Ignition delay-time study of dimethoxymethane/air and CH₄/dimethoxymethane/air mixtures over a wide temperature range at high pressure

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1 Introduction

Dimethoxymethane (DMM) is the smallest polyoxymethylene dimethyl ether (OME). OMEs (CH₃-O-(CH₂-O)_n-CH₃) can be used as Diesel fuel or as additives to Diesel fuel [1]. Studies in internal combustion engines have shown that the addition of OMEs can reduce soot emissions [2-5], increases the efficiency [6], and has a positive influence in the context of the soot-NO_x tradeoff [7, 8]. DMM as pure fuel in Diesel engines exhibits the same advantages as Diesel/DMM mixtures [9, 10]. OMEs are produced from syngas in a gas-to-liquid process with methanol as intermediate [2]. Syngas required for this process can be produced from methane [11], coal [12, 13], biomass [14], or CO_2/H_2 mixtures (with H₂ produced by electrolysis of water, power-to-liquid (PtL), e-fuel) [9, 15-17]. Despite the increasing importance of DMM and OMEs, there are only few studies on DMM oxidation and pyrolysis in reactors (jet-stirred reactor studies of Daly et al. ($\phi = 0.444$, 0.889, and 1.778, 800–1200 K, 1.07 bar) [18], Sun et al. ($\phi = 0.5, 460-820$ K, 0.974 bar, $\phi = 0.2, 0.5, and 1.5, 500-1200$ K, 10.13 bar) [19], Vermeire et al. ($\phi = 0.25, 1.0, 2.0, \text{ and } \infty, 500-1100 \text{ K}, 1.07 \text{ bar}$) [20], flow-reactor studies of Marrodán et al. ($\phi = 0.05, 1.0, 1.43, 373 - 1073$ K, 20, 40, and 60 bar) [21] and ($\phi = 0.0286, 1.0, 1.43,$ 2.5 and ∞ , 573–1373 K, 1.013 bar)) [22], premixed flames (Dias et al. ($\phi = 0.24, 0.05$ bar) [23] and Dias and Vandooren (C₂H₄/DMM mixture, $\phi = 2.5, 0.05$ bar)) [24] and shock tubes (H-ARAS and TOF-MS study of DMM pyrolysis at 1000–1700 K and pressures of about 1 bar by Golka et al. [25] and H-ARAS, TOF-MS, and GC/MS study at 1100-1430 K and pressures of 1.2 to 2.5 bar by Peukert et al. [26]). The only study on ignition delay times of DMM was performed by Jacobs et al. [27] in a shock tube, a rapid compression machine and a laminar flow reactor at pressures of 1-40 bar and temperatures between 590 and 1215 K at stoichiometric conditions. Due to the lack of ignition data for the validation of DMM mechanisms we performed shock-tube ignition-delay time measurements at engine relevant conditions ($\phi = 0.5, 1, 2; 30$ bar).

DMM can also be used to increase the reactivity of methane as fuel. This is important for using engines in the HCCI mode in a polygeneration process [28] without preheating the reactants. Polygeneration means that power and valuable chemicals are produced at the same time by using fuel rich conditions. The equivalence ratio determines the kind of product species, at $\phi = 2$, syngas (CO, H₂) is the main product, whereas at higher equivalence ratios, also larger hydrocarbons like C₂H₄ and ben-

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zene are formed [29, 30]. Lower inlet temperatures lead to lower final temperatures after ignition so that soot formation can be avoided at high equivalence ratios. A limiting case of a polygeneration process in an engine is the pure chemical energy storage in an engine externally driven by renewable electrical power and a methane / argon mixture as working fluid [31]. We previously tested dimethyl ether, diethyl ether and *n*-heptane as additives to methane [29, 30] in oxidative polygeneration processes and performed now ignition delay-time studies of CH₄/DMM mixtures at $\phi = 2$ and a pressure of 30 bar. Two concentrations of DMM were used, 5 mol% of the fuel, which is typically the required the concentration needed in the engine and 20 mol% for a wider validation range.

2 Experimental setup

The ignition delay time measurements were performed in a shock tube with a constant inner diameter of 90 mm and lengths of the driver and driven sections of 6.4 and 6.1 m, respectively. Allowable postignition peak pressures are 500 bar and the maximum test time is extended up to 15 ms by driver-gas tailoring. Helium was used as the main driver gas component and Ar was added to match the acoustic impedance of the driver gas with the one of the test gas. The driver gas was mixed *in situ* via two high-pressure mass flow controllers (Bronkhorst Hi-Tec flowmeter F-136AI-FZD-55-V and F-123MI-FZD-55-V). Test gas mixtures were 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 using a one-dimensional shock model with an estimated temperature uncertainty of <15 K. The shock velocity was measured over two intervals using three piezoelectric pressure transducers. 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 1P28 photomultiplier tube. The pressure was recorded at the same position using a piezoelectric pressure transducer. Ignition delay times were defined as the interval between the rise in pressure due to the arrival of the reflected shock wave at the measurement port and the extrapolation of the steepest increase in CH* chemiluminescence to its zero level on the time axis.

