



Experimental and numerical low-temperature oxidation study of ethanol and dimethyl ether



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ABSTRACT

Low-temperature combustion (LTC) receives increasing attention because of its potential to reduce NO_x and soot emissions. For the application of this strategy in practical systems such as internal combustion engines and gas turbines, the fundamental chemical reactions involved must be understood in detail. To this end, reliable experimental data are needed including quantitative speciation to assist further development of reaction mechanisms and their reduction for practical applications.

The present study focuses on the investigation of low-temperature oxidation of ethanol and dimethyl ether (DME) under identical conditions in an atmospheric-pressure laminar flow reactor. The gas composition was analyzed by time-of-flight (TOF) mass spectrometry. This technique allows detection of all species simultaneously within the investigated temperature regime. Three different equivalence ratios of $\phi = 0.8, 1.0, \text{ and } 1.2$ were studied in a wide, highly-resolved temperature range from 400 to 1200 K, and quantitative species mole fraction profiles have been determined.

The experiments were accompanied by numerical simulations. Their results clearly show the expected different low-temperature oxidation behavior of both fuels, with a distinct negative temperature coefficient (NTC) region only observable for DME. With detailed species information including intermediates, differences of the kinetics for both fuels are discussed. Small modifications of the mechanisms served to identify sensitivities in the model. The experimental results may assist in the improvement of kinetic schemes and their reduction.

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1. Introduction

For a transformation of the global energy system towards increasing sustainability, it is desirable to improve conventional or to design novel combustion processes, while at the same time, environmentally-friendly fuels and routes to their production should be identified. Future combustion processes must feature substantially reduced pollutant emissions while maintaining high efficiency. A promising concept in that respect is low-temperature combustion (LTC). The LTC regime can be realized, for example, by high dilution of the fuel-oxidizer mixture through exhaust gas recirculation [1]. The low-temperature behavior is important for homogeneous charge compression ignition (HCCI) engines [2–5], characterized by low soot and low NO_x emissions [6–10]. Combustion at low temperatures may feature different reaction

pathways from those occurring in the common high-temperature combustion regime. Low-temperature kinetics could lead to combustion instabilities, and appropriate control strategies may be needed [11].

The reaction schemes for many fuels in the low-temperature regime have recently been reviewed by Battin-Leclerc [12] and Zádor et al. [13]. However, detailed kinetic studies for the low-temperature regime are scarce, and the examination of reaction mechanisms for combustion in a highly diluted regime is of particular importance. Ethanol as an established alternative fuel and its isomer dimethyl ether (DME) are interesting targets for an in-depth analysis under such conditions.

A significant number of studies exists on both ethanol and DME combustion. Ethanol combustion reactions have been investigated experimentally and in mechanistic studies [14–19], with the mechanism of Cancino et al. [17] as the only ethanol oxidation mechanism in the intermediate-temperature regime. The thermal decomposition of ethanol in a flow reactor was investigated in an early study by Rotzoll [20] and, more recently, by Li et al. [21]. Ethanol combustion was studied in low-pressure flames [18,22–26],

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and ethanol oxidation was investigated at 1100 K in a flow reactor by Norton and Dryer [27]. Haas et al. [28] have investigated the low- and intermediate-temperature oxidation of ethanol in a flow reactor under knock-relevant conditions, while Alzueta and Hernández [29] have addressed the influence of NO on ethanol oxidation. More recently, Leplat et al. [23] and Dagaut and Togbé [30] have investigated the oxidation of ethanol in a jet-stirred reactor (JSR) at atmospheric and high pressure in the ranges of 890–1250 K and 770–1220 K, respectively. Although Frassoldati et al. [19] have modeled low-pressure propene–oxygen–argon flames blended with DME or ethanol at higher temperatures, a comparative study of the low-temperature chemistry of the isomeric fuels ethanol and DME, especially in the regime below ~ 800 K, is still lacking.

Mechanisms for oxidation and pyrolysis of DME in the low- and high-temperature regimes have been reported in [31–34]. Hidaka et al. [35] and Sivaramakrishnan et al. [36] investigated the pyrolysis of DME, while Pfahl et al. [37] studied its autoignition. A wide range of combustion conditions for DME was addressed in several flame experiments [26,38–42]. Also, DME oxidation was investigated by Dagaut et al. [43,44] in a JSR, and its thermal decomposition and oxidation in a flow reactor were studied by Fischer, Curran and the group of Dryer et al. [31–33]. Moreover, Liu et al. [45] and Alzueta et al. [46] have investigated the influence of NO on DME oxidation. Species concentrations in previous work have commonly been determined by Fourier-transform infrared (FT-IR) spectroscopy or online gas chromatography (GC). Mass spectrometric detection of species in DME oxidation in a flow reactor has only been used by Guo et al. [47] and in our own work [48].

