Ignition Delay Time Study of Aromatic LIF Tracers in a Wide Temperature and Pressure Range

J. Herzler, M. Fikri, C. Schulz
IVG, Institute for Combustion and Gas Dynamics – Reactive Fluids,
University of Duisburg-Essen,
Duisburg, Germany

1   Introduction

Tracer-LIF imaging is an important technique for non-intrusive measurements of fuel concentration, temperature, and equivalence ratio in practical combustion systems, in particular in IC engines [1]. Several fluorescence tracers have been suggested, among which ketones [2] and aromatics [3] have become the most popular. In compression-heated environments, such as IC engines, tracers can be used even under conditions where the lifetime of the tracer is only on the order of a few milliseconds. For these conditions, the optical properties of some tracers have been studied in shock tubes [4] where with further increasing temperature the gradual loss of signal was observed due to the decomposition of the tracers. Under high-temperature conditions, tracers can partially decompose together with the base fuel in the pre-ignition phase. Thus, the addition of the tracers to fuels for LIF experiments has two important implications. On one hand, the measured fluorescence signals could be misinterpreted in case of the decomposition of the tracer because of either disappearing of the fluorescing species or formation of fragments with different fluorescence properties. On the other hand, the tracer and its fragments can potentially influence the ignition and combustion characteristics of the base fuel.

Few studies investigated this chemical effect of tracers relative to that of the fuels they track. A theoretical study by Westbrook and Sick investigated the stability of biacetyl relative to reference fuels (primary reference fuels, PRF, i.e., mixtures from n-heptane and iso-octane) based on kinetics models, however, without experimental validation [5]. In this computational study, it was found that the decomposition kinetics of the tracer vs. fuel considerably changes when the temperature is changed from low to high because unimolecular decomposition of the fuel becomes an important reaction pathway. This can cause errors in the quantification of the LIF signals. Detailed reaction mechanisms for many fuels exist, for many alkanes and also for more complex substances like alcohols, aromatics, ketones, ethers and esters [6]. Most of these are, however, limited to the high-temperature range where chemistry is significantly less complex than at lower temperatures (700–1000 K) where the chemical reaction channels become

strongly fuel-specific. The low temperature domain is, however, crucial for questions regarding the decay of fuel and tracers for ignition and combustion conditions relevant for IC engines. Therefore, the ignition of aromatic LIF tracers was studied in a wide temperature range at engine relevant conditions in this work.

The choice of the "appropriate" tracer obeys different criteria and depends on the application. In particular the evaporation properties should match those of the fuel. Therefore, low-volatile tracers are typically compatible with Diesel surrogates whereas high-volatile tracers are typically applied for gasoline. In addition, the spectroscopy of the tracer should be convenient to permit the use of available laser sources. Also, fluorescence intensities of many tracers are strongly influenced by the presence of oxygen because of collisional quenching. This effect can be exploited to determine fuel-to-air ratio in pre-combustion mixing. The most important criterion is related to the signal intensity which is strong for many aromatics. Additional to the frequently used tracers toluene, acetone, and 3-pentanone, novel tracers with improved properties were suggested and investigated [7]. An aromatic tracer, suggested because of its increased signal intensity is anisole [8]. It has a relatively low boiling point which makes it compatible to gasoline-type fuels. In contrast, 1,3,5-trimethylbenzene (TMB) has evaporation characteristics comparable to Diesel and kerosene. All these tracers provide fluorescence signals up to two orders of magnitude stronger than those of toluene under identical conditions and are therefore highly attractive for various applications as discussed, e.g., by Hirasawa et al. [9]. There is, however, only very limited mechanistic information about their decomposition and combustion in situations relevant for tracer applications. The ignition delay times of 1,3,5-TMB were studied in shock tubes at pressures of 10 and 20 bar in the temperature range of 1100 to 1500 K at equivalence ratios of 0.5, 1.0, and 2.0 by Diévart et al. [10], at pressures of 1,5, 20 bar, at temperatures between 1080 and 1560 K and equivalence ratios of 0.5, 1, 2 by Rao et al. [11], and at pressures of 4–6 bar, temperatures between 1235 and 1810 K, and equivalence ratios of 0.41–1.33 by Miyama [12]. Roubaud et al. [13] measured the ignition delay times of 11 different alkylbenzenes in a rapid compression machine in the 600–910 K range at 5–25 bar. They found that 1,3,5-TMB ignites only at temperatures above 900 K and pressures above 16 bar. There are also some studies at lower pressures, initial concentrations or higher temperatures, e.g., the reaction kinetics of pure 1,3,5-TMB was recently studied in an atmospheric plug-flow reactor between 750 and 950 K [14] and the oxidation of 1,3,5-TMB was studied at high pressures and low concentrations in a high-pressure single-pulse shock tube [15]. There are no ignition delay time studies of anisole. The oxidation of anisole was studied by Nowakowska et al. [16] in a jet-stirred reactor at dilute conditions between 673 and 1173 K at a pressure of 1067 mbar and by Pecullan et al. [17] in an atmospheric flow reactor at 1000 K.

