A Shock Tube Chemical Kinetic Study of Ethanol Oxidation at Elevated Pressures

Andrew Laich

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A SHOCK TUBE CHEMICAL KINETIC STUDY OF ETHANOL OXIDATION AT ELEVATED PRESSURES

by

ANDREW R. LAICH
B.S. University of Michigan – Dearborn, 2017

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Sciences in the Department of Mechanical and Aerospace Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Spring Term
2020

Major Professor: Subith S. Vasu
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ABSTRACT

Understanding the combustion chemistry of ethanol is critical for continued proliferation and use in future internal combustion engines (ICEs) that will operate in a downsized, turbo-charged, high compression configuration. Detailed chemical kinetic reaction mechanisms already exist for ethanol, which have been validated over a range of operating conditions; however, capturing the conditions that may be seen in future ICEs requires extension of these conditions, namely at elevated pressure. Investigating the kinetics of ethanol existing in a combustion system first involve, for example, understanding a key global metric like ignition delay time (IDT) and measuring major or minor species in a time resolved fashion capturing both formation and decomposition stages. A shock tube facility offers ideal (thermodynamically) operation that can be used to study the high pressure kinetics across a wide range of temperatures, all the while enabling non-intrusive temporal in situ measurements within the given test time.

Oxidation of ethanol was carried out behind reflected shock waves at elevated pressures by measuring IDTs and carbon monoxide (CO) time-histories, the latter of which utilized a distributed feedback quantum cascade laser centered at a wavelength in the infrared (IR). With the gathered data, various ignition regimes and sensitive chemistry were investigated for high pressure CO formation. Since CO is an important product of combustion, having an accurate prediction of its formation is necessary to preliminarily understand the efficiency and sustainability of future engine designs. Moving forward, hazardous products like CO among other harmful emissions will have stricter governmental constrains, which further supports studies as these that aid in the continued refinement of such chemical kinetic mechanisms.
to Robin E. and Sandra A. Laich
ACKNOWLEDGMENTS

I would like to thank my advisor and mentor Dr. Subith Vasu for his continued guidance and assistance throughout my graduate studies. I am grateful to him for his willingness to accept me in his laboratory and in support of my research endeavors here at UCF and beyond. I would also like to thank my thesis committee members Dr. Jayanta Kapat and Dr. Louis Chow for their willingness and time to be on this committee. I am also grateful to Dr. William J. Pitz (LLNL) and Dr. S. Scott Goldsborough (ANL) for feedback regarding the interpretation of ignition phenomena and chemical kinetic model sensitivity and pathway analyses. This work would not have been possible without the help of my many coworkers and friends at the Vasu Lab; specifically, Dr. Sneha Neupane (now at ONL) and Mr. Ramees Rahman performed many of the shock tube experiments presented. Finally, I would like to thank my family for their constant encouragement and support. Though over 1000 miles separates me from my mother and father, the many visits and phones calls have been something that has helped us grow even closer.

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CHAPTER 1: INTRODUCTION

1.1 Motivation

The continued study of ethanol combustion chemistry aiding in high fidelity chemical kinetic reaction mechanism will aid in the future design and optimization of transportation engines. By simultaneously performing research on selected biofuels (like ethanol, among others) and the engines that will be compatible with these fuels, the effort to increase efficiency while minimizing overall environmental impact can be realized. This is the main mission of the Department of Energy (DOE) through the collaborative Co-Optimization of Fuels and Engines Initiative. By measuring various chemical kinetic targets like species concentration histories and ignition delay times at the desired elevated pressure throughout temperature ranges, the validity of current and to-be-developed fuel mechanisms can be broadened. Shock tubes are nearly ideal reactors for studying gas phase chemical kinetics, as they provide well controlled changes in temperature and pressure, a well defined time-zero, and typically ensure uniformity of the flow during test time. In addition, non-intrusive optical diagnostics like laser absorption spectroscopy provide in-situ measurements of these important parameters, including temperature and other intermediate sparsely formed species. In this work, shock tube and laser absorption spectroscopy were utilized to carry out ignition delay times and concentration time-histories during the oxidation of ethanol at high and low fuel loading. The experimental data were used for model comparison assessing the current state of ethanol sub-mechanisms.
CHAPTER 2: HIGH-PRESSURE SHOCK TUBE STUDY OF ETHANOL OXIDATION: IGNITION DELAY TIME AND CO TIME-HISTORY MEASUREMENTS

2.1 Introduction

Ethanol (C2H5OH) is a prominent renewable fuel that can be produced in a sustainable manner and used as a neat fuel or additive in spark ignition (SI) engines for octane boosting. With the addition of alcohols such as ethanol in fuel blends, a reduction in harmful emissions, poly-aromatic hydrocarbons, particulates, and soot can be realized [1, 2]. A study also shows the potential use of ethanol as an additive in diesel fuels where it was observed that smoke opacity and NOx were reduced in blends containing ethanol or n-butanol [3].

In the literature there are many studies investigating the chemical kinetics of ethanol at low and high pressures throughout a wide temperature range. These include laminar flame speed measurements [4-9], ignition delay time (IDT) measurements in shock tubes [9-19] and rapid compression machines (RCM) [12, 14, 20, 21], and speciation experiments performed in a RCM [21], flow reactor [22-25], jet-stirred reactor [26-28], and shock tube [17, 29-31]. In addition, ethanol preignition was studied in a shock tube using conventional and high-speed end wall imaging diagnostics [12, 15]. Considering high pressure ignition data in the literature, Heufer and Olivier [13] measured IDTs in a shock tube of stoichiometric ethanol-air mixtures at 13, 19, and 40 bar in the temperature range of 800 and 1400 K. Cancino et al. [11] measured IDTs in a shock tube for ethanol-air mixtures with stoichiometric conditions at 10, 30, and 50 bar and at lean mixtures (\( \phi = 0.3 \)) at 30 bar in the temperature range of 650 -1220 K. The studies of Heufer et al. and Cancino et al. pushed the domain of IDT data to higher pressures where the latter study
Table 1: Summary of ethanol ignition and speciation studies in a shock tube and RCM with associated optical diagnostics.

