

Shock Tube Measurements of Ignition Delay Times for the Butanol Isomers

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1. Introduction

Butanol is a bio-fuel candidate with several important advantages over ethanol. It has a larger energy density, it is not hygroscopic, which means it can be transported in gasoline pipelines, it can be blended with gasoline in higher concentrations, and it has a lower vapor pressure [1]. As a result, there is significant interest in developing a chemical kinetic mechanism in order to accurately model butanol combustion.

One of the simplest methods to evaluate the global accuracy of a chemical kinetic mechanism is by measuring the ignition delay time of a fuel behind the reflected shock wave in a shock tube. Although ignition delay time measurements of the butanol isomers exist, no single study has measured delay times for all isomers over a wide range of conditions. These measurements are needed in order to allow direct comparisons of model simulations with a consistent set of data.

Here, ignition delay time was measured for all four isomers of butanol. Conditions covered temperatures between 1050 and 1600 K, pressures between 1.5 and 43 atm, and equivalence ratios of 1.0 and 0.5 in mixtures containing 4% O₂ dilute in argon. Several other data sets were collected at 1.0-1.5 atm in order to replicate conditions used by previous researchers. Additional data were collected at 23 atm for stoichiometric 1-butanol mixtures in air at temperatures as low as 800 K. To our knowledge, these are the first low temperature measurements of 1-butanol ignition delay time at near-constant volume conditions. These low-temperature measurements were performed using driver inserts and driver gas tailoring to insure near-constant-volume test conditions.

2. Experimental Setup

Ignition delay times were determined by measuring OH* emission associated with the $A^2\Sigma^+ \rightarrow X^2\Pi$ transition near 306 nm. Ignition delay time was defined as the time between the arrival of the reflected shock at the observation port and the extrapolation of the maximum slope of the emission signal to the baseline. Representative data are shown in *Figure 1*.

Mixtures were prepared manometrically inside a heated mixing tank. The mixing tank was heated so that the vapor pressure of the fuel at the tank temperature was greater than the partial pressure of the fuel by at least a factor of three. It was observed that tank temperature and mixing time had no effect on the experimental results. Fuel concentration inside the shock tube was verified by measuring the absorption of 3.39 μm HeNe laser light along the diameter of the shock tube. Beer's law was used to determine the fuel mole fraction. The absorption cross-section of the butanol isomers was

measured in separate experiments using known quantities of butanol, and these values agreed to within 2.5% with cross-section measurements from the PNNL database [2].

It was observed that butanol isomers have a tendency to adsorb onto the shock tube walls, even at partial pressures lower than the vapor pressure at the shock tube wall temperature. These losses can be significant in high pressure experiments. To overcome this problem, a passivation technique was developed. The shock tube was overfilled beyond the desired initial driven pressure, and the excess gas was then evacuated from the shock tube until the desired driven pressure was achieved. This method allowed the initial overfilling of the shock tube to saturate the absorption sites of the shock tube so that once the excess gas was evacuated, the test gas had the desired mole fraction of fuel. This method was validated using the in-situ absorption technique described above.

In addition to the direct fuel concentration measurements inside the shock tube, several other checks were performed to ensure the accuracy of the low pressure data in this study. These extra measures were taken because the current data in this study showed disagreement with data from some previous researchers. The extra measures included: verifying accuracy of incident shock velocity measurements, repeating experiments with different 2-butanol sources, assessing shock tube cleanliness effect on ignition delay time, performing ignition delay time measurements of n-heptane using the same apparatus and comparing with previous data [3], changing driver/driven gas bottles, and several others.

2.1 Low Pressure Measurements

Measurements at pressures between 1.0 and 3.5 atm were taken on the Stanford stainless steel high-purity low-pressure shock tube (LPST). The driven section of this shock tube has an inner diameter of 14.13 cm. Helium was used as a driver for all low pressure experiments which resulted in approximately 1.2 ms of near-constant-volume test time. Temperature and pressure behind the reflected shock were calculated using ideal shock relations with known initial temperature, pressure, mixture composition, and incident shock speed. Incident shock speeds were determined from shock arrival times at a series of pressure sensors near the endwall of the shock tube. The measured shock speeds were linearly extrapolated to the endwall in order to determine endwall shock speed. Ignition times were measured at the endwall and confirmed with measurements at a sidewall location 2 cm away from the endwall.

