<sup>a</sup>, Yasuyuki Sakai<sup>b</sup>, Christof Schulz<sup>a</sup>

<sup>a</sup>Institute for Combustion and Gas Dynamics – Reactive Fluids,  
University of Duisburg-Essen, 47048 Duisburg, Germany

<sup>b</sup>Graduate School of Engineering,  
University of Fukui, 3-9-1 Bunkyo, Fukui 910-8507, Japan

## 1 Introduction

Diethyl ether (DEE) can be produced from ethanol by catalytic dehydrogenation [1] and is therefore of interest as a biomass-derived fuel component. It has a surprisingly high cetane number of 125 when compared with alkane with the same molecular size (e.g., 22 for butane and 30 for pentane). DEE is typically used to support cold-start in gasoline and Diesel engines [2], or as ignition improver for ethanol [3] and is even considered as alternative Diesel fuel [4, 5]. In addition, DEE is used as a model fuel to test safety-relevant ignition processes on hot surfaces.

Understanding the ignition chemistry of DEE is therefore of high practical interest. Di Tommaso et al. [6] 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 [7]. 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 [8, 9]. Inomata et al. [10] 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. [2] 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 [11].

Griffiths and Inomata [12] 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. [13] 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  $\mu\text{m}$ , 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  $\phi$  of 0.5, 1, and 2. Werler et al. [14] extended the temperature range for ignition delay time measurements down to 550 K using a shock tube and a rapid compression machine. At these conditions, the model of Yasunaga [15] could not reproduce the experimental data. Based on a sensitivity analysis, the rate coefficient for the  $\text{HO}_2 + \text{DEE}$  hydrogen abstraction reaction was increased by a factor of five, which improved the agreement between simulation and experiment. However, the model did not contain reactions of peroxy ( $\text{RO}_2$ ) radicals derived from reactions of  $\text{O}_2$  with initial radicals of DEE ( $\text{C}_2\text{H}_5\text{OCHCH}_3$  and  $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2$ ). These reactions are known to critically influence the radical pool that is responsible for low-temperature auto ignition [16].

Very recently, Sakai et al. [17] 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- $\text{RO}_2$ ) and 2-ethoxyethylperoxy ( $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OO}$ , s- $\text{RO}_2$ ) radicals using transition state theory based on quantum-chemical calculations. Different reactions paths including intramolecular hydrogen shift to hydroperoxyalkyl (QOOH) radicals, concerted  $\text{HO}_2$  elimination and back dissociation to  $\text{R} + \text{O}_2$  for  $\text{RO}_2$ , as well as unimolecular decomposition of QOOH radicals were considered. Although reaction of  $\text{O}_2$  with QOOH leading to low-temperature chain branching has not yet been taken into account, these new results enabled the development of an improved mechanism for the low temperature regime. The goal of the present study is to check the performance of this model based on new experimental data of ignition delay times of a reference fuel (PRF95: 95% *iso*-octane and 5% *n*-heptane, representative for gasoline) doped 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. [18, 19]. 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  $10 \pm 1.5$  and  $40 \pm 1.5$  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 ( $431 \pm 5$  nm) emission from  $\text{CH}^*$  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  $\text{CH}^*$  chemiluminescence to its zero level on the time axis [20].

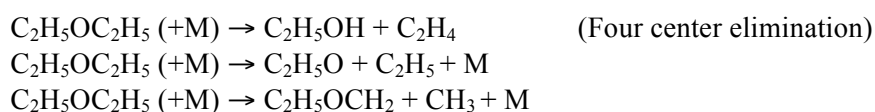
## 3 Modeling

In this work a detailed kinetics model for DEE and gasoline surrogates is assembled. The initial kinetics model for gasoline surrogates was taken from Mehl et al. [21]. This model was developed and validated against shock tube, RCM and jet-stirred reactor data covering a wide range of conditions (3–50.7 bar, 650–1200 K). This mechanism, however, does not contain reactions of DEE. Most of DEE reactions were therefore adopted from a pentane mechanism [22] and updated with unimolecular reactions of 1-ethoxyethylperoxy (s- $\text{RO}_2$ ) and 1-ethoxyethylperoxy (p- $\text{RO}_2$ ) which are relevant in the low temperature regime and were recently characterized by Sakai et al [17] (this model is referred to as “Sakai model” below). In the combined DEE/PRF95 mechanism, we initially kept the  $\text{C}_0$ - $\text{C}_2$  mechanism from Mehl et al. [21] invariant. However, the simulations with the combined model gave longer ignition delay times for pure DEE when compared with the prediction of the initial model of Sakai