<table>
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</thead>
<tbody>
<tr>
<td>Natarajan and Bhaskaran [18]</td>
<td>1981</td>
<td>Shock tube</td>
<td>1, 2</td>
<td>1300-1700</td>
<td>Ethanol/O2/Ar</td>
<td>0.5-2.0</td>
<td>Ignition: Visible Light</td>
</tr>
<tr>
<td>Curran et al. [19]</td>
<td>1992</td>
<td>Shock tube</td>
<td>2.0, 3.5, 4.5</td>
<td>1100-1900</td>
<td>Ethanol/O2/Ar</td>
<td>0.25-1.5</td>
<td>Ignition: CO2*, OH*, pressure</td>
</tr>
<tr>
<td>Hidaka et al. [30]</td>
<td>2005</td>
<td>Shock tube</td>
<td>1.4-3.6</td>
<td>1000-1700</td>
<td>Ethanol/Ar</td>
<td>∞</td>
<td>Absorption Spectroscopy: C2H5OH at 3.39 µm</td>
</tr>
<tr>
<td>Heufer and Olivier [13]</td>
<td>2010</td>
<td>Shock tube</td>
<td>13, 19, 40</td>
<td>800-1400</td>
<td>Ethanol/O2/N_2</td>
<td>1.0</td>
<td>Ignition: CH*, pressure</td>
</tr>
<tr>
<td>Noorani et al. [16]</td>
<td>2010</td>
<td>Shock tube</td>
<td>2, 10, 12</td>
<td>1070-1760</td>
<td>Ethanol/O2/Ar</td>
<td>0.5, 1.0, 2.0</td>
<td>Ignition: CH*</td>
</tr>
<tr>
<td>Lee et al. [12]</td>
<td>2012</td>
<td>Shock tube and RCM</td>
<td>34-93</td>
<td>705-1300</td>
<td>Ethanol/O2/N_2 and Ethanol/O2/N_2/Ar</td>
<td>1</td>
<td>Ignition: CH*, pressure; Schlieren imaging in shock tube</td>
</tr>
<tr>
<td>Mittal et al. [20]</td>
<td>2014</td>
<td>RCM</td>
<td>10-50</td>
<td>825-985</td>
<td>Ethanol/O2/N_2/Ar</td>
<td>0.3-1.0</td>
<td>Ignition: pressure</td>
</tr>
</tbody>
</table>
also proposed a detailed kinetic model for ethanol-air mixtures at intermediate temperatures and high pressures. Lee et al. [12] measured IDTs in a shock tube and RCM at elevated pressures between 67 and 93 bar in the temperature range of 775 – 1000 K. Mittal et al. [20] investigated autoignition of ethanol-oxidizer mixtures in a RCM at various equivalence ratios of 0.3 – 1, pressures between 10 – 50 bar, and temperatures of 825 – 985 K. Most recently, Zhang et al. [14] measured IDTs in a RCM in fuel lean and rich conditions over 650 – 1250 K and at 20 and 40 bar where binary mixtures of ethanol and dimethyl ether (DME) to probe the low temperature chemistry of ethanol. Furthermore, Mathieu et al. [17] measured IDTs from 1.3 – 53 atm in the temperature range of 938 – 1590 K; this study also included H₂O time-history measurements near 1.38 atm from 1300 – 1615 K using laser absorption spectroscopy. Other shock tube studies on ethanol implementing laser absorption spectroscopy include Pinzón et al. [29] who measured H₂O time-histories from 1500 – 1677 K at 1.31 atm, Hidaka et al. [30] who measured ethanol time-histories from 1000 – 1700 K between 1.4 and 3.6 atm, and Choudhary et al. [31] who measured ethanol, ethylene, and CO time-histories during pyrolysis at 10 atm from 1200 – 1600 K. A summary listing relevant RCM and shock tube ignition/speciation studies is presented in Table 2.
Table 2: A continuation of summary of ethanol ignition and speciation studies in a shock tube and RCM with associated optical diagnostics.

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</thead>
<tbody>
<tr>
<td>Aghsaee et al. [9]</td>
<td>2014</td>
<td>Shock tube</td>
<td>1.06, 2.07</td>
<td>1047-2518</td>
<td>Ethanol/O2/Ar/Ne</td>
<td>1.0, ∞</td>
<td>TOF-MS Sampling: C2H4, H2O, C2H5OH, CH3, CHO, CH4, C2H2, CO, CO2; Ignition: OH* and OH time-histories Ignition: Pressure and High speed imaging; GC Sampling: C2H5OH and 11 stable intermediates Ignition: OH* and high speed end wall imaging</td>
</tr>
<tr>
<td>Barraza et al. [21]</td>
<td>2016</td>
<td>RCM</td>
<td>3-10</td>
<td>880-1150</td>
<td>Ethanol/O2/N2/Ar</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Figueroa-Labastida et al. [15]</td>
<td>2018</td>
<td>Shock tube</td>
<td>2-4</td>
<td>900-1340</td>
<td>Ethanol/O2/N2 and Ethanol/O2/Ar</td>
<td>0.5 and 1.0</td>
<td></td>
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</table>
Table 3: A continuation of summary of ethanol ignition and speciation studies in a shock tube and RCM with associated optical diagnostics.

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<tbody>
<tr>
<td>Pinzón et al. [29]</td>
<td>2018</td>
<td>Shock tube</td>
<td>1.31</td>
<td>1250-1677</td>
<td>Ethanol/Ar</td>
<td>∞</td>
<td>Absorption Spectroscopy: H2O at 1388.140 nm</td>
</tr>
<tr>
<td>Zhang et al. [14]</td>
<td>2018</td>
<td>Shock tube and RCM</td>
<td>20-40</td>
<td>650-1250</td>
<td>Ethanol/DME/O2/N2</td>
<td>0.5-2.0</td>
<td>Ignition: pressure</td>
</tr>
<tr>
<td>Mathieu et al. [17]</td>
<td>2019</td>
<td>Shock tube</td>
<td>1.3-53</td>
<td>938-1615</td>
<td>Ethanol/O2/N2 and Ethanol/O2/Ar</td>
<td>0.5-2.0</td>
<td>Ignition: OH* and pressure Absorption Spectroscopy: H2O at 1388.140 nm</td>
</tr>
<tr>
<td>Choudhary et al. [31]</td>
<td>2019</td>
<td>Shock tube</td>
<td>10</td>
<td>1200 - 1600</td>
<td>Ethanol/Ar</td>
<td>∞</td>
<td>Absorption Spectroscopy: C2H5OH at 9.53 μm, CO at 4.85 μm, C2H4 at 10.532 μm</td>
</tr>
</tbody>
</table>
With significant progress made to improve ethanol mechanisms, there are still major discrepancies, which underscore the need for continued validation of important kinetic targets. Time-history measurements of species including carbon monoxide (CO) during ethanol oxidation in shock tubes is very limited, especially at elevated pressures. This lack of data limits construction and refinement of chemical kinetic mechanisms for real combustor applications, especially since CO is an important intermediate species playing a larger role in the way future combustion devices will be designed. The current work is aimed at measuring CO time-histories in a shock tube at higher pressure, near 20 atm, and to the best of the authors’ knowledge, this condition has not been investigated before. Implementing laser absorption spectroscopy provides an ideal method to make in situ measurements of concentration time-histories in a shock tube facility that can be used in validating a chemical kinetic mechanism and component sub-mechanisms. This study presents the addition of CO time-history measurements at higher pressure to ethanol literature and compares the performance of model predictions across a temperature range to better aid in the understanding of associated sensitive pathways. We will first report the ignition delay time data for all mixtures and test conditions, followed by results of measured CO time-histories behind reflected shock waves with comparison to model predictions. Through a sensitivity and rate of production analysis, along with the measured concentrations, new insights into the elementary reactions and pathways most sensitive to CO formation are gained.
2.2 Experimental Setup

The procedure and instrumentation for shock tube experiments have been previously detailed in our earlier work [32-34], thus only a brief description will be provided here. Experiments were performed with three different mixtures, covering high fuel loading at an equivalence ratio of 1 and low fuel loading at equivalence ratios of 1.0 and 0.5. The high fuel loading condition ranged from 960 – 1113 K near 22 atm, and low fuel loading ranged from 1229 – 1580 K near 20 atm. Only ignition delay data were taken for high fuel loading experiments, while low fuel loading included both ignition data and CO time-history measurements. A summary of the test conditions is provided in Table 3.

Table 3: Summary of current ethanol oxidation experiments.

