Influence of dimethyl ether and diethyl ether addition on the flame structure and pollutant formation in premixed *iso*-octane flames

Meirong Zeng [a,b,*], Julia Wullenkord [a], Isabelle Graf [a], Katharina Kohse-Höinghaus [a,**]

[a] *Department of Chemistry, Bielefeld University, Universitätsstraße 25, D-33615 Bielefeld, Germany*
[b] *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, PR China*

ABSTRACT

While the combustion reactions of many individual fuels in flames have been studied in detail, often providing numerous experimental species profiles in combination with the development and critical testing of kinetic models, similar work on fuel mixtures has remained scarcer, especially for blends of conventional and biogenic fuels. In the present study, we have thus chosen *iso*-octane, one of the primary reference fuels that determine octane number and knocking tendency of gasoline, as the base fuel, and dimethyl ether (DME) and diethyl ether (DEE) as potentially bio-derived fuel components. Premixed low-pressure flames of *iso*-octane without and with different amounts of DME or DEE, of up to 50% of the fuel in the mixture, have been investigated systematically to analyze the change of the flame structure and species composition upon blending. All flames were studied at a pressure of 40 mbar (4 kPa) with 50% argon dilution and a cold gas velocity of 60 cm s^{-1}. The carbon-to-oxygen ratio was fixed at 0.47 while the equivalence ratio changed from 1.47 to 1.84. Up to 70 species in the range of C_0–C_9 were identified and quantified in each flame by electron ionization molecular-beam mass spectrometry (EI-MBMS). Moreover, about 300 experimental species profiles were provided.

The aim of this study is thus threefold. First, a new species dataset for a pure *iso*-octane flame is reported, since speciation data under premixed flame conditions for this fuel is surprisingly scarce. Second, the effects of DME and DEE addition in increasing amounts to the *iso*-octane base flame are investigated with special attention to the flame structure and pollutant species formation. Third, a joint combustion model for *iso*-octane, DME, and DEE mixtures consisting of 379 species and 1931 reactions is proposed that was examined against the present data and reference experiments for a larger range of conditions. Key pathways of interesting species, including aldehydes, alkenes, and soot precursors were revealed with the present mixture model. DME and DEE addition were found to have a similar influence on the flame structure of *iso*-octane, except for some C_2 and C_3 intermediates. The addition of DME as well as of DEE decreases the formation of soot precursors while it enhances the production of formaldehyde.

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1. Introduction

Future combustion strategies for road transportation will aim for optimized fuel–engine performance and are likely to use approaches that may, for example, adapt the fuel's reactivity and emission behavior by using tailored mixtures of conventional and biogenic fuels. Especially for homogeneous charge compression ignition (HCCI) concepts and their variants that offer high thermal efficiency at low NO$_x$ and particulate matter (PM) emissions, dual-fuel strategies [1–4] appear promising, since HCCI combustion is sensitive to chemical kinetics. Therefore, blending of fuels with different chemical properties is an efficient way to adjust the fuel characteristics and thus meet various operation conditions, especially regarding ignition and combustion behavior [5,6]. Several global parameters have been considered regarding fuel blends for HCCI engines, such as cetane number (CN), research octane number (RON), and oxygen content, and an accepted strategy is to use combinations of fuels with high octane and high cetane numbers [5,7]. However, the combustion behavior of prototypical fuel mixtures, including intermediate species formation and potential chemical interactions of the fuel components' chemical reaction pathways, is often not as well studied and understood as the reactions of the individual fuel compounds.

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* Corresponding author at: National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, PR China.
** Corresponding author.
E-mail addresses: zengmr@mail.ustc.edu.cn (M. Zeng), kkh@uni-bielefeld.de (K. Kohse-Höinghaus).

In the present study, we address the premixed flame combustion of *iso*-octane as the base fuel and of its mixtures with varying amounts of dimethyl ether (DME, CN> 55 [8]) and diethyl ether (DEE, CN> 125 [9]). This choice was motivated by the generally recognized important properties of the respective fuels. *iso*-Octane, or 2,2,4-trimethylpentane (RON= 100), is a significant component in primary reference fuels to assess the octane number and knocking tendency under spark ignition (SI) or HCCI conditions [5,10,11], and it is also commonly used as a representative branched alkane in jet fuel surrogates [12,13]. DME and DEE, both proposed as bio-derived neat fuels or fuel additives [9,14], have attractive properties, including high cetane number, high oxygen content, and the typical C-O-C structure that results in low ignition temperatures and low emissions of NO_x, PM, and soot. Both fuels have therefore been considered as clean high-efficiency alternative fuels in compression ignition (CI) engines, including diesel and HCCI engines [6,8].

The individual combustion chemistries of neat *iso*-octane, DME, and DEE have been investigated in numerous previous studies. Global combustion parameters including ignition delay times [15–17] and laminar flame speeds [18–20] have been reported for *iso*-octane [15,18], DME [16,19], and DEE [17,20], respectively. Species concentration measurements were performed under different homogeneous conditions in flow reactors for *iso*-octane [21] and DME [22], in jet-stirred reactors (JSRs) for *iso*-octane [23] and DME [24–26], in shock tubes for *iso*-octane [27] and DEE [28] as well as in laminar premixed flames that include transport behavior for all three fuels [29–32]. These mostly quite recent investigations focused on the respective combustion properties and, in part, the development of kinetic reaction models. It should be noted, however, that laminar premixed *iso*-octane flames were studied almost 20 years ago [29,30], and the experimental temperature profiles from Bakali et al. [30] were adjusted in the simulation by Blanquart et al. [33] to match the consumption of *iso*-octane and O_2.