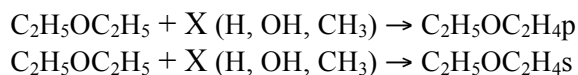
(which uses a different C<sub>0</sub>-C<sub>2</sub> mechanism). Therefore the C<sub>0</sub>-C<sub>2</sub> submechanism in the Sakai model was used in the combined DEE/PRF95 mechanism. The corresponding C<sub>0</sub>-C<sub>2</sub> reactions were taken from Curran mechanism [23] for *iso*-octane and some reactions were changed according to recent papers. During this blending process we ensured that the combined mechanism still reproduces the ignition delay times on which both individual mechanism were built. The combined mechanism yields ignition delay times for *n*-heptane and DEE that differ by about 10% compared to the values obtained from the original mechanisms. The resulting detailed kinetics model for DEE-blended gasoline surrogates consists of 1458 chemical species and 6114 elementary reactions. We note that cross reactions between different fuels were not considered.

In the previous model of Yasunaga et al. that was assembled based on natural gas, *n*- and *iso*-butane, DEE-specific reactions were added. These main reaction channels are:

Unimolecular decomposition of DEE:



Abstraction reactions from DEE:



At high temperature, C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>4</sub>s decomposes to acetaldehyde (CH<sub>3</sub>CHO) and ethyl (C<sub>2</sub>H<sub>5</sub>) radicals, and C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>4</sub>p decomposition mainly leads to C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>5</sub>O formation. At low temperature, O<sub>2</sub> addition to C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>4</sub>p and C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>4</sub>s yields the p-RO<sub>2</sub> p-RO<sub>2</sub> peroxy radicals that open the low temperature reaction paths.

In the model proposed in this work (Sakai model) several reactions specific for diethyl ether and relevant for the low-temperature regime were added (except the subsequent reactions QOOH + O<sub>2</sub>) as described in the introduction. All these modifications substantially improve the prediction of ignition delay times of DEE compared to the former model of Yasunaga et al. [15] (for brevity not shown here).

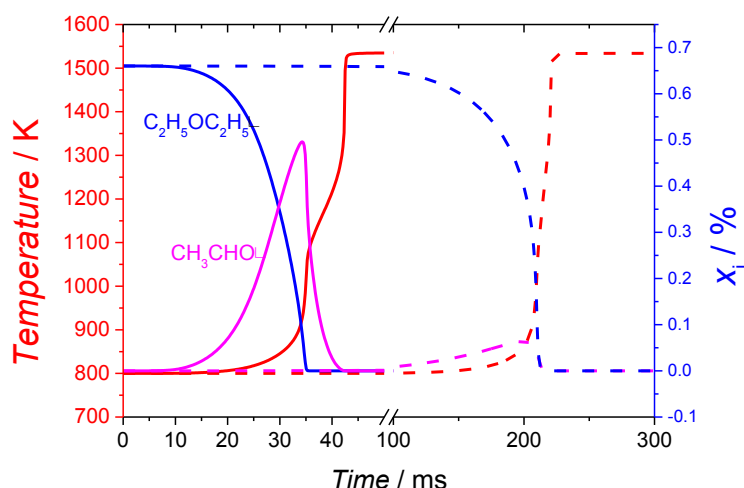


Figure 1. Concentration-time profiles of C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> and CH<sub>3</sub>CHO and temperature history of a stoichiometric reaction  $x_{\text{DEE}} = 0.66\%$ ,  $x_{\text{O}_2} = 3.97\%$  balanced in argon.

Figure 1 shows the predictions of Yasunaga [15] and Sakai model [17] for a stoichiometric mixture of DEE/O<sub>2</sub>/Ar at 800 K and 40 bar. It clearly shows that the Yasunaga model predicts much longer ignition delay and produces much less CH<sub>3</sub>CHO which is the main intermediate during the depletion of DEE. Also, the temperature histories differ. The first-stage ignition from the model in this work is much more pronounced. Kinetics modeling under given experimental conditions was performed using CHEMKIN under constant volume, accounting for heat release of the reactions.

