



## High-pressure oxidation of ethane



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### 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  $C_2H_5O_2$  potential energy surface were adopted from the recent theoretical work of Klippenstein. In the present work, the internal H-abstraction in  $CH_3CH_2OO$  to form  $CH_2CH_2OOH$  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  $C_2H_5 + O_2$  reaction yields ethylperoxyl rather than  $C_2H_4 + HO_2$ , the chain branching sequence  $CH_3CH_2OO \rightarrow CH_2CH_2OOH \xrightarrow{+O_2} OOC_2H_4OOH \rightarrow \text{branching}$  is not competitive, because the internal H-atom transfer in  $CH_3CH_2OO$  to  $CH_2CH_2OOH$  is too slow compared to thermal dissociation to  $C_2H_4$  and  $HO_2$ .

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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  $C_2H_6$  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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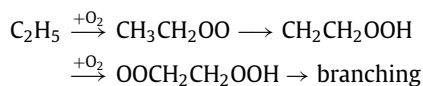
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by Lamoureux et al. [14], Aul et al. [16], and Zhang et al. [18] have characterized ignition delays for ethane in a wide range of temperature (1100–2700 K), pressure (1–21 bar), and equivalence ratio. Experiments performed by Gersen et al. [19] in a rapid compression machine (RCM) at 930–1000 K and 20–40 bar extended the available data to higher pressure. However, these pressures are still below those relevant for modern internal combustion engines.

Chemical mechanisms for ethane oxidation have been developed by several groups [5,20–22]. Two of the more recent models were developed specifically for high pressure application. Naik and Dean [21] suggested a model for the oxidation of ethane at high pressure and evaluated it against literature data. In a previous study from this laboratory [22], a kinetic model for the oxidation of the mixtures of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> was established and evaluated against the results of high-pressure flow-reactor experiments of C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> mixtures (C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub>=13%, at maximum). Models developed for heavier hydrocarbons or components of natural gas (e.g., [23–26]) include by necessity subsets for ethane, but specific evaluation against ethane data has been limited.

To extend the available data toward conditions relevant to engines and gas turbines, this paper reports the results of ethane oxidation experiments in a laminar flow reactor at pressures of 20–100 bar and temperatures of 600–900 K under a wide range of stoichiometries. The data are supplemented by ignition delay times measured in a rapid compression machine (RCM) at temperatures of 900–1025 K and pressures of 10–80 bar under stoichiometric and fuel-lean ( $\phi = 0.5$ ) conditions. A chemical kinetic model for ethane oxidation at increased pressure was established, based mostly on previous work [27]. The mechanism was updated with special emphasis on the peroxide chemistry. In particular, 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 [28]. 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 studied at a high level of theory, allowing us to reevaluate the importance of the sequence

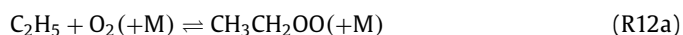


for low temperature ethane oxidation. The kinetic model was evaluated by comparison to the present data as well as to data reported in literature.

## 2. Chemical kinetic model and ab initio calculations

A chemical kinetic model for ethane oxidation at increased pressure was established. The model, which is discussed in more detail below, was based on previous work on high-pressure oxidation of hydrogen [29], hydrogen/carbon monoxide [30], methane [22,27], acetylene [31], ethylene [32], and methanol [33]. In the present work, it was updated with special emphasis on the peroxide chemistry and evaluated by comparison to the present data as well as to data reported in literature.

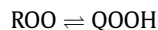
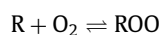
The key reaction in oxidation of ethane at intermediate temperature is C<sub>2</sub>H<sub>5</sub> + O<sub>2</sub>. This reaction, which involves multiple wells and multiple product channels, was recently studied by Klippenstein [28], along with other reactions on the C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> potential energy surface, at a high level of theory. At the conditions of the present study ( $T > 600$  K and high pressure), the reaction mainly proceeds by addition of molecular oxygen to the ethyl radical,



The fate of the ethylperoxy radical is important for the oxidation rate of ethane. Ethane is intermediate between the smallest alkane methane, which does not exhibit negative-temperature-coefficient (NTC) behavior and the larger alkanes such as propane and butane,

which have distinct NTC behavior. As pointed out by Carstensen and Dean [34], experimental studies addressing the ignition of C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub> mixtures appear to come to contradicting conclusions as to whether or not ethane oxidation shows NTC behavior. Knox and Norrish [35] reported distinct cool flame behavior for ethane while Dechaux and Delfosse [36] found no evidence of NTC behavior. In earlier studies, Townend and coworkers [37,38] and Chirkov and Entelis [39] both observed a temperature range where the maximum rate of oxidation of ethane remained almost constant.

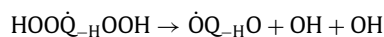
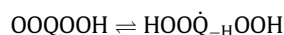
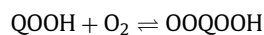
It is of interest whether the ethylperoxy radical participates in a chain-branching sequence similar to that of higher alkanes at temperatures below the NTC region. The initial steps are [40],



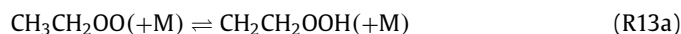
Once formed, QOOH may decompose to form the more reactive OH radical,



or it may recombine with O<sub>2</sub>, starting a chain-branching sequence,



In both cases, the internal hydrogen abstraction reaction ROO  $\rightleftharpoons$  QOOH, or for ethane,



may constitute a rate-limiting step. This reaction has previously been investigated theoretically [41–43] but only estimates of the high-pressure limit have been reported. In the present work, we determine the rate constant for this step as a function of temperature and pressure, based on the potential energy surface (PES) and methods of Klippenstein [28].

### 2.1. Theory: CH<sub>3</sub>CH<sub>2</sub>OO isomerization

#### 2.1.1. Methodology

The rovibrational properties of the stationary points on the PES were determined at the CCSD(T)/cc-pVTZ level. The B2PLYP-D3 double-hybrid density functional method [44,45], with a cc-pVTZ basis set was employed in the mapping of the torsional modes. High level energy estimates were derived from estimates for (i) the CCSD(T) complete basis set (CBS) limit obtained from extrapolation of calculations for the aug'-cc-pVQZ and aug'-cc-pV5Z basis sets, (ii) higher order corrections from CCSDT(Q)/cc-pVDZ calculations, (iii) core-valence corrections from CCSD (T,full)/CBS calculations based on extrapolation of results for the cc-pcVTZ and cc-pcVQZ basis sets, (iv) relativistic corrections from CI/aug-cc-pcVTZ calculations, (v) diagonal Born–Oppenheimer corrections (DBOC) obtained at the HF/cc-pVTZ level, and (vi) anharmonic zero-point energy (ZPE) corrections calculated at the B3LYP/cc-pVTZ level.

The majority of the electronic structure calculations were performed with the MOLPRO software package of Werner and Knowles [46]. The CCSDT(Q) calculations were performed with the MRCC code of Kallay [47], while the DBOC were obtained with the CFOUR code of Stanton and Gauss [48]. The density functional theory calculations were performed with G09 [49].

The MESS code [50] was employed to obtain ab initio transition state theory based master equation (AI-TST-ME) predictions of the

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