Due to the described lack of ignition data of 1,3,5-TMB and anisole at engine relevant conditions, we measured ignition delay times of these species at 10, 20, and 40 bar at lean ($\phi = 0.5$) and stoichiometric conditions in the 770–1600 K range in a high-pressure shock tube.

2   Experimental Setup

Ignition delay times were measured 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 post-ignition peak pressures are 500 bar and the maximum test time is extended up to 16 ms by driver-gas tailoring. Helium was used as the main driver gas component and argon 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 by using two high-pressure mass flow controllers (Bronkhorst Hi-Tec flowmeter). The driver gas composition is dependent on the Mach number and was calculated by a spreadsheet analysis prior to the experiment. For the calculation, equations by

Oertel [18] and Palmer and Knox [19] were used. Test gas mixtures were prepared manometrically in a mixing vessel and stirred for one hour to ensure homogeneity. The mixing vessel and the driven section of the shock tube were heated to 100°C to ensure complete evaporation of low-volatile species.

The temperature T_5 and pressure p_5 behind the reflected shock waves are computed from the incident shock velocity using a one-dimensional model with an estimated temperature uncertainty of below 15 K. The shock velocity was measured over two intervals (60 and 40 cm) using three piezoelectric pressure transducers (PCB 112A05). 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. The pressure was recorded at the same position using a piezoelectric pressure transducer (PCB 112A05) that was shielded with a thin high-temperature silicone layer. 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 (Figure 1). For short ignition delay times below 200 μs an uncertainty of about 20 μs can be assumed, whereas at the longest ignition delay times an uncertainty of about 200 μs must be considered. Pressure measurement at 15 mm in front of the end flange of inert mixtures showed a pressure increase of about 5%/ms for the first 2.8 ms, followed by a constant pressure up to the measurement time of 16 ms. This pressure increase was considered in the simulations.

3   Results and Discussion

Ignition delay times of 1,3,5-TMB and anisole were determined at 10, 20, and 40 bar at lean ($\phi = 0.5$) and stoichiometric conditions in the 770–1600 K range and compared with simulations with mechanisms from literature. The results are shown in Figures 1 and 2.

Simulations with the mechanism of Gudiyella and Brezinsky [15] show a very good agreement with all experimental ignition delay times for 1,3,5-TMB at stoichiometric conditions, see dashed lines in Figure 1. At lean conditions ($\phi = 0.5$), the measured values with the exception of the one at the lowest temperature (about 850 K) are also very well predicted by the mechanism of Gudiyella and Brezinsky [15] for 10 and 20 bar. For 40 bar, only at the highest temperatures above 1340 K, very good agreement of experiments and simulations with the mechanism of Gudiyella and Brezinsky [15] at $\phi = 0.5$ can be observed; with decreasing temperature, the differences between simulations (too short ignition delay times) and measurements increase. The observed trends are also valid for simulations with the mechanism of Diévart et al. [10] that agree quite well with the measurements and simulations with the mechanism of Gudiyella and Brezinsky [15] at temperatures above 1300 K. For lower temperature, this mechanism [10] predicts increasingly too long ignition delay times.

