Ignition delay times of diethyl ether measured in a high-pressure shock tube and a rapid compression machine

M. Werler [b], L.R. Cancino [a], R. Schiessl [b], U. Maas [b], C. Schulz [a], M. Fikri [a,*]

[a] IVG, Institute for Combustion and Gas Dynamics – Reactive Fluids, University of Duisburg-Essen, Germany
[b] ITT, Institute of Technical Thermodynamics, Karlsruhe Institute of Technology, Karlsruhe, Germany

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Abstract

Ignition delay times of diethyl ether (DEE)/air/argon mixtures were studied in a shock tube in the temperature range from 900 to 1300 K at pressures of 10, 20, and 40 bar and in a rapid compression machine (RCM) at various equivalence ratios between 500 and 1060 K at pressures between 2.5 and 13 bar. Between 2.5 and 5.5 bar, the RCM results show that ignition delay times of DEE exhibit a region (between 590 and 800 K) where ignition delay times are weakly temperature dependent only, while above 833 K and below 590 K, the ignition delay times are strongly temperature dependent. Two-stage ignition was observed in the temperature range from 500 to 665 K in the RCM measurements. At the conditions of the shock tube, a strong pressure and temperature dependence of the ignition delay times was observed, but no non-thermal (NTC) behavior was found in the investigated temperature range. Simulations based on detailed chemistry using the mechanism of Yasunaga et al. (2010) [15] indicate that at high pressures ignition delay times show a high sensitivity towards the two H-atom abstraction reactions by HO_2 from diethyl ether. By increasing the rate coefficients of these two reactions relative to the original values by a factor of five, the mechanism well describes our measurements and still well reproduces the original data of Yasunaga et al. (2010) [15].
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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 high cetane number of 125, is used to support cold-start in gasoline and Diesel engines [2], is used as ignition improver for ethanol [5] and is even considered as alternative Diesel fuel [3,4]. In addition, DEE is used as a model fuel

* Corresponding author. Address: IVG, Institute for Combustion and Gas Dynamics – Reactive Fluids, University of Duisburg-Essen, 47048 Duisburg, Germany. Fax: +49 (0) 203 3798159.
 E-mail address: mustapha.fikri@uni-due.de (M. Fikri).

to test safety-relevant ignition processes at hot surfaces. Understanding its ignition chemistry is therefore of high practical interest.

Tommaso et al. [6] presented a density functional theory study of DEE oxidation to identify the formation of hazardous intermediates, such as peroxides. Other works investigated low-temperature reactions of ethers in general [7,8]. Recently, the effects of blending Diesel fuel with DEE on the combustion behavior were studied in a direct-injection Diesel engine [9] where DEE increased the ignition delay times despite the much higher cetane number of DEE. Laminar burning velocities of DEE/air mixtures were measured at various equivalence ratios, initial temperatures, and pressures in a spherical bomb by schlieren photography [10,11]. Inomata et al. [12] studied the ignition delay times of DEE and acetaldehyde in air and found that the mixture is extremely reactive and the ignition delay times decreased monotonically with increasing temperature. Clothier [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 [13].

Griffiths and Inomata [14] studied oscillatory cool flames of DEE between 430 and 590 K experimentally and numerically. The low-temperature reactivity of DEE was associated with the primarily-formed hydroperoxide. Yasunaga et al. [15] studied the pyrolysis and the oxidation of DEE at 900–1900 K and 1–4 bar behind reflected shock waves. Time-resolved infrared absorption at 3.39 μm, time-resolved emission at 431 nm and absorption at 306.7 nm were applied to monitor the decay of DEE, ignition onset, and OH induction times [15]. 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.

These studies have shed light onto many aspects of DEE auto-ignition. However, there is a lack of ignition studies for the engine-relevant range of low and intermediate temperatures combined with high pressures. The purpose of this study is to provide ignition delay data in a wide temperature and pressure range for a variety of equivalence ratios. Measurements were conducted in a shock tube and in a rapid compression machine (RCM) which are largely complementary with respect to accessible temperatures and timescales [16].

This paper is organized as follows: First, both experiments (shock tube and RCM) are described, as well as the methodologies used for data evaluation. Ignition delay times are then presented as a function of temperature and pressure and compared with results of a kinetics mechanism. The results are compared in an Arrhenius diagram, and are discussed on the background of an uncertainty analysis with respect to the temperature and pressure assigned to ignition events under RCM and shock-tube conditions.

2. Methodology

2.1. High-pressure shock tube

The shock-tube facility used for measuring ignition delay times is described in detail in [17,18]. The shock tube has a constant inner diameter of 90 mm, the length of the driver and driven sections are 6.4 and 6.1 m, respectively. Allowable peak pressures are 500 bar and the maximum test time is extended up to 15 ms by driver-gas tailoring. All experiments are conducted behind reflected shock waves in the 900–1300 K range at pressures of 10 ± 1.5, 20 ± 1.5, and 40 ± 1.5 bar at stoichiometric conditions (with O_2 diluted with argon). The mixtures are prepared manometrically in a mixing vessel and stirred for one hour to ensure homogeneity. The temperature T_5 and pressure p_5 behind the reflected shock waves are computed from the incident shock velocity, with an estimated temperature uncertainty below 15 K. Bandpass-filtered (430 ± 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 end-wall and the extrapolation of the steepest increase in CH^* chemiluminescence to its zero level on the time axis [19]. Figure 1 shows an example signal trace for a stoichiometric DEE/O_2 mixture at $p_5 = 20.6$ bar and $T_5 = 1015$ K with an ignition delay time of 5 ms.
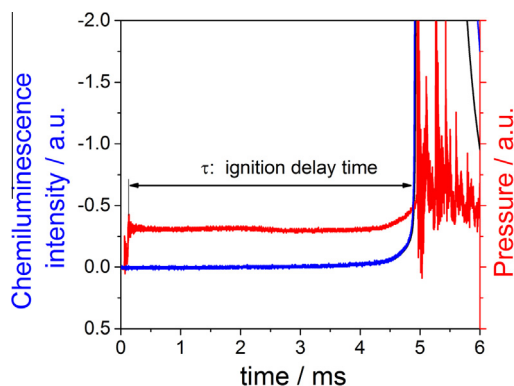

Fig. 1. Temporal variation of pressure, CH^* chemiluminescence ($\lambda = 431 \pm 5$ nm) for a stoichiometric DEE/air mixture with $T_5 = 1015$ K and $p_5 = 20.6$ bar. Initial mole fractions are: $x_{DEE} = 0.66\%$, $x_{O2} = 3.97\%$ balanced with argon.