<table>
<thead>
<tr>
<th>$T_s$ [K]</th>
<th>$P_s$ [atm]</th>
<th>$T_s$ [K]</th>
<th>$P_s$ [atm]</th>
<th>$T_s$ [K]</th>
<th>$P_s$ [atm]</th>
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<tbody>
<tr>
<td>$X_{\text{ethanol}} = 0.25%$</td>
<td>$X_{\text{ethanol}} = 0.25%$</td>
<td>$X_{\text{ethanol}} = 6.54%$</td>
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<td>$\varphi = 0.5$</td>
<td>$\varphi = 1.0$</td>
<td>$\varphi = 1.0$</td>
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<tr>
<td>1230</td>
<td>19.7</td>
<td>1252</td>
<td>20.5</td>
<td>960</td>
<td>22.5</td>
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<tr>
<td>1232</td>
<td>17.8</td>
<td>1272</td>
<td>19.8</td>
<td>975</td>
<td>23.3</td>
</tr>
<tr>
<td>1281</td>
<td>19.1</td>
<td>1322</td>
<td>19.7</td>
<td>977</td>
<td>23.5</td>
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<tr>
<td>1309</td>
<td>19.5</td>
<td>1359</td>
<td>18.9</td>
<td>986</td>
<td>24</td>
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<tr>
<td>1309</td>
<td>18.8</td>
<td>1364</td>
<td>19.1</td>
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<tr>
<td>1340</td>
<td>18.7</td>
<td>1454</td>
<td>20.3</td>
<td>1090</td>
<td>22.1</td>
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<td>17.8</td>
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<td>1464</td>
<td>19.1</td>
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2.2.1 Shock Tube Facility

The double-diaphragm shock tube facility at the University of Central Florida (UCF) has an inner diameter of 14.17 cm and is compatible with plastic or metal diaphragms. A stacked double-diaphragm setup was used with two scored polycarbonate diaphragms, which ruptured at
a known pressure. Before each experiment, the driver and driven section of the shock tube were first vacuumeed with Agilent DS 102 rotary vane pumps. The driven pressure was then lowered to a level of $1 \times 10^{-5}$ Torr with an Agilent V301 turbo-molecular pump, which occurred in less than 1 h. Vacuum pressures were measured with a convection gauge (Lesker KJL275804LL) and an ionization gauge (Lesker KJLC354401YF). For measuring the shock velocity, there are five time-of-arrival PCB 113B26 pressure transducers connected to four Agilent 53220A timer-counters. This velocity is then extrapolated to the end wall to calculate temperature ($T_3$) and pressure ($P_3$) behind the reflected shock wave in the test location using 1D ideal shock relations assuming vibrationally equilibrated and chemically frozen test gases. Uncertainties in temperatures and pressures behind reflected shock waves were at worst ±12.2 K and ±0.324 atm, and at best ±9.2K and ±0.281 atm, for all experiments. These uncertainties originate from the determination of incident shock velocity based on the timer-counter values and port-to-port distances. The aforementioned uncertainties in temperature result in an estimated uncertainty in ignition delay time of at worst 28.0% and at best 21.5%.

### 2.2.2 Fuel/Oxidizer Mixture Preparation

All oxidation mixtures were prepared in a 33L stainless steel mixing tank that was fitted with a magnetically driven stirrer. Before making each mixture, the mixing tank was vacuumeed overnight to ensure the accuracy of the mixture. Ultra high purity (99.999%) argon and oxygen, and industrial grade (99.998%) nitrogen were supplied by nexAir and the ethanol used was supplied by Acros Organics (99.5+%). It should also be noted that the mixing tank and manifold was heated to 110C to ensure no condensation of ethanol occurred during the mixture
preparation and subsequent filling. Vaporization of ethanol was done using a heated schlenk tube connected to the manifold. The ethanol mixtures were prepared manometrically using 100 Torr (MKS E27D), 10000 Torr (MKS 628D), and 3000 psia (MKS 750C) Baratron pressure transducers. Upon completion of the mixture, it was left to mix for at least 2 h before use. The initial pressure for each experiment was measured with the Baratron pressure transducers mentioned above, which were attached to the manifold.

2.2.4 Pressure and Emission Diagnostics for Ignition Delay Times

Diagnostics used for these experiments included pressure measurements, emission detection, and a fixed-wavelength direct-absorption laser setup at the test location 2 cm from the end wall. Reflected shock pressure ($P_s$) was measured with a sidewall mounted Kistler 603B1 pressure transducer with RTV coating, and chemiluminescence emission was captured using a sidewall located Thorlabs GaP transimpedance amplified detector fitted with Edmund optics filters for CH* (430 ±10 nm) and Thorlabs filter for OH* (310 ±5 nm). Details of these diagnostics used for interpretation of ignition delay times will be discussed further with comparisons of the methods employed.

2.2.5 Laser Absorption Diagnostic for CO Time-histories Near 4.9 µm

Absorption measurements of CO were made using a continuous wave distributed feedback quantum cascade laser (CW-DFB QCL) supplied by Alpes Lasers. The mid-IR QCL allowed access to the strong P(23) transition line of CO near 4.9 µm where interfering absorption
from H2O and CO2 are limited, enabling accurate measurements of CO. At this selected transition CO2 and H2O are the most likely species to interfere, though other hydrocarbons like methane (CH4), formaldehyde (CH2O), ethylene (C2H4), ethanal (CH3CHO), and ethenol (C2-H3OH) are forming though absorb negligibly at the wavenumber used. Figure 1 (a and b) shows the absorption cross-sections of CO, H2O and CO2 from HITRAN 2016 [35] plotted over a wavenumber range, and a zoomed view with the selected measurement wavenumber. Due to the line strength and mitigation of likely interfering species during oxidation experiments, the wavenumber of 2046.30 cm⁻¹ was chosen to target the P(23) transition of CO and enable ppm-level measurements in shock tube experiments. Figure 2 shows the expected absorbance traces of CO, CO2 and H2O at this wavelength during ethanol oxidation using species predictions from Metcalfe et al. [36] and HITRAN cross-section values, and indicates that the absorbance from the potential interfering species is essentially negligible. Note that there is minimal interference from H2O, which peaks near ignition and remains constant throughout the remaining CO decay. This was accounted for in the total uncertainty for the entire time-history. This characterization investigation provided confidence in making CO concentration measurements with minimal interference.
Figure 1: Comparison of CO, CO2 and H2O absorption cross-section data taken from HITRAN showing (a) broad spectrum with two main branches of CO and (b) the wavenumber of 2046.30 cm⁻¹ chosen for CO measurements at 1380 K and 19.3 atm.
Figure 2: Predicted absorbances of CO, H2O and CO2 at 1380 K and 19.3 atm during the oxidation of (a) 0.25% C2H5OH / 1.5% O2 / 98.25% Ar and (b) 0.25% C2H5OH / 0.75% O2 / 99% Ar. The reaction mechanism of Metcalfe et al. [36] was used for these simulations. Absorbances due to other interfering species are minimal and essentially negligible.
A fixed-wavelength direct-absorption technique was used to measure CO time-histories at 2046.30 cm⁻¹ to target the P(23) transition of CO. Figure 3 shows a schematic representing the optical setup for this diagnostic at the shock tube test location. The wavelength of the laser was verified before and after each experiment with the use of a Bristol 771 wavemeter. Two HgCdTe (MCT) detectors (Vigo PIV-4TE-5-2x2) were used to measure focused laser light intensity and obtain the absorbance of the laser beam during experiments. This absorbance is related to mole fraction and measured laser intensities via the Beer-Lambert Law, given by equation 1, where \( \alpha \) is the absorbance, \( I_{\text{trans}} \) is the intensity of light that passes through the shock tube during the experiment, \( I_{\text{ref}} \) is the reference intensity through the shock tube under vacuum, \( \sigma \) [cm² molecule⁻¹] is the absorption cross-section, \( P_5 \) [atm] is the pressure behind the reflected shock wave, \( R \) [cm³ atm K⁻¹ mole⁻¹] is the universal gas constant, \( T_5 \) [K] is the temperature behind the reflected shock wave, \( X_{\text{CO}} \) is the mole fraction of CO, and \( L \) [cm] is the optical path length.