2.2 High Pressure Measurements

Measurements at pressures between 17 and 48 atm were taken on the Stanford stainless steel high-pressure shock tube (HPST). The driven section of this shock tube has an inner diameter of 5 cm. In all high pressure experiments, a driver insert was used in order to eliminate the facility-dependent pressure rise behind the reflected shock [4]. Helium was used as a driver for all high pressure experiments where the driven gas was diluted in argon. A 10% argon/ 90% helium driver gas was used in some 1-butanol experiments in air in order to extend the test time. This tailored driver gas mixture was successfully used in order to achieve near-constant-volume test times of approximately 3 ms [5]. Temperature and pressure behind the reflected shock were

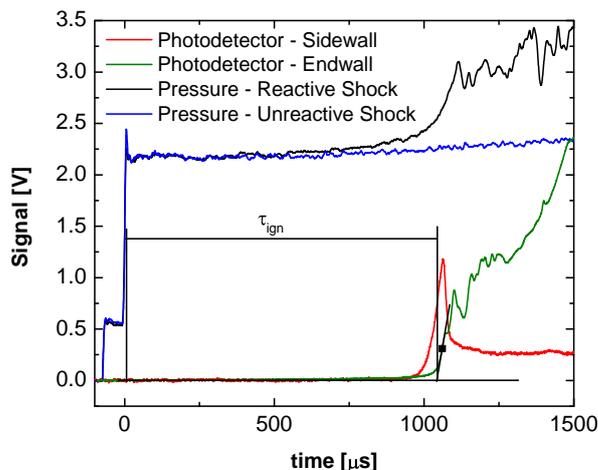


Figure 1: Ignition delay time measurement of 2-Butanol, $X_{O_2} = 0.04$, $\Phi = 1$. Initial reflected shock conditions: $T = 1306$ K, $P = 1.58$ atm.

inferred from the measurement of incident shock speed by the same method used in the low pressure experiments. Ignition times were measured at a sidewall location 1 cm away from the endwall. The optical configuration resulted in a temporal resolution of approximately 15 μs for the sidewall ignition time measurements.

2.3 Modeling

The experiments were modeled with the Chemkin-Pro solver using a chemical kinetic mechanism and thermodynamic data published by Grana et al. (2010) [6]. Version 1006 was used according to the downloadable mechanism on the group's webpage. All experiments were modeled using constant volume, constant internal energy assumptions. As shown by the flat pressure trace of an unreactive shock in *Figure 1*, this constant volume assumption is valid for dilute mixtures even for long ignition times. The constant internal energy assumption is valid because ignition times are too short for significant heat transfer to occur out of the shock tube [7].

All the experimental data were scaled to an average pressure for a particular data set. The pressure scaling was determined using the experimental data in this study. Depending on the isomer and specific conditions, it was found that ignition delay time scales inversely with pressure to the power of 0.5-0.8.

3. Experimental Results

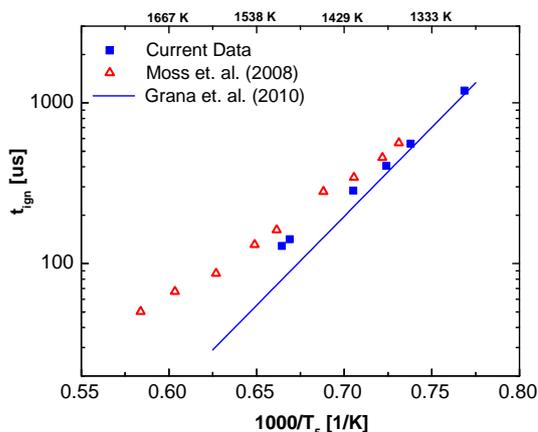


Figure 2: 1-Butanol, $P = 1.2$, $X_{O_2} = 0.03$, $\phi = 1$. Moss et al. (2008) [8] data are not scaled to a common pressure. $P \approx 1.1-1.35$ atm

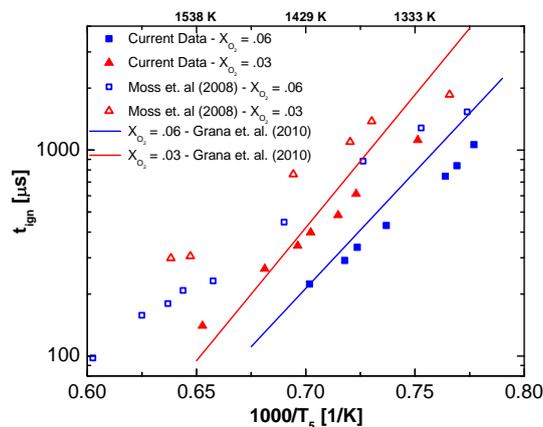


Figure 3: 2-Butanol, $P = 1.2$, $\phi = 1$. Moss et al. (2008) [8] data are not scaled to a common pressure. $P \approx 1.1-1.35$ atm

Figures 2 and 3 show our attempt to replicate experiments at conditions used by Moss et al. (2008) [8]. There is fairly good agreement between experiments for 1-butanol. In addition, agreement is observed with data by Black et al. (2009) [9] (not shown). However, significant disagreement is seen between two sets of 2-butanol experiments at conditions used by Moss et al (2008) [8]. Although ignition delay times are similar at lower temperatures, there is significant divergence at higher temperatures. Similar divergence is observed for i-butanol and t-butanol data. In general, the Grana et al. (2010) [6] mechanism agrees more closely with the data in this study than with the Moss et al (2008) [8] data.