## 4 Results and discussions

Ignition delay times were measured in a high-pressure shock tube at 10±1.5 and 40±1.5 bar in the 650–1250 K range for two equivalence ratio ( $\phi = 0.5, 1$ ). Below 650 K, no ignition was observed within the test time of 15 ms. Figure 2a compares the measured ignition delay times for PRF95 at two equivalence ratios and 40 bar with the prediction of the model of Mehl et al [21]. The simulation was performed under constant volume assumption and without the consideration of the gas-dynamic facility effects. The model agrees well with the data at high temperature but overpredicts the measurements at intermediate temperature. Deviation of the model at high pressure and low temperature was also observed for pure *n*-heptane in [21]. Figure 2 (b) shows ignition delay time data for mixtures of PRF doped with 10% DEE at  $\phi = 0.5$  and 1 and at 10 and 40 bar. At first glance, one notices that lean mixtures (open symbols) are less reactive than stoichiometric mixtures (filled symbols). This effect is due to the chain branching reactions that are mainly dependent on fuel concentration at low and intermediate temperatures. At high temperature, ignition delay times for both equivalence ratios converge and ignition becomes primarily controlled by the reaction  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ , so that the reactivity depends merely on the O<sub>2</sub> concentration in this regime. Addition of 10 Vol.% DEE to the base fuel at 40 bar increases the reactivity of the fuel substantially especially in the low temperature range ( $T < 950$  K). At high temperature the difference in the reactivity between the PRF95 and the PRF95/DEE mixtures are not too large at 40 bar.

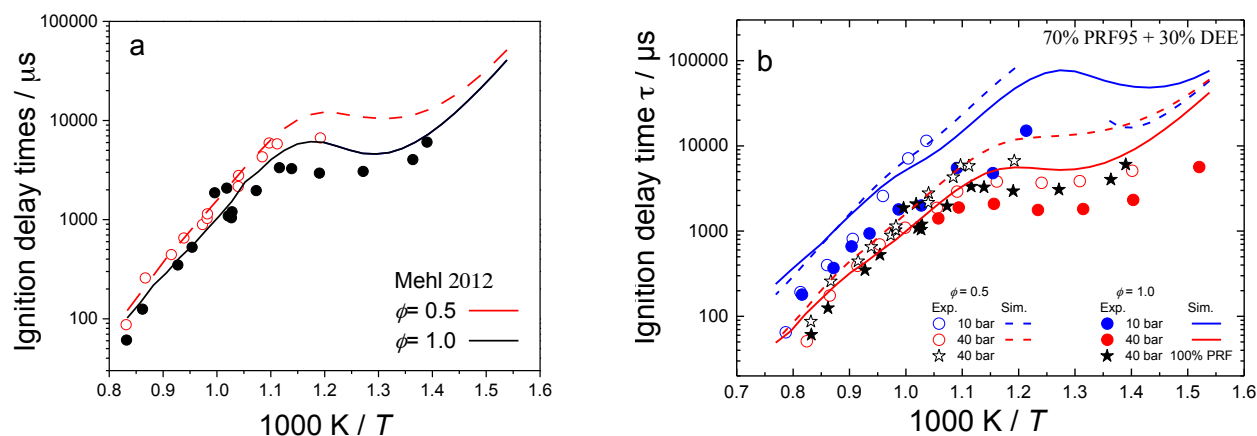


Figure 2. Ignition delay times of PRF95 and PRF doped with 10 Vol.% diethyl ether at equivalence ratios  $\phi = 0.5$  (open symbols), 1 (filled symbols) and pressures of 10 and 40 bar.

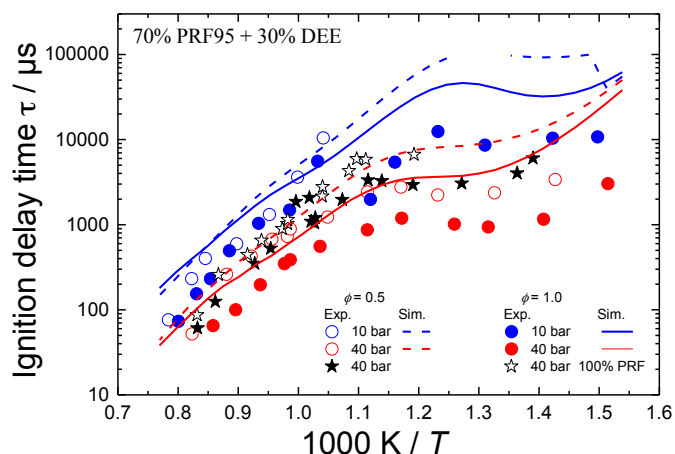


Figure 3. Ignition delay times of PRF95 and PRF doped with 30 Vol.% diethyl ether at equivalence ratios  $\phi = 0.5$  (open symbols), 1 (filled symbols) and pressures of 10 and 40 bar.

The reactivity of the mixture increases drastically when the amount of DEE was increased to 30% relative to the reference fuel in the low temperature as well as in the high temperature range, particularly for the stoichiometric conditions as shown in Figure 3. At 10 bar the ignition delay times values of the doped mixture for the lean and the stoichiometric conditions exhibits the same activation energy but the absolute values are slightly similar, but the deviation becomes large when the pressure is increased to 40 bar. It is also noticeable that increasing the amount of DEE addition leads to a more pronounced NTC behavior, which is shifted to lower temperature relative to that for the reference fuel. In general, the model captures the trend of data well but does not reproduce the absolute values. Ongoing work focuses on the second  $O_2$  addition to QOOH. This will improve the prediction of the model.