To spectrally characterize the absorption cross-section of CO at this wavelength over the range of experimental conditions, cross-section measurements were carried out by shock heating a non-reactive mixture of 0.75% CO in 2.5% He and 96.75 Ar. The data collected were aggregated into an empirical correlation using a polynomial fit with an adjusted R-squared value of 0.97, with the expression given by equation 2 and values of coefficients in Table 4. The adjusted R-squared value is a metric that allows for an unbiased fit of the data, as higher order polynomial fits and multiple sets of data (pressure and temperature) were used for the fit. By optimizing the adjusted R-squared value, we have ensured the higher order polynomial fits have not overfit the data. Note that with increasing fit order this will continually increase the R-squared value, however the adjusted R-squared value will increase to a maximum then being to fall.
Multiple sources of uncertainty are responsible for the overall uncertainty in CO concentration measurements. These include the uncertainty of measured absorbances based on the noise \((2\sigma)\) of measured transmitted and reference intensity signals, uncertainty in path length (diameter of the shock tube), \(T_5/P_5\) (as previously discussed), the mixture prepared, and the absorption cross-section. Since the absorption cross-section was based on an entire set of characterization experiments, the uncertainty associated with the cross-section also depends on uncertainties of \(T_5/P_5\), path length, absorbances, and the used mixture. The combination of all described uncertainties in an error propagation analysis results in an overall uncertainty of CO for lean mixtures of 8.8% and 5.7% for stoichiometric mixtures on average.

\[
\alpha = -\ln \left( \frac{I_{\text{trans}}}{I_{\text{ref}}} \right) = \sigma_{\text{CO}}(v, T, P) \frac{P_5}{RT_5} X_{\text{CO}} L
\]

\[
\sigma_{\text{CO}}(T, P) = a + bT + cP + dT^2 + eTP + fT^3 + gT^2P
\]

Table 4: Constant values calculated within a 95% confidence interval of the polynomial fit for the CO absorption cross-section expression.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>(-3.61 \times 10^{-18})</td>
</tr>
<tr>
<td>(b)</td>
<td>(6.206 \times 10^{-21})</td>
</tr>
<tr>
<td>(c)</td>
<td>(1.284 \times 10^{-18})</td>
</tr>
<tr>
<td>(d)</td>
<td>(-2.896 \times 10^{-24})</td>
</tr>
<tr>
<td>(e)</td>
<td>(-1.950 \times 10^{-22})</td>
</tr>
<tr>
<td>(f)</td>
<td>(3.264 \times 10^{-28})</td>
</tr>
<tr>
<td>(g)</td>
<td>(6.925 \times 10^{-26})</td>
</tr>
</tbody>
</table>
Figure 3: Schematic of shock tube and laser setup used to perform CO time-history measurements.

2.3 Results and Discussion

2.3.1 High Fuel Loading Ignition Delay Time Measurements

For high fuel concentration measurements of ignition delay time, a stoichiometric mixture of 6.54% ethanol/19.64% O2/73.82% N2 was used in the temperature range of 1229 – 1580 K near 22 atm. These experiments presented some difficulty in defining time-zero due to having a diatomic compound in the bath gas of the mixture, which is known to result in reflected shock bifurcation in the system causing a non-uniform pressure rise [37, 38]. Thus, we sought after use of the schlieren spike from a laser (near 3.4 µm) that was aligned through the shock tube (not the CO laser described previously); however, due to the immense emission, the
expected observation of distinct incident/reflected schlieren spikes were not presented. Instead a blended form of the two spikes in the laser signal was observed. To resolve this, time-zero was interpreted as the midpoint of the rise in laser signal, which correlates very well with the pressure rise due to the arrival of the reflected shock wave, and moreover the pressure trace itself, as can be seen in Figure 4.

![Figure 4](image.png)

Figure 4: Relationship of raw transmitted laser signal and pressure trace showing similar coinciding trends during an ethanol-air oxidation experiment at 977 K and 23.5 atm.

With a defined time-zero, the next step is to find the time corresponding to the onset of ignition. In this study, we adopted several methods to define ignition delay time. These include the first and maximum observed peak of OH* emission, as well as maximum rate of change in the pressure profile. Due to the deflagrative process followed by the arrival of a blast wave (inherent of mild ignition [39] that was observed in nearly every experiment), OH* emission
signals in some cases posed difficulty in interpretation. For example, in Figure 5 many OH* peaks of similar strength in the signal were captured. As was discussed by Davidson and Hanson [40], ignition delay times for mixtures consisting of high fuel concentrations can appropriately be defined based on pressure. Accordingly, the primary definition of ignition delay time is based on the maximum rate of change in pressure rise and is compared to other methods with generally good agreement with a variation of typically 3.6% from the average. Table 5 and Figure 6 present IDT data according to various definitions.

Figure 5: Multi-peak features of raw OH* emission detected during oxidation of ethanol in air (phi=1.0) at 977 K and 23.5 atm.
Table 5: Summary of ignition delay times defined using various methods for evaluation of the high fuel loading case.

<table>
<thead>
<tr>
<th>$T_s$ [K]</th>
<th>$p_s$ [atm]</th>
<th>OH* First Peak [ms]</th>
<th>OH* Max Peak [ms]</th>
<th>$d\dot{P}/dt$ Max [ms]</th>
</tr>
</thead>
<tbody>
<tr>
<td>960</td>
<td>22.5</td>
<td>2.240</td>
<td>2.240</td>
<td>2.238</td>
</tr>
<tr>
<td>975</td>
<td>23.3</td>
<td>1.785</td>
<td>1.853</td>
<td>1.824</td>
</tr>
<tr>
<td>977</td>
<td>23.5</td>
<td>1.237</td>
<td>1.513</td>
<td>1.257</td>
</tr>
<tr>
<td>986</td>
<td>23.9</td>
<td>1.013</td>
<td>1.150</td>
<td>1.000</td>
</tr>
<tr>
<td>1069</td>
<td>21.2</td>
<td>0.357</td>
<td>0.371</td>
<td>0.355</td>
</tr>
<tr>
<td>1090</td>
<td>22.1</td>
<td>0.292</td>
<td>0.311</td>
<td>0.285</td>
</tr>
<tr>
<td>1113</td>
<td>22.9</td>
<td>0.165</td>
<td>0.165</td>
<td>0.158</td>
</tr>
</tbody>
</table>

Figure 6: Comparison of various methods used to define the ignition delay time during the oxidation of a stoichiometric mixture of 6.54% ethanol in air.