All measurement values for anisole at $\phi = 0.5$ agree well with the simulations using the mechanism of Ranzi et al. [19] whereas the mechanism of Nowakowska et al. [15] predicts too long ignition delay times in the whole measurement range (Figure 2). At stoichiometric conditions, the measured ignition delay times are very well predicted for temperatures above 1100 K by the mechanism of Ranzi et al. [19] whereas at lower temperatures the experimentally observed reduction of the activation energy is not reproduced by the simulations so that much too long ignition values are predicted at the lower temperature end of the measurements. Simulations with the mechanism of Nowakowska et al. [15] show also for stoichiometric conditions too long ignition delay times in the whole temperature range. The observed reduction of the activation energy is also not predicted by this mechanism [15].
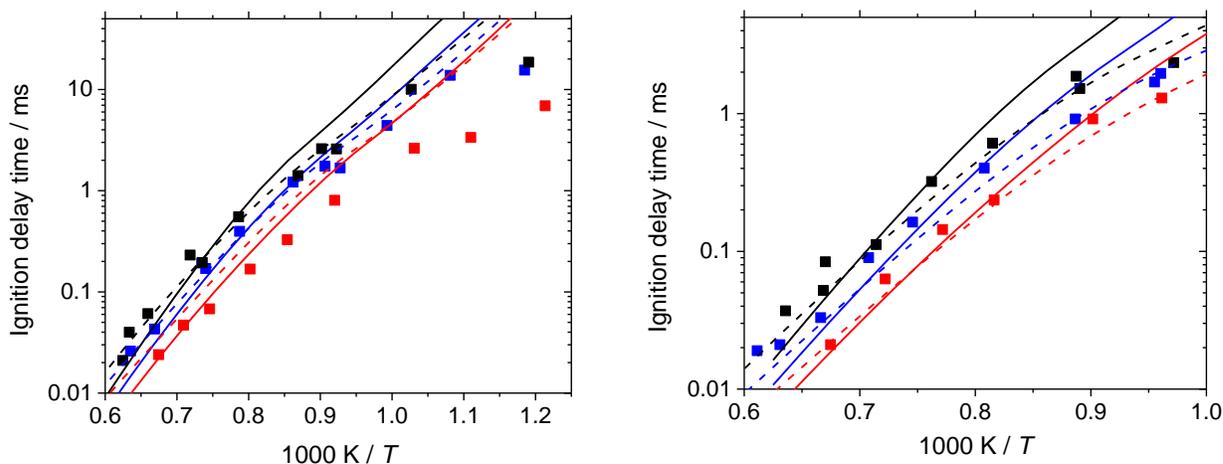
Figure 1: Measured and simulated ignition delay times of 1,3,5-TMB/air mixtures: Left figure: ϕ = 0.5, right figure: ϕ = 1.0. Black lines and symbols: 10 bar, blue lines and symbols: 20 bar, red lines and symbols: 40 bar. Squares: Experimental values, full lines: Simulations with the mechanism of Diévart et al. [10], dashed lines: Simulations with the mechanism of Gudiyella and Brezinsky [15].
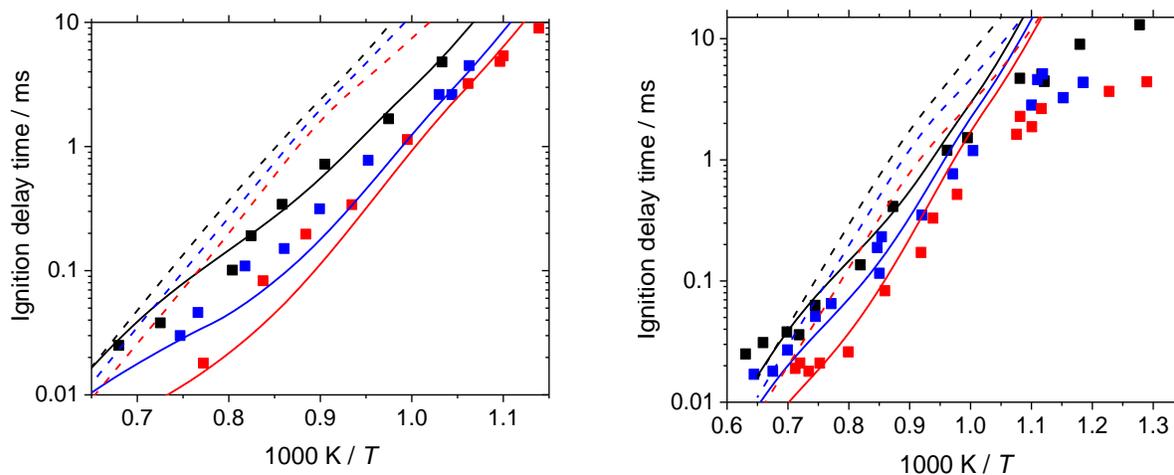

Figure 2: Measured and simulated ignition delay times of anisole/air mixtures: Left figure: ϕ = 0.5, right figure: ϕ = 1.0. Black lines and symbols: 10 bar, blue lines and symbols: 20 bar, red lines and symbols: 40 bar. Squares: Experimental values, full lines: Simulations with the mechanism of Ranzi et al. [10, 20], dashed lines: Simulations with the mechanism of Nowakowska et al. [16].