Here, we report quantitative mole fractions of reactants, products and intermediates for both DME and ethanol oxidation, using simultaneous mass spectrometric detection for all species. A laminar flow reactor was coupled to an electron ionization (EI) time-of-flight (TOF) mass spectrometer and used for a systematic study of the low-temperature oxidation for the two C_2H_6O -isomers over a wide temperature range of 400–1180 K at equivalence ratios of $\phi = 0.8, 1.0, \text{ and } 1.2$. With online detection of the complete stable species pool, a superior temperature resolution was achieved through continuous ramping of the reactor temperature. Identical conditions were chosen for both fuels so that a direct comparison is feasible. A major aspect of our present paper is to report the experimental data for the interesting low-temperature oxidation regime. Modeling was performed in addition for a better understanding of the chemistry in this system, but not with an aim to develop a new model. An analysis of the low-temperature combustion chemistry with mechanisms available in the literature was performed to elucidate details of the reaction pathways. Minor changes in the kinetic models served to emphasize sensitive reactions in the established mechanisms.

2. Experiment

Systematic studies of the oxidation of ethanol and DME were performed under near-identical conditions for both fuels. The experimental setup was described in detail in [48], and thus only details relevant to this study are given here. An overview of the setup is given in Fig. 1. The experimental results for DME oxidation have been previously reported in [48] without a kinetic model.

2.1. Experimental conditions

For both fuels, the exhaust gas composition was determined as a function of the reactor temperature. To achieve high temperature resolution, i. e. measurements at a multitude of individual temperature values, the entire reactor length was heated with applying a constant ramp of 0.16 K/s generated by a temperature controller (Horst HT60). By this procedure, mass spectra were obtained in

steps of 8.7 K. The temperature range for DME started from 1115 K and ended at 410 K, and for ethanol from 1178 K to 421 K. The reactor wall temperature was observed and controlled with a Ni–Cr/Ni thermocouple positioned at 350 mm downstream of the beginning of the heated reactor section (see Fig. 1a) and inserted between the reactor wall and the heating tape. Due to small inhomogeneities across the tube, the absolute temperature error was higher ($<5\%$) than the stated uncertainty of the thermocouple ($<0.4\%$). The gases were fed premixed to the flow reactor with 97% argon dilution. Under these highly diluted conditions, self-sustaining combustion is suppressed. The flow rates of the gases were regulated by calibrated mass flow controllers. The flow velocity at 400 K was 0.25 m/s, resulting in laminar flow conditions. Table 1 presents the gas flow rates (in g/min) for both fuels and for the investigated stoichiometry series ($\phi = 0.8, 1.0, 1.2$). For comparison, temperature profiles along the centerline of the reactor were measured for different isothermal reactor wall temperatures with a non-reactive isothermal argon gas flow at 0.5 slm (Fig. 1b).

2.2. Vaporizer system for ethanol fuel

Liquid ethanol flow rates of 8.2–11.2 $\mu\text{l}/\text{min}$ were provided with a vaporizer system, shown schematically in Fig. 1a. The system consists of a syringe pump (Protea, PM-1000) suitable for these small feeding rates. The liquid fuel was fed through a 55.5 mm-long stainless steel tube into the vaporizer chamber, the main length of which (51.5 mm) extended into this chamber. The end of the tube was crimped to provide a small drop size of the liquid fuel and to improve the vaporization.

The vaporizer chamber with an inner diameter of 4 mm and a length of 117 mm was heated electrically by a heating tape (Horst, HSQ and HT60 control) and the outer wall temperature, controlled by a Ni–Cr/Ni thermocouple, was kept constant at $393 \text{ K} \pm 1.6 \text{ K}$. At a position of 10 mm from the chamber inlet, a preheated argon flow (88% of the main argon flow rate) was introduced to pick up the vaporized ethanol in the gas stream into the reactor inlet. The pressure inside the vaporizer chamber and the flow reactor was controlled via a valve and set to 970 mbar. The preheated argon flow and the pressure control were instrumental in assuring a steady ethanol flow.

2.3. Species detection

Since the coupling of the reactor to the mass spectrometer was described previously [48], only some details are given here. Species detection was performed at the reactor outlet using an EI-TOF mass spectrometer. A gaseous sample was taken via a needle valve at the reactor outlet and guided with a 110 cm transfer line to the ion source. With low pressure behind the valve ($<1 \text{ mbar}$), significant delay between reactor outlet and detection was avoided. However, although the mass spectrometric method allows simultaneous detection of almost all species, only stable species could be detected with this sampling technique. Ionization was performed at an electron energy of 20 eV so that it was necessary to consider fragmentation of the fuels. The relevant fragmentation patterns were measured from cold gas samples and used for a rigorous fragmentation correction. For the detection of species in the oxidation of both fuels, 10^6 sweeps were averaged, leading to a total measurement time of 52 s/spectrum. The mass resolution of $R = 1600$ allowed to determine the elemental composition so that C_2H_4 could be separated from CO and C_2H_6 from CH_2O .

2.4. Data evaluation

The calibration procedure used in this study was adapted from [49–51] and described in detail in [48]. To follow the discussion of

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