



## High-pressure oxidation of ethane



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### ARTICLE INFO

#### Article history:

Received 25 November 2016

Revised 2 January 2017

Accepted 30 March 2017

#### Keywords:

Ethane

Ignition

High pressure

Reaction kinetics

### ABSTRACT

Ethane oxidation at intermediate temperatures and high pressures has been investigated in both a laminar flow reactor and a rapid compression machine (RCM). The flow-reactor measurements at 600–900 K and 20–100 bar showed an onset temperature for oxidation of ethane between 700 and 825 K, depending on pressure, stoichiometry, and residence time. Measured ignition delay times in the RCM at pressures of 10–80 bar and temperatures of 900–1025 K decreased with increasing pressure and/or temperature. A detailed chemical kinetic model was developed with particular attention to the peroxide chemistry. Rate constants for reactions on the C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> potential energy surface were adopted from the recent theoretical work of Klippenstein. In the present work, the internal H-abstraction in CH<sub>3</sub>CH<sub>2</sub>OO to form CH<sub>2</sub>CH<sub>2</sub>OOH was treated in detail. Modeling predictions were in good agreement with data from the present work as well as results at elevated pressure from literature. The experimental results and the modeling predictions do not support occurrence of NTC behavior in ethane oxidation. Even at the high-pressure conditions of the present work where the C<sub>2</sub>H<sub>5</sub> + O<sub>2</sub> reaction yields ethylperoxyl rather than C<sub>2</sub>H<sub>4</sub> + HO<sub>2</sub>, the chain branching sequence CH<sub>3</sub>CH<sub>2</sub>OO → CH<sub>2</sub>CH<sub>2</sub>OOH  $\xrightarrow{+O_2}$  OOC<sub>2</sub>H<sub>4</sub>OOH → branching is not competitive, because the internal H-atom transfer in CH<sub>3</sub>CH<sub>2</sub>OO to CH<sub>2</sub>CH<sub>2</sub>OOH is too slow compared to thermal dissociation to C<sub>2</sub>H<sub>4</sub> and HO<sub>2</sub>.

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### 1. Introduction

Investigation of ethane oxidation at high pressure and intermediate temperature is important from both fundamental and practical perspectives. From a practical point of view, ethane is the major non-methane component in natural gas, which is used in gas turbines and gas engines for power generation and transportation; variations in ethane fraction in natural gas may result in significant changes in the ignition properties of the fuel [1]. In addition, the use of ethane as an engine fuel is growing, in the first instance for ships transporting feedstock ethane. Knowledge of ethane oxidation is important for evaluating the potential of knock in the engines using these fuels, as well as for the development of HCCI engines [2] and assessing possible spontaneous ignition in lean-premixed gas turbines [3]. From a fundamental perspective, the oxidation of C<sub>2</sub>H<sub>6</sub> plays an important role in the hierarchical struc-

ture of the reaction mechanisms of hydrocarbon fuels. To develop and verify these chemical kinetic models for hydrocarbon oxidation, measurements of the combustion characteristics at high pressure are essential.

While hydrocarbon ignition even at high temperatures relies on intermediate-temperature chemistry, this range of temperature, particularly at high pressure, has only been sparsely studied. Species concentrations have been reported from reactor experiments. Hunter et al. [4] studied ethane oxidation at temperatures of 915–966 K and pressures up to 10 atm in a flow reactor. A jet-stirred reactor was used by Dagaut et al. [5] to study ethane oxidation at temperatures of 800–1200 K and pressures of 1–10 atm. Tranter and co-authors [6–8] studied the pyrolysis and oxidation of ethane behind a reflected shock at pressures between 40 and 1000 bar over temperatures of 1000–1500 K by measuring major stable products using gas chromatography (GC).

A number of studies report the measurement of autoignition delay times for ethane [9–18]. Beerer and McDonell [17] evaluated the ignition delay of ethane and other lower alkanes in a flow reactor in the ranges of 785–935 K and of 7–15 atm. Shock tube studies

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