3 Results and Discussion

Ignition delay times of DMM/air ($\phi = 0.5, 1, 2$) and CH₄/DMM/air mixtures ($\phi = 2$) were measured between 600 and 1500 K at a pressure of 30 bar. The results of the measurements are presented in Figures 1–4. The experiments were compared to simulations with four reaction mechanisms [13, 19-21]. Vermeire et al. [20], Marrodán et al. [21] and Sun et al. [19] developed their mechanisms based on their DMM oxidation reactor experiments whereas He et al. [13] developed a mechanism for OME3 with a DMM submechanism validated with their RCM and HCCI measurements for OME3 ignition. The mechanism of He et al. [13] predicts the measured ignition delay of pure DMM at low and high temperatures very well, only in the intermediate temperature range between 700 and 1000 K up to a factor of two too long ignition delay times are predicted (Figure 1). Simulations with the mechanism of Vermeire et al. [20] show too long ignition delay times (up to a factor of 4) in the whole temperature range, especially in the intermediate temperature range (Figure 1). The mechanisms of Marrodán et al. [21] and Sun et al. [19] predict the measured values at high temperatures very well (Marrodán et al. [21] for T > 1100 K, Sun et al. [19] for T > 1000 K), whereas at lower temperatures increasingly too long ignition delay times are predicted (up to a factor of 10 and more) (Figure 2). The trends of the dependence on the equivalence ratio are well represented by all four mechanisms [13, 19-21].

The addition of 5 mol% DMM shortens the ignition delay times of methane [30] for about 80% (Figure 3). The ignition delay times of the 5 mol% DMM / 95 mol% methane/air mixture at $\phi = 2$ are very well predicted in the whole temperature range by the mechanisms of He et al. [13], Vermeire et al.

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[20] and Sun et al. [19] whereas the mechanism of Marrodán et al. [21] predicts a factor of about 3 too long ignition delay times (Figures 3 and 4). The agreement of experiments and simulations for the mixture with 20 mol% DMM is very well for the mechanism of He et al. [13], where deviations can only be observed in the temperature range from 750 to 850 K (Figure 3). The mechanism of Sun et al. [19] predicts the measurements also very well for T > 950 K (Figure 4). The mechanisms of Vermeire et al. [20] and Marrodán et al. [21] predict too long ignition delay times in the whole temperature range especially at lower temperatures.



Figure 1. Ignition delay times of DMM/air mixtures at 30 bar. Blue squares and lines: $\phi = 0.5$, black squares and lines: $\phi = 1.0$, green squares and lines: $\phi = 2.0$. Squares: experiments, full lines: simulations with the mechanism of Vermeire et al. [20], dashed lines: simulations with the mechanism of He et al. [13].



Figure 2. Ignition delay times of DMM/air mixtures at 30 bar. Blue squares and lines: $\phi = 0.5$, black squares and lines: $\phi = 1.0$, green squares and lines: $\phi = 2.0$. Squares: experiments, full lines: simulations with the mechanism of Marrodán et al. [21], dashed lines: simulations with the mechanism of Sun et al. [19]



Figure 3. Ignition delay times of CH₄/DMM/air mixtures and CH₄ ($\phi = 2$) at 30 bar. Black squares and lines: [CH₄]/[DMM] = 19/1, red squares and lines: [CH₄]/[DME] = 4/1, blue circles: 100% CH₄ [30]. Squares and circles: experiments, full lines: simulations with the mechanism of Vermeire et al. [20], dashed lines: simulations with the mechanism of He et al. [13].



Figure 4. Ignition delay times of CH₄/DMM/air mixtures ($\phi = 2$) at 30 bar. Black squares and lines: [CH₄]/[DMM] = 19/1, red squares and lines: [CH₄]/[DME] = 4/1. Squares: experiments, full lines: simulations with the mechanism of Marrodán et al. [21], dashed lines: simulations with the mechanism of Sun et al. [19].

4 Conclusions

Ignition delay times of DMM and DMM/CH₄ mixtures were measured in a wide temperature range at pressures of about 30 bar and compared to simulations with different mechanisms from literature [13, 19-21]. None of the mechanisms could predict the measured values in the entire temperature range; the best agreement was observed with the mechanism of He et al. [13], where deviations could be observed only for the intermediate temperature range. The addition of small amounts of DMM (5 mol%) to methane very significantly decreases the ignition delay times at $\phi = 2$. The measurements agree very well with simulations, only the mechanism of Marrodán et al. [21] predicts too long ignition delay times. With 20 mol% DMM only the mechanism of He et al. [13] predicts the measurements very well except in a small temperature regime from 750 to 850 K.

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