## 4 Conclusions

Ignition delay times of lean and stoichiometric mixture 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 Mehl [21] was embedded in a new DEE mechanism, in which important low-temperature species such as QOOH were considered. The prediction of the measured ignition delay time data was satisfactory but does still not reproduce the absolute values. The implementation of the reaction channels for  $O_2$ QOOH is underway.

## Acknowledgements

Funding by the German Research Foundation (DFG) in the framework of the project FI 1712/1 is gratefully acknowledged. We thank Natascha Schlösser for technical support.

## References

1. B. Bailey, J. Eberhardt, S. Goguen, J. Erwin, *SAE Paper* 972978 (1997).
2. P. Q. E. Clothier, A. Moise, H. O. Pritchard, *Combust. Flame* 81 (1990) 242-50.
3. G. Nagarajan, A. N. Rao, S. Renganarayanan, *Int. J. Amb. Energy* 23 (2002) 149-158.
4. M. P. Ashok, C. G. Saravanan, *Energy Fuels* 21 (2007) 1878-1882.

5. A. S. Ramadhas, S. Jayaraj, C. Muraleedharan, *Int. J. Global Energy Issues* 29 (2008) 329 - 336.
6. S. Di Tommaso, P. Rotureau, O. Crescenzi, C. Adamo, *Phys. Chem. Chem. Phys.* 13 (2011) 14636-14645.
7. D. C. Rakopoulos, C. D. Rakopoulos, E. G. Giakoumis, A. M. Dimaratos, *Fuel* 109 (2013) 325-335.
8. Y. Di, Z. Huang, N. Zhang, B. Zheng, X. Wu, Z. Zhang, *Energy Fuels* 23 (2009) 2490-2497.
9. F. Gillespie, W. K. Metcalfe, P. Dirrenberger, O. Herbinet, P.-A. Glaude, F. Battin-Leclerc, H. J. Curran, *Energy* 43 (2012) 140-145.
10. T. Inomata, J. F. Griffiths, A. J. Pappin, *Proc. Combust. Inst.* 23 (1991) 1759-1766.
11. P. Q. E. Clothier, A. Moise, H. O. Pritchard, *Combust. Flame* 81 (1990) 242-250.
12. J. F. Griffiths, T. Inomata, *J. Chem. Soc., Faraday Transactions* 88 (1992) 3153-3158.
13. K. Yasunaga, F. Gillespie, J. M. Simmie, H. J. Curran, Y. Kuraguchi, H. Hoshikawa, M. Yamane, Y. Hidaka, *J. Phys. Chem. A* 114 (2010) 9098-9109.
14. M. Werler, L. R. Cancino, R. Schiessl, U. Maas, C. Schulz, M. Fikri, *Proc. Combust. Inst.* 35 (2015) 259-266.
15. K. Yasunaga, F. Gillespie, J. M. Simmie, H. J. Curran, Y. Kuraguchi, H. Hoshikawa, M. Yamane, Y. Hidaka, *J. Phys. Chem. A* 114 (2010) 9098-9109.
16. C. K. Westbrook, *Proc. Combust. Inst.* 28 (2000) 1563-1577.
17. Y. Sakai, H. Ando, H. K. Chakravarty, H. Pitsch, R. X. Fernandes, *Proc. combust. Inst.* 35 (2015).
18. M. Fikri, J. Herzler, R. Starke, C. Schulz, P. Roth, G. T. Kalghatgi, *Combust. Flame* 152 (2008) 276-281.
19. J. Herzler, M. Fikri, K. Hitzbleck, R. Starke, C. Schulz, P. Roth, G. T. Kalghatgi, *Combust. Flame* 149 (2007) 25-31.
20. A. Vandersickel, M. Hartmann, K. Vogel, Y. M. Wright, M. Fikri, R. Starke, C. Schulz, K. Boulouchos, *Fuel* 93 (2012) 492-501.
21. M. Mehl, W. J. Pitz, C. K. Westbrook, H. J. Curran, *Proc. Combust. Inst.* 33 (2011) 193-200.
22. A. Miyoshi, *J. Phys. Chem. A* 115 (2011) 3301-3325.
23. H. J. Curran, P. Gaffuri, W. J. Pitz, C. K. Westbrook, *Combust. and Flame* 129 (2002) 253-280.