In previous end wall imaging experiments, observed localized hot spots leading to a gradual heat release preceding homogeneous transition to detonation were observed; thus calling into question the experimental non-homogeneities and deviation from constant internal energy, constant volume (U, V) assumptions [12, 15, 41]. It was noted by Figueroa-Labastida et al. [15]
that the governing factors of preignition are fuel concentration and equivalence ratio, with their observations revealing preignition in 5% ethanol/30% oxygen mixtures (φ = 0.5) in the temperature range of 992 – 1042 K. Their high-speed imaging supported localized, non-homogeneous ignition marked as mild ignition, with pressure and camera intensity showing similar profiles of early heat release. Much like Figueroa-Labastida et al. [15], what seemed to be preignition effects were observed with pressure and OH* traces similarly capturing the gradual heat release (as shown in Figure 7). However, when compared to the predictions of several kinetic mechanisms modeled in Chemkin-Pro[42] assuming constant-U, V, there is good agreement for stoichiometric conditions used in the current study (see Figure 8). However, this is misleading as experiments affected with preignition should not be simulated with a 0-D, constant U, V model assumption, as this phenomenon is inhomogeneous and 3-D. It should be noted that the higher pressure and undiluted mixture composition (or higher fuel loading) further promote preignition at these temperatures [15, 43].

It is possible that the early energy/heat release observed in this study is not substantial enough to completely deviate from homogenous behavior and is more indicative of a transition from mild to strong ignition (mixed regime). As was observed in previous side wall imaging studies [12, 41, 44-48], the presence of nonhomogeneous “hot spot” ignition initiates away from the end wall and at many different locations in mild ignition cases, though can still occur similarly near the end wall. Thus, these results suggest the early heat release as seen in the pressure traces is confined closely to the end wall that start off in a nonhomogeneous behavior, but quickly transition into a homogeneous event, which is fully captured in the pressure trace. Moreover, the early heat release events as observed in the pressure traces happen over a very
short period and with minimal dP/dt rise prior, rather than in a gradual manner as observed in previous works [12, 13, 15] among others, which is typical in preignition events (mild ignition). In addition, the use of N\textsubscript{2} as a bath gas is understood to produce a thicker flame, which is less prone to initiate a flame kernel from localized hot spots. This may also explain why the ignition delay times were not observed to be shorter than the predictions, even though early heat release is evident. It should also be noted that the diameter of the shock tube (14.17 cm) can mitigate perturbations due to flame propagation, as this was shown through scaling analysis in works by Medvedev et al. [49, 50]. However, previous work [12, 15] utilizing similar diameter shock tubes and N\textsubscript{2} bath gas, have observed preignition. To better understand this, more experiments will be done at lower temperatures where the deviation between experiment and model predictions due to preignition should present significant differences. Currently, it is difficult to understand and interpret the preignition effects observed. Therefore, future efforts will also include novel end wall and side wall (3D) imaging techniques to further the understanding of mild and transitional ignition events in the UCF shock tube facility.

Previous studies reporting ethanol preignition, as in Figueroa-Labastida et al. [15], point to ignition chemistry which is strongly influenced by chemical induction processes that have high sensitivity to perturbations from gas-phase chemistry, mixing, fluid dynamics, temperature, and catalytic end wall and surface effects [43, 44, 51]. These preignition events have been observed to be independent of facility cleanliness, and other impurities likely to cause this occurrence [15, 41, 43]. The current work outlines additional conditions that exhibit preignition, and further supports that continued studies investigating the properties associated with this phenomenon are necessary by employing a combination of pressure time-histories and imaging
techniques to truly understand and decipher the differences in various types of ignition. With this in consideration, the experiments that are affected by these inhomogeneities should not be used to validate chemical kinetic mechanisms; knowing at which conditions these effects arise is not only important for shock tubes, but in the application of internal combustion engines. We have considered the authors’ requests [15, 40, 43] regarding the inclusion of pressure traces when observing these ignition events, and they are provided in the supplementary material. In addition, though there is overlap in temperature and pressure conditions with previous works, it is beneficial to amass ignition data on an important fuel such as ethanol from multiple shock tube (and RCM) facilities, as in the previous propene work of Burke et al. [52].
Figure 7: Measured pressure and normalized OH* emission showing early heat release during leading to detonation for ethanol-air oxidation at (a) 1090 K and 22.1 atm, and (b) 986 K and 23.9 atm.
Figure 8: Ignition delay time data for the current high fuel loading experiments compared with literature data and model predictions performed in Chemkin-Pro using the chemical kinetic mechanisms of Mittal et al.[20], Zhang et al. [14], and Metcalfe et al. [36] assuming constant-U, V

2.3.2 Low Fuel Loading Ignition Delay Time Measurements

For these tests, lean (0.25% ethanol/1.5% O2/98.25% Ar) and stoichiometric (0.25% ethanol/0.75% O2/99% Ar) mixtures were used in an intermediate to high temperature range near 20 atm. Time-zero was defined by the schlieren spike observed in the CO laser measurements, and the onset of ignition was determined through CH* and OH* peak emission. Table 6 shows data collected where the variation between the two definitions was typically less than 3.8% from the average. There is generally good agreement when comparing experiments and predictions, with a consistent slight overprediction for the stoichiometric mixture throughout the temperature spread. The lean mixture shows larger spread in data collected at lower
temperatures. Measured ignition delay times are plotted against model predictions in Figure 8. During these low fuel loading experiments, mild or mixed ignition was not observed. When comparing the ignition delay trend from both mixtures across the temperature ranges, an identical slope, i.e. activation energy, remains constant across the different equivalence ratios as expected (see supplemental material).
Table 6: Summary of ignition delay times based on OH* and CH* emissions for both low fuel loading mixtures at equivalence ratios of 0.5 and 1.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$T_s$ [K]</th>
<th>$P_s$ [atm]</th>
<th>OH* Max Peak [ms]</th>
<th>CH* Max Peak [ms]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi = 0.5$</td>
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<td>19.7</td>
<td>2.054</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>1232</td>
<td>17.8</td>
<td>0.833</td>
<td>0.771</td>
</tr>
<tr>
<td></td>
<td>1281</td>
<td>19.1</td>
<td>0.309</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>1305</td>
<td>19.5</td>
<td>0.449</td>
<td>0.393</td>
</tr>
<tr>
<td></td>
<td>1309</td>
<td>18.8</td>
<td>n/a</td>
<td>0.396</td>
</tr>
<tr>
<td></td>
<td>1340</td>
<td>18.7</td>
<td>0.283</td>
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<tr>
<td></td>
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<td>20.4</td>
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<td>0.183</td>
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<td></td>
<td>1391</td>
<td>19.3</td>
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<tr>
<td></td>
<td>1405</td>
<td>17.8</td>
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<td>0.137</td>
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<tr>
<td></td>
<td>1464</td>
<td>19.1</td>
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<td>0.055</td>
</tr>
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<tr>
<td></td>
<td>1580</td>
<td>19.5</td>
<td>0.040</td>
<td>0.043</td>
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</tbody>
</table>
Figure 9: Ignition delay time data defined by peak OH* emission taken for this current low fuel loading study compared with model predictions performed in Chemkin-Pro using the chemical kinetic mechanisms of Mittal et al.[20], Zhang et al. [14], and Metcalfe et al. [36] assuming constant-U, V for equivalence ratios of (a) 0.5 and (b) 1.0.
2.3.3 Low Fuel Loading Carbon Monoxide Time-history Measurements