As a first objective of the present work, we thus aim at providing new experimental data for laminar premixed *iso*-octane flame combustion. The base *iso*-octane–oxygen–argon flame at an equivalence ratio of $\phi = 1.47$ (C/O= 0.47, Ar mole fraction $x_{Ar} = 0.5$) and a pressure of 40 mbar was investigated including detailed measurements of C_0–C_9 species with electron ionization molecular-beam mass spectrometry (EI-MBMS). Secondly, laminar premixed flames of *iso*-octane/DME mixtures and *iso*-octane/DEE mixtures, including pure DME and DEE flames as a reference, were investigated with the same setup and methodology using constant pressure and C/O ratio to ensure consistent conditions. Attention was given to explore tendencies of intermediate species formation between the neat fuels and fuel mixtures. Thirdly, a first attempt was made to propose a kinetic model for these fuel mixtures. As a first step, established *iso*-octane models from the literature [34–36] were examined against the present experimental results to ensure confidence in the joint experiment–modeling approach for the base flame. A combined kinetic model including also the sub-mechanisms for DME from [37] and DEE from [32] was then assembled and tested, in particular to explain key reactions of fuel decomposition and intermediate species formation as well as effects of DME or DEE addition to *iso*-octane under laminar premixed flame conditions.

It is evident that such low-pressure flame conditions are quite far from direct engine relevance, although the detailed species measurements permit severe testing of the model in a limited parameter space. In continuation of earlier studies on the ignition behavior of alkane–ether fuel mixtures [16,38–40], we have thus also performed some numerical tests of the present mixture model to predict ignition delay times of DME addition to *iso*-octane and laminar flame speeds of such mixtures.

2. Experiments

Laminar premixed flames of the neat fuels *iso*-octane, DME, and DEE, as well as of different mixtures of *iso*-octane and DME or DEE were stabilized on a homemade flat bronze burner (65 mm diameter) that is moveable in vertical and horizontal directions. All flames were systematically studied at the same pressure of 40 mbar (4 kPa) with oxygen as the oxidizer and 50% argon dilution at a carbon-to-oxygen ratio of C/O= 0.47. The cold gas flow velocity was kept fixed at 60 cm s^{-1} (333 K, 4 kPa). Conditions for the seven flames investigated here are presented in Table 1.

Calibrated mass-flow controllers were used to establish the gas flows of DME, O_2, and Ar. Liquid *iso*-octane (purity of 99%, boiling point ∼372 K) and DEE (purity of 99%, boiling point ∼307 K) were metered by a syringe pump and gasified in two separate vaporizers heated to 433.15 K and 373.15 K, respectively. Both, vaporized *iso*-octane and DEE, each combined with argon as diluent, were passed into the third vaporizer for mixing and then fed to the burner. Compositions of cold gas mixtures of *iso*-octane and DEE (or DME) were controlled with gas chromatography to ensure constant composition of the two inlet fuels in accordance with the set values by the two syringe pumps.

An electron ionization molecular-beam mass spectrometer was used to detect stable and reactive species. A detailed description of the experimental setup can be found elsewhere [41,42]. Briefly, gas samples were extracted from the flame by a quartz nozzle (300 μm orifice, 25° opening angle) and expanded into the first pumping stage chamber (kept at <10^{-4} mbar) to quench the reaction, and then directed through a copper skimmer to the ion source of the mass spectrometer (at <10^{-6} mbar). The EI-MBMS setup consists of a two-stage Wiley-McLaren ion source with a reflectron time-of-flight (TOF) detection unit and provides a mass resolution of $m/\Delta m \sim 4000$ that enables determination of the exact elemental composition of C/H/O species. Soft ionization (with electron energies of 10.5, 11.5, and 12.5 eV for the detection of intermediates, 16 and 17 eV for major species) was applied to minimize undesired fragmentation processes. Moreover, fragmentation corrections were considered for fragment ions originating from the fuel and selected intermediate species. The individual fragment pattern was determined by independent cold-gas energy scans. Ions were detected using a multichannel plate with a multichannel scaler for data recording. The molecular-beam sampling technique preserves the gas composition of the sample and enables detection of reactive species such as radicals.

The mole fraction evaluation of the molecular-beam experiment followed previously reported procedures [41,42]. Briefly, the integrated mass signal S_i of a species *i* can be expressed as a function of its mole fraction x_i as given in Eq. (1):

$$S_i = x_i \cdot c \ \cdot \ \varphi \ \cdot SW \cdot D(M_i) \cdot FKT(h) \cdot \int \sigma_i(\tau) \cdot f(E - \tau)d\tau \qquad (1)$$

Here, c is an instrument factor, φ is the number of ionizing particles, SW is the number of sweeps, $D(M_i)$ is the mass discrimination factor, FKT is a temperature- and position-dependent sampling function, and $\int \sigma_i(\tau) \cdot f(E - \tau)d\tau$ is the convolution of the energy distribution with the ionization cross section, with τ as the integration variable. Mass discrimination effects have been determined in the previous study of Schenk et al. [41] and the factors were set to unity for all species except for H_2 which was internally calibrated as described below. Eq. (1) can be simplified if the signal is detected *versus* a reference species R (in this case argon) in the same measurement:

$$\frac{S_i}{S_R} = \frac{x_i}{x_R} \cdot \frac{D(M_i)}{D(M_R)} \cdot \frac{\int \sigma_i(\tau) \cdot f(E - \tau)d\tau}{\int \sigma_R(\tau) \cdot f(E - \tau)d\tau} = \frac{x_i}{x_R} \cdot k_{i/R}(E) \qquad (2)$$

The species- and energy-related terms can be condensed into a calibration factor $k_{i/R}$. Relying on element balances for C, O, and H