A comparison of the measured ignition delay times of 1,3,5-TMB of this work with shock-tube experiments of Diévart et al. [10] at 10 and 20 bar and equivalence ratios of 0.5 and 1.0 shows a very good agreement of both measurements for all conditions, see Figure 3. The shock-tube experiments of Rao et al. [11] at 20 bar and equivalence ratios of 0.5 and 1.0 exhibit a very similar activation energy but the absolute values are about 40% shorter for ϕ = 0.5 and about 25% shorter for stoichiometric conditions. The comparison shows also that this work extended the temperature range of the former studies especially to lower temperatures and higher pressures (40 bar).
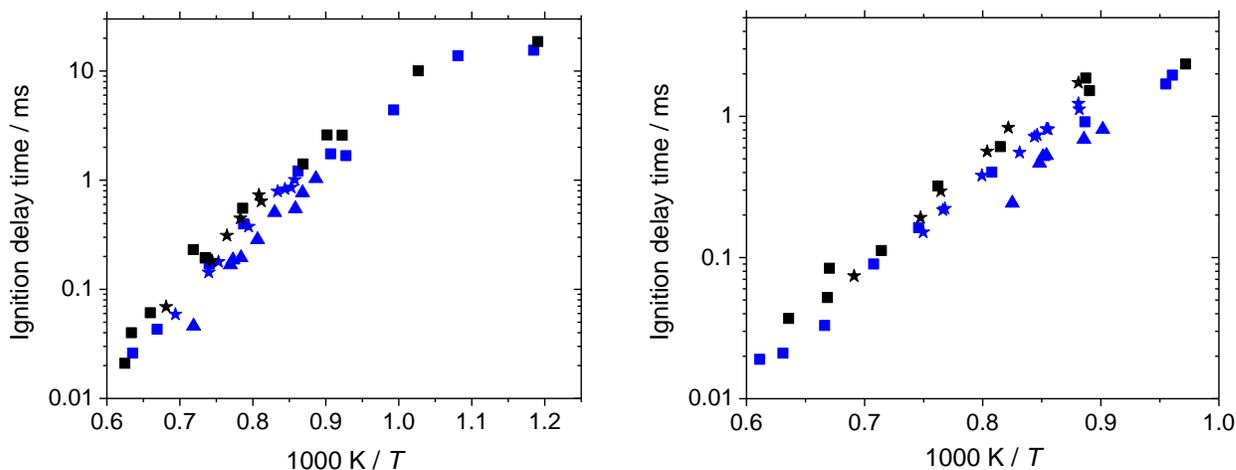
Figure 3: Measured ignition delay times of 1,3,5-TMB/air mixtures: left figure: ϕ =0.5, right figure: ϕ = 1.0. Black symbols: 10 bar, blue symbols: 20 bar. Squares: This work, stars: Diévart et al. [10], triangles: Rao et al. [11].

4   Summary

Ignition delay times of the LIF tracers 1,3,5-TMB and anisole were determined at 10, 20, and 40 bar at lean (ϕ = 0.5) and stoichiometric conditions in the 770–1600 K temperature range and compared to simulations with various mechanism from literature and with experimental values for 1,3,5-TMB at 10 and 20 bar. The measured 1,3,5-TMB data agree very well with simulations with the mechanism of Gudiyella and Brezinsky [15] whereas the mechanism of Diévart et al. [10] predicts too long ignition for lower temperatures. Simulations with both mechanisms [10, 15] exhibit significantly too slow ignition delay times for ϕ = 1, 40 bar and low temperatures. A comparison of the anisole measurements and the simulations with the mechanism of Ranzi et al. [20] shows a very good agreement for all data with the exception of the experiments at temperatures below 1000 K at ϕ = 1 where the mechanism cannot reproduce the observed reduction of the activation energy. Simulations with the mechanism of Nowakowska et al. [16] predict too long ignition delay time for all conditions. A comparison of the 1,3,5-TMB measurements of this work with data of Diévart et al. [10] at 10 and 20 bar show a very good agreement whereas experiments of Rao et al. [11] at 20 bar exhibit slightly faster ignition delay times.

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