Carbon monoxide concentration time-histories were measured during ethanol oxidation behind reflected shock waves using the CO absorption diagnostics centered at 2046.30 cm$^{-1}$. Figure 10 and Figure 11 compare measured CO time-histories for lean and stoichiometric mixtures, respectively, with model predictions using Chemkin-Pro assuming constant-$U$, $V$. Temperature rise due to ignition was minimal (around 40 K) for these experiments as estimated with an isentropic compression assumption, and so CO time-histories are shown throughout the ignition process. Here we have plotted experimental results against predictions by three models including Metcalfe et al. [36], Mittal et al. [20], and Zhang et al. [14]. The Metcalfe et al. mechanism, which is a detailed chemical kinetic model for the oxidation of small hydrocarbon and oxygenated hydrocarbon species, is used as the base ethanol mechanism found in AramcoMech 1.3 onwards. With respect to shock tube studies, this mechanism has been validated between 833 – 2500 K and 0.5 – 260 atm for lean/rich mixtures. The other authors included have built upon this base mechanism to better predict the observations (ignition) of their experiments, particularly at high pressure and low temperature.
Figure 10: Experimental pressure traces and CO time-histories represented by solid lines compared to various model predictions represented by the dashed/dotted lines carried out in Chemkin-Pro assuming a constant-U, V model for the stoichiometric mixture at (a) high temperature and (b) low temperature experiments.
Figure 11: Experimental pressure traces and CO time-histories represented by solid lines compared to various model predictions represented by the dashed/dotted lines carried out in Chemkin-Pro assuming a constant-U, V for a mixture at an equivalence ratio of 0.5 for (a) high temperature and (b) low temperature experiments.
As can be seen from data presented in Figs. 10 and 11, the predictions show a tendency to underpredict the rate of CO formation up to the max yield, which is more apparent during lower temperature experiments when compared to those at high temperatures for both lean and stoichiometric conditions (Figs. 10b and 11b). The models show similar performance, though differences arise for the lean mixture at lower temperatures. For experiments performed at an equivalence ratio of 1.0, the Metcalfe et al. mechanism [36] seems to show peak CO formation occurring slightly sooner at intermediate/low temperatures when compared to other models.

A sensitivity analysis was first performed using the Metcalfe et al. mechanism to determine the reactions that are critical to controlling the species time-histories. The sensitivity coefficient is the partial derivative of the species mole fraction history with respect to the reaction rate constant normalized by the species mole fraction history and rate constant, defined as $S(X_{\text{species}}, k_i, t) = \left( \frac{d X_{\text{species}}(t)}{d k_i} \right) \left( \frac{k_i}{X_{\text{species}}(t)} \right)$. For both mixtures (see Fig. 13), there are several elementary reactions that show high sensitivity to CO time-histories at the lower temperatures of this study, which include the following:

$$H+O_2=O+OH \quad \text{R1}$$

$$CH_3+HO_2=CH_3O+OH \quad \text{R144}$$

$$C_2H_5OH+HO_2=sC_2H_4OH+H_2O_2 \quad \text{R369}$$
Figure 12: Results of Chemkin-Pro sensitivity analysis for CO based on the Metcalfe et al. [36] mechanism at simulation conditions for (a) stoichiometric mixture at 1252 K and 20.5 atm, and (b) mixture with equivalence ratio of 0.5 at 1232 K and 17.8 atm.
One of the most important elementary reactions for ignition is also very sensitive to the early stages of CO formation, given by R369. When comparing the model predictions to lower temperature experimental data, these early stages of CO formation have immense discrepancy, which may be impart due to a low reaction rate for R369. Though in a previous study by Barraza-Botet et al. [21], it was observed that the adjustment of the A-factor for R369 had negligible effect on the prediction of intermediate species. Compensating for the discrepancy of early stage CO formation by this reaction may have undesired effects on ignition delay time prediction, as this reaction is most sensitive to OH at the point of ignition. Looking throughout the formation of CO, R1 and the bimolecular reaction of methyl radical and hydroperoxyl radical (R144) are most sensitive to the formation of CO. The chain branching reaction of R1 is well studied in the literature and the reaction mechanism used for this sensitivity analysis uses the reaction rate provided by Hong et al. [53], which was estimated to have an uncertainty of 4.6% at 1500 K and 8.8% at 1100 K. This provides minimal margin for adjustment to account for the discrepancy observed. Furthermore, there is high sensitivity at elevated temperatures for this reaction that can cause significant deviations in the model predictions (where there is fair agreement with experiments already). Thus, attention was directed to R144, CH3+HO2=CH3O+OH.

This reaction has been most recently studied by Sangwan et al. [54] in an experimental capacity at 295 K and 1 bar, which agrees well with the theoretical calculations of Jasper et al. [55] using direct variable reaction coordinate transition state theory (VRC-TST). The theory used by these authors was developed to accurately treat barrierless reactions with estimated errors less
than 25%. The calculated reaction rate by Jasper et al. [55] confirms previous experimental investigations and prior revisions of the reaction rate, including work by Scire et al. [56] (who performed an indirect experimental study of this reaction rate and a detailed error analysis that reduced the overall uncertainty). The experiment performed in the study [56] was carried out in a lean CO oxidation system with methane in a flow reactor, which revealed that at low pressures with low concentrations of methane, CO oxidation was stifled as methane consumed OH faster than CO; however, at higher pressures methane increased the rate of CO oxidation. It was identified that reaction R144, CH3+HO2=CH3O+OH, was a key feature in this process at these conditions resulting in CH3O and OH that expedited CO oxidation. The importance of this reaction (R144) in mechanisms is underscored at high pressure and low/intermediate temperature hydrocarbon combustion, and this pathway has been previously said to be a major chain propagation reaction at these conditions [57, 58]. Considering the extent of previous insights into this reaction, a slight adjustment of the rate well within the specified uncertainty factor of Scire et al. [56] of ± 2.24 and Sangwan et al. [54] of ± 1.8 yields significant effect on the overall prediction of the CO time-history. This has a favorable impact when compared to low temperature data collected, as shown in Figs. 13 and 14, where the rate constant for elementary reaction R144 was increased by a factor of 1.75 via adjustment of the A-factor. It should be noted that this is only a suggestion providing insight from what has been experimentally observed in this study. This reaction rate has one of the highest sensitivities in combustion reactions; changing it will affect predictions for many different fuels. To instate such a change to mechanisms would require validation over a wide variety of targets and fuels. As was stated before, R369 also contributes to the formation of CO much earlier in the experiment. With an
adjustment of the A-factor value for R369 from $3.5 \times 10^{-5}$ (specified in the Metcalfe et al. mechanism taken from Zhou et al.[59]) to $5.5 \times 10^{-5}$, better agreement with the model earlier in the profile is observed; however, this is outside the specified uncertainty based on calculations of Zhou et al. [59] who estimated the rate of R369 via an analogy with n-butanol+HO2. Barraza-Botet et al. [21] noted that perhaps the allowable uncertainty is less stringent than that estimated by Zhou et al. (uncertainty factor of ± ~ 2.5). Recently, however, Zhao et al. [60] calculated the rate of R369 based on transition-state theory and canonical variational transition-state theory to be slower than the rate of Zhou et al., though it is within the uncertainty factor of 3 specified by Zhao et al.

