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Proceedings of the Combustion Institute xxx (2014) xxx–xxx

 Proceedings  
 of the  
 Combustion  
 Institute
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# Experimental study of the kinetics of ethanol pyrolysis and oxidation behind reflected shock waves and in laminar flames

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## Abstract

The pyrolysis and oxidation of ethanol mixtures at high temperature is studied in a shock tube in the 1047–2518 K range at initial pressures of 1.06 and 2.07 bar. Pyrolysis and oxidation intermediates were investigated with high-repetition-rate time-of-flight mass spectrometry (TOF-MS). Ignition delay times were determined from chemiluminescence measurements and the OH concentration was determined with high time resolution from ring dye laser absorption measurements. Laminar flame speeds of ethanol in air were measured in a spherical bomb for initial temperatures between 318 and 473 K at 1, 2, and 5 bar and for equivalence ratios from 0.7 to 1.5. The measurements were compared to simulations based on various mechanisms from the literature. This comparison showed that the mechanism developed by Ranzi et al. (2012) provides the best agreement with the measured data for ethanol oxidation at high temperature.

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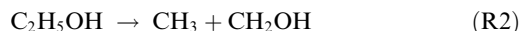
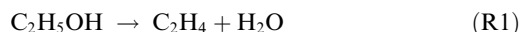
**Keywords:** Ethanol; Detailed kinetics mechanism; Shock tube; Ignition delay time; Laminar flame speed

## 1. Introduction

Ethanol as a fuel component for internal combustion engines has an increasing importance, partially because of regulatory requirements [1]. As a biomass-derived fuel, ethanol can help reduce the dependence on fossil fuels [2]. Due to its oxygen content, like other oxygenates, it is considered as being able to reduce soot formation

[3,4], although some works also show adverse effects where ethanol enhances soot formation [5]. Additionally, its anti-knock properties [6] can be beneficial to further increase the compression ratio of IC engines. However, unlike higher alcohols, ethanol combustion is prone to generate large quantities of acetaldehyde [7].

Ethanol pyrolysis proceeds via different channels where the reactions steps:



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<http://dx.doi.org/10.1016/j.proci.2014.05.063>

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are the most dominant channels at high temperature [8]. Li et al. [9] studied ethanol pyrolysis in a flow reactor at 1.7–3.0 bar and 1045–1080 K. Species concentrations have been measured by FTIR absorption and gas chromatography and the reaction rate of  $C_2H_5OH \rightarrow C_2H_4 + H_2O$  was determined. In addition, the multichannel unimolecular decomposition was calculated on the basis of RRKM theory and the rate  $k_1$  was verified. A deviation from the rate adopted from [10] has been postulated. More recently, Sivaramkrishnan et al. [11] also studied ethanol decomposition according to reactions (R1)–(R3). H-atoms are instantaneously formed from fast dissociation reactions of  $CH_2OH$  and  $C_2H_5$  which are products of reactions (R2) and (R3), respectively. Atomic resonance absorption spectroscopy (H-ARAS) was used to determine the rates of (R1)–(R3). H-atom concentration histories were found to depend on the overall rate coefficient  $k_{overall} = k_1 + k_2 + k_3$  at short times and only the branching ratio of  $k_2 + k_3/k_{overall}$  determines the asymptote at longer times. From the difference, the rate coefficient  $k_1$  was determined.

Earlier investigations of ethanol oxidation in diffusion flames [12] and shock tubes [13,14] showed that H abstraction from ethanol takes place via three channels leading to three  $C_2H_5O$  isomers that are then consumed to form the usual combustion intermediates:  $C_2H_4$ ,  $CH_3$ ,  $CH_2O$ , and  $CH_2OH$ . Acetaldehyde is one additional intermediate that appears during ethanol combustion.

Natarajan and Bhaskaran [15] studied ethanol ignition delay times and proposed an oxidation mechanism. Dunphy et al. [16] proposed a mechanism based on methanol oxidation including reactions of ethanol, acetaldehyde, and the  $C_2H_5O$ . Later, Norton and Dryer [17] constructed a mechanism for ethanol oxidation based on a review of published rates of the elementary reactions of  $C_2H_5OH$ ,  $CH_3CHO$ ,  $C_2H_4$ ,  $CH_4$ , and related species. In contrast to [15,16], they considered H-abstraction from all three distinct sites ( $CH_3$ ,  $CH_2$ , and  $OH$ ) in ethanol and consequently included all three isomers of  $C_2H_5O$ . They concluded that H-abstraction from the  $CH_3$  site is the primary source of  $C_2H_4$  from  $CH_2CH_2OH$ .

Marinov has developed a detailed mechanism for ethanol oxidation [10] and validated it against experimental data of laminar flame speeds [18], ignition delays [15,16], and product concentrations from a jet-stirred and turbulent-flow reactors [19]. The ethanol multi-channel decomposition process was analyzed by RRKM/master-equation theory. Several works [20,21] were devoted to validate Marinov's mechanism [10]. Discrepancies between simulations and flow-reactor experiments were attributed to the uncertainties in the kinetics of the decomposition reaction of ethanol [22].

Laminar flame speeds of ethanol combustion were measured in constant-volume vessels [23,24], counterflow flames [18,25], and heat-flux burners [26,27]. The effect of the mixture composition, in terms of equivalence ratio, initial conditions, temperature, and pressure were studied by several authors. However, there are still unexplained discrepancies between these studies.

Modeling of ethanol chemistry is of specific interest because it is considered as a base alcohol that also supports the understanding of the oxidation of higher alcohols. Earlier mechanisms have shed light on the main aspect of ethanol combustion. The development and validation of new mechanisms requires reliable experimental data, in particular species concentration measurements. We use complementary experimental approaches by studying the pyrolysis and oxidation of ethanol behind reflected shock waves. Multiple species concentrations of fuel, intermediates, and products, OH, as well as ignition delay times and laminar flame speeds were measured to rigorously check and constrain available mechanisms.

## 2. Experimental

### 2.1. Shock-tube measurements

The experiments were conducted in two different diaphragm-type shock-tube facilities behind reflected shock waves between 1047 and 2518 K at 1.06 and 2.07 bar. The driver section of the shock tube has a length of 2.5 m and the driven section has a length of 6.3 m with a constant inner diameter of 80 mm. Driver and driven sections are pumped down to  $1.8 \times 10^{-3}$  mbar in between experiments. The driver section is equipped with a magnetic valve to feed the driver gas (here: He) into the driver section. A set of four pressure transducers (PCB-112A05), equally spaced by 150 mm, are used to measure shock velocities. The fourth pressure transducer is located 15 mm from the end plate. Pressure and temperature behind the reflected shock wave ( $p_5$  and  $T_5$ ) are calculated from shock-wave equations [28] using the initial pressure, temperature ( $p_1$  and  $T_1$ ) and the measured velocity of the incident shock wave. The end-flange contains a 60  $\mu$ m conical nozzle that connects the shock tube to the high-repetition-rate time-of-flight mass spectrometer (TOF-MS, Kaesdorf). This allows measuring multiple species simultaneously with a 10- $\mu$ s time resolution during the pyrolysis and oxidation of ethanol. The TOF-MS is equipped with an electron impact ion source (5–85 eV) with two-stage ion extraction and a two-stage micro-channel plate for ion detection either in linear or in reflectron mode. The maximum kinetic energy of the ions is 10 keV which is high enough to generate detectable signals for molecular masses up to 1000 u. Ionization is initiated when

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