The minor changes discussed seem to favorably shift the stoichiometric and lean conditions (Figs. 13 and 14) based on comparisons with current experiments; however, a shift of peak prediction is only partial to understanding the discrepancies observed in time-history trends. For example, the trend in the time-histories during CO formation and decomposition, as well as the ppm level throughout these processes. Furthermore, these changes directly impact the predictions of ignition delay times for both high and low fuel loadings. As shown in Fig.15, slightly better agreement is observed for the low fuel loading stoichiometric case due to overprediction as mentioned previously. For the low fuel loading lean and high fuel loading cases deviation is significant (Figs. 15b and 16), which is primarily due to the adjustment of R369. Though changing this reaction rate yields improved agreement in early stages of CO formation, this is not recommended as it adversely affects the prediction of ignition delay times. In addition, these changes also impact the predictions of CO time-histories where there is already
good agreement at specific conditions, for example in Fig. 11a. By comparing the “tweaked” mechanism to Metcalfe et al. predictions, undesired disagreement is observed as shown in Fig. 17. This may suggest that the governing reactions for ethanol decomposition that lead to highly reactive species resulting in accelerated reactivity play a larger role in early stages, which agrees with the assessment of Barraza-Botel et al. [21] who noted model underprediction of ethanol consumption rate at earlier times. To better understand the pathways of CO formation and depletion during ethanol oxidation, an analysis was performed on the stoichiometric mixture. One of the most important elementary reactions for ignition is also very sensitive to the early stages of CO formation, given by R369. When comparing the model predictions to lower temperature experimental data, these early stages of CO formation have immense discrepancy, which may be impart due to a low reaction rate for R369. Though in a previous study by Barraza-Botel et al. [21], it was observed that the adjustment of the A-factor for R369 had negligible effect on the prediction of intermediate species. Compensating for the discrepancy of early stage CO formation by this reaction may have undesired effects on ignition delay time prediction, as this reaction is most sensitive to OH at the point of ignition. Looking throughout the formation of CO, R1 and the bimolecular reaction of methyl radical and hydroperoxyl radical (R144) are most sensitive to the formation of CO. The chain branching reaction of R1 is well studied in the literature and the reaction mechanism used for this sensitivity analysis uses the reaction rate provided by Hong et al. [53], which was estimated to have an uncertainty of 4.6% at 1500 K and 8.8% at 1100 K. This provides minimal margin for adjustment to account for the discrepancy observed. Furthermore, there is high sensitivity at elevated temperatures for this reaction that can
cause significant deviations in the model predictions (where there is fair agreement with experiments already). Thus, attention was directed to R144, CH3+HO2=CH3O+OH.

This reaction has been most recently studied by Sangwan et al. [54] in an experimental capacity at 295 K and 1 bar, which agrees well with the theoretical calculations of Jasper et al. [55] using direct variable reaction coordinate transition state theory (VRC-TST). The theory used by these authors was developed to accurately treat barrierless reactions with estimated errors less than 25%. The calculated reaction rate by Jasper et al. [55] confirms previous experimental investigations and prior revisions of the reaction rate, including work by Scire et al. [56] (who performed an indirect experimental study of this reaction rate and a detailed error analysis that reduced the overall uncertainty). The experiment performed in the study [56] was carried out in a lean CO oxidation system with methane in a flow reactor, which revealed that at low pressures with low concentrations of methane, CO oxidation was stifled as methane consumed OH faster than CO; however, at higher pressures methane increased the rate of CO oxidation. It was identified that reaction R144, CH3+HO2=CH3O+OH, was a key feature in this process at these conditions resulting in CH3O and OH that expedited CO oxidation. The importance of this reaction (R144) in mechanisms is underscored at high pressure and low/intermediate temperature hydrocarbon combustion, and this pathway has been previously said to be a major chain propagation reaction at these conditions [57, 58]. Considering the extent of previous insights into this reaction, a slight adjustment of the rate well within the specified uncertainty factor of Scire et al. [56] of ± 2.24 and Sangwan et al. [54] of ± 1.8 yields significant effect on the overall prediction of the CO time-history. This has a favorable impact when compared to low
temperature data collected, as shown in Figs. 14 and 15, where the rate constant for elementary reaction R144 was increased by a factor of 1.75 via adjustment of the A-factor. It should be noted that this is only a suggestion providing insight from what has been experimentally observed in this study. This reaction rate has one of the highest sensitivities in combustion reactions; changing it will affect predictions for many different fuels. To instate such a change to mechanisms would require validation over a wide variety of targets and fuels. As was stated before, R369 also contributes to the formation of CO much earlier in the experiment. With an adjustment of the A-factor value for R369 from 3.5 x 10^{-5} (specified in the Metcalfe et al. mechanism taken from Zhou et al.[59]) to 5.5 x 10^{-5}, better agreement with the model earlier in the profile is observed; however, this is outside the specified uncertainty based on calculations of Zhou et al. [59] who estimated the rate of R369 via an analogy with n-butanol+HO2. Barraza-Botet et al. [21] noted that perhaps the allowable uncertainty is less stringent than that estimated by Zhou et al. (uncertainty factor of ± ~ 2.5). Recently, however, Zhao et al. [60] calculated the rate of R369 based on transition-state theory and canonical variational transition-state theory to be slower than the rate of Zhou et al., though it is within the uncertainty factor of 3 specified by Zhao et al.

The minor changes discussed seem to favorably shift the stoichiometric and lean conditions (Figs. 14 and 15) based on comparisons with current experiments; however, a shift of peak prediction is only partial to understanding the discrepancies observed in time-history trends. For example, the trend in the time-histories during CO formation and decomposition, as well as the ppm level throughout these processes. Furthermore, these changes directly impact the
predictions of ignition delay times for both high and low fuel loadings. As shown in Fig.16, slightly better agreement is observed for the low fuel loading stoichiometric case due to overprediction as mentioned previously. For the low fuel loading lean and high fuel loading cases deviation is significant (Figs. 16b and 17), which is primarily due to the adjustment of R369. Though changing this reaction rate yields improved agreement in early stages of CO formation, this is not recommended as it adversely affects the prediction of ignition delay times. In addition, these changes also impact the predictions of CO time-histories where there is already good agreement at specific conditions, for example in Fig. 12a. By comparing the “tweaked” mechanism to Metcalfe et al. predictions, undesired disagreement is observed as shown in Fig. 18. This may suggest that the governing reactions for ethanol decomposition that lead to highly reactive species resulting in accelerated reactivity play a larger role in early stages, which agrees with the assessment of Barraza-Botet et al. [21] who noted model underprediction of ethanol consumption rate at earlier times. To better understand the pathways of CO formation and depletion during ethanol oxidation, an analysis was performed on the stoichiometric mixture.
Figure 13: Mechanism predictions before and after increasing the A-coefficient for R144 by a factor of 1.75 and R369 by a factor of 1.57 for the stoichiometric mixture of ethanol.
Figure 14: Model performance before and after increasing the A-coefficient for R144 by a factor of 1.75 and R369 by a factor of 1.57 for the lean mixture of ethanol.

Figure 15: Model predictions of ignition delay time before and after increasing the A-coefficient for R144 by a factor of 1.75 and R369 by a factor of 1.57 for (a) the stoichiometric mixture and (b) the lean mixture of $\phi = 0.5$. 
Figure 16: Model predictions before and after increasing the A-coefficient for R144 by a factor of 1.75 and R369 by a factor of 1.57 for the stoichiometric mixture of 6.54% ethanol in air.

Figure 17: Model predictions before and after increasing the A-coefficient for R144 by a factor of 1.75 and R369 by a factor of 1.57 for an equivalence ratio of 0.5 with 0.25% ethanol.
Figure 18: Pathway for CO production from ethanol oxidation at an equivalence ratio of 1. Blue text represent the CH3 radicals produced in intermediate steps.

At first, unimolecular decomposition of ethanol undergoes through reaction 394 and 395.

\[ \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]  
\[ \text{R}394 \]

\[ \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{CH}_3 \]  
\[ \text{R}395 \]

More than 95% of initial decomposition proceed through these two steps until enough of H,OH and CH3 radicals are produced in the combustion mixture. The H atoms released by
CH2OH (R173), OH atoms released from ethanol (reaction 396) and CH3 released by reaction 395 initiates the production of sC2H4OH by H abstraction reactions.

\[
\text{CH2OH} (+\text{M}) = \text{CH2O} + \text{H} (+\text{M}) \quad \text{R173}
\]

\[
\text{C2H5OH} = \text{C2H5} + \text{OH} \quad \text{R396}
\]

The production of sC2H4OH plays an important role in initial CO formation from ethanol, as was previously discussed. To elaborate this, the rate of production analysis of CO at t=1.4ms (when CO mole fraction increases gradually) is shown in Fig. 19a. It can be seen that CO production from CH3CO dominates over traditional HCO pathway (HCO+M=H+CO+M) at t=1.4ms. The pathway diagram shows that CH3CO is produced from CH3CHO which is produced from sC2H4OH. Figure 19 confirms that at t=1.4ms, there is appreciable amount of CH3CHO in the combustion mixture which confirms this. Beyond t=2.2ms, the concentration of CH3CHO approaches zero. A rate of production analysis at t=2.6 ms shows that traditional HCO pathway dominates at this stage. Moreover, the role of CO production from CH3CO pathway is incremental, as evident from Fig. 19b.
Figure 19: Absolute rate of production of CO at (a) t=1.4 ms and (b) t=2.6 ms.
To understand how this pathway of CO production changes from CH3CO to HCO pathway, the reaction pathway was further examined. The reason for this is attributed as follows:

The reaction of CH3CHO to produce CH3CO (reaction 335) consumes H radicals produced in the combustion mixture. This is also evident from Fig. 21 as concentration of H radical starts to increase once all of CH3CHO is consumed. Once H radicals start to accumulate in the reaction mixture, then reaction 155 consumes H radicals at much higher rate (as it is not competing with reaction 335 now) to produce more HCO which results in further production of CO. Accumulation of H atoms in the reaction mixture also triggers the reaction with O2 to release energy by reaction 1. Following production of OH by reaction 1, some amount of CO gets converted to CO2 by reaction 36.

\[ \text{CH}_3\text{CHO} + \text{H} \rightarrow \text{CH}_3\text{CO} + \text{H}_2 \]  

R335

Figure 20: Modeled concentration of (a) CH3CHO vs time and (b) H radicals vs time for stoichiometric ethanol oxidation.
CH2O + H = HCO + H2  \quad \text{R155}

H + O2 = O + OH  \quad \text{R1}

CO + OH = CO2 + H  \quad \text{R36}

2.4 Conclusions

Ignition delay times and CO time-histories measurements were carried out behind reflected shock waves in a shock tube. Ignition delay times were measured for the high fuel loading mixture of 6.54% ethanol/19.64% O2/73.82% N2, while CO time-histories in addition to ignition delay times were measured for low fuel loading mixtures (0.25% ethanol) at equivalence ratios of 0.5 and 1.0 in Ar/O2. Ignition delay times of ethanol/O2/N2 mixtures showed a transition from mild to strong ignition (mixed) with good agreement with predictions by literature mechanisms assuming constant-U, V in the simulations. The pressure traces of these experiments revealed an early heat release indicative of preignition, though it is suggested that the early heat release is not substantial and gradual enough to deviate from a rather homogeneous event. Continued care must be taken when interpreting various ignition events and regimes when using such data for chemical kinetic mechanism development and validation. The combination of pressure and novel 3D imaging techniques should be implemented in future shock tube studies to better understand different ignition schemes, especially, considering the inhomogeneous nature
of these events. To the best of our knowledge, current CO measurements provide the first of its kind at these conditions behind reflected shock waves in a shock tube. Measured CO time-histories had better agreement with predictions at elevated temperatures, while there was observed deviation at lower temperatures. A sensitivity analysis revealed lower temperature sensitivity at the studied pressures to the bimolecular methyl radical and hydroperoxyl radical reaction (R144) CH3+HO2=CH3O+OH and the H-atom abstraction reaction (R369) at the alpha site of ethanol C2H5OH+HO2=sC2H4OH+H2O2. The production of sC2H4OH plays an important role in the initial formation of CO, as is evident through the pathway and sensitivity analyses. With adjustments made to both elementary reaction rates, better model predictions are suggested; however, adjustment of R369 is not recommended due to the importance for overall reactivity (ignition). Greatest sensitivity in the overall trend was observed with R144 and the rate was increased by a factor of 1.75, within the uncertainty factor estimated by Scire et al. [56] and Sangwan et al. [54]. Though these changes aided in a major shift in the concentration histories, certain trends and ppm level discrepancies still exist throughout formation/decomposition. An analysis elaborating on ethanol decomposition and pathways to CO formation/decomposition was presented to aid in this understanding. The results of this study show the value of CO time-histories in accessing mechanism performance at various conditions. Specifically, current measurements emphasize the need for better understanding of low temperature, high pressure species formation during ethanol combustion, which are target conditions for practical combustion devices.

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CHAPTER 3: SUMMARY

The main objective of this thesis is to aid in the further refinement of current ethanol mechanisms. Improving the predictability of IDTs and species’ concentration time-histories their application can provide higher fidelity in the research and design of future engines. First, IDTs were measured for the high and low fuel loading ethanol mixtures, where the former mixture showed inhomogeneous ignition. Given the high pressure and large concentration of fuel, energy release during oxidation experiments were expected, and so the early energy/heat release observed was commented upon. Though characteristics similar to inhomogeneous (mild) ignition were observed, it was hypothesized that the early release was contained closer to the end wall, and thus significant deviation from constant U, V behavior was not apparent in model comparisons. At longer test-times (lower temperature), this would be expected to become more apparent. Previous studies in the literature at these conditions comment on the ignition effects, and the data gathered in this study was compared to those data with good agreement.

In addition, absorption cross section data was acquired for CO near 20 atm using a laser absorption setup. Using this same diagnostic setup and the found cross section data, CO time-histories were measured during the oxidation of ethanol at elevated pressures. The spectral transition to measure CO was chosen specifically for its large absorption cross section and mitigation of potential interference from species formed during oxidation. From the data collected, a sensitivity and pathway analyses revealed critical elementary reaction that play into overall reactivity as well as the early stage formation of CO. The information presented and subsequent discussion regarding the relevant pathways is meant to inform modelers when
updating the chemical kinetic mechanisms. It was discussed that the methyl radical reaction (R144) though being very sensitive to CO (and IDT) predictions, was not recommended, but instead emphasizes ethanol decomposition reactions. With ethanol decomposition reaction (R359) adding to the methyl radical pool by forming CH3 in addition to forming CH2OH, pathways following this, directly and indirectly form CO and play a role in overall reactivity as well.

Future work on ethanol inhomogeneous ignition events in a shock tube should involve advanced imaging techniques to fully understand the 3D phenomenon. Incorporating such a diagnostic at elevated pressures is difficult due to the optical access required for imaging, and may not be appropriate, though multi-pressure or chemiluminescence implementation may be sufficient to study such inhomogeneities. This not only sheds light on regimes which promote preignition in a shock tube but can offer insights into what is expected in-cylinder of internal combustion engines (both spark and compression ignition). In addition, ethanol pyrolysis and oxidation experiments should be carried out where ethanol decomposition time-histories are investigated at these elevated pressures. Further experiments covering wider range of pressures (> 20 atm) and equivalence ratios will be useful in expanding current and future kinetic mechanism.
LIST OF REFERENCES