Figure 4 shows the variation of 1-butanol ignition delay times as a function of pressure. As expected, ignition time clearly decreases as a function of pressure. The Grana et al. (2010) [6] mechanism agrees moderately well with the experimental data. At low pressures, the mechanism predicts that the global activation energy for ignition is higher than is measured in the experiments. This suggests that divergence in ignition delay times could occur between simulations and experiments at temperatures outside of the range used in this study. Although the slope of the experimental data and the simulation are similar at high pressures, the ignition time predicted by the simulations is approximately 40% longer than that of the experimental data.

Figure 5 shows a comparison of ignition delay time for the four isomers of butanol at 1.5 atm. The ignition time is lowest for 1-butanol and highest for t-butanol. i-Butanol and 2-butanol have similar ignition delay times. t-Butanol appears to have a slightly higher activation energy compared to the other isomers, though less than predicted in the simulations. Similar relationships are also observed at higher pressures. However, the ignition delay time of i-butanol at high pressures is much more similar to that of 1-butanol than 2-butanol.

Figure 6 shows the variation of ignition delay time as a function of equivalence at low pressures for 1-butanol. There is a slight inverse dependence of ignition delay time on equivalence ratio. At high pressures, this dependence is even weaker. This relationship is also predicted by the simulations as shown in Figure 6. Similar observations were made for the other isomers, although their sensitivity appears to be slightly larger than that of 1-butanol. The ignition delay time of t-butanol is particularly sensitive to equivalence ratio at low pressures.

Figure 7 shows measurements of ignition delay times of 1-butanol in stoichiometric air mixtures at high pressures. A comparison with similar data by Heufer et al. (2011) [10] is also shown. It is important to note that the data by Heufer et al. (2011) [10] is subject to a facility dependent non-reactive pre-ignition pressure rise that is not present in the current study. Furthermore, it is observed in this study and in the study by Heufer et al. (2011) [10] that there is significant pre-ignition heat release for 1-butanol ignition delay times measured at temperatures below 1000K. This phenomenon causes shock tubes to deviate from their ideal constant-volume behavior, and the deviation may be facility dependent. The facility-dependent differences described above mean that that data in the current study may not be comparable to the data by Heufer et al. (2011) [10] at low temperatures. As shown in Figure 7, this is evident by the agreement between the two studies at high temperatures, and disagreement at low temperatures. The Grana et al. (2010) [6] mechanism over predicts the ignition delay time over the entire temperature range at the conditions described in Figure 7. Furthermore, the Grana et al. (2010) [6] mechanism does not predict the rollover of ignition delay times observed either in this study or in the study by Heufer et al. (2010) [10].

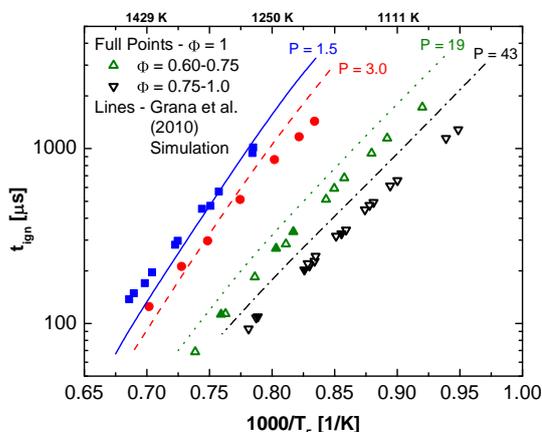


Figure 4: 1-Butanol, $X_{O_2} = 0.04$, $\phi = 1$

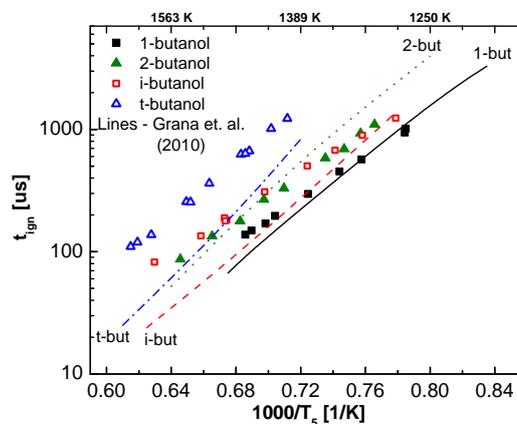


Figure 5: $P = 1.5$ atm, $X_{O_2} = 0.04$, $\phi = 1$

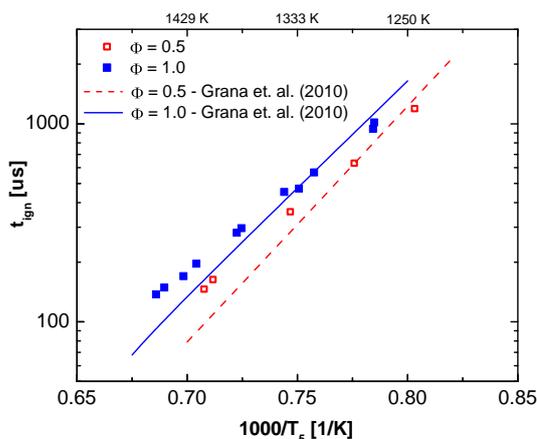


Figure 6: 1-butanol, $X_{O_2} = 0.04$, $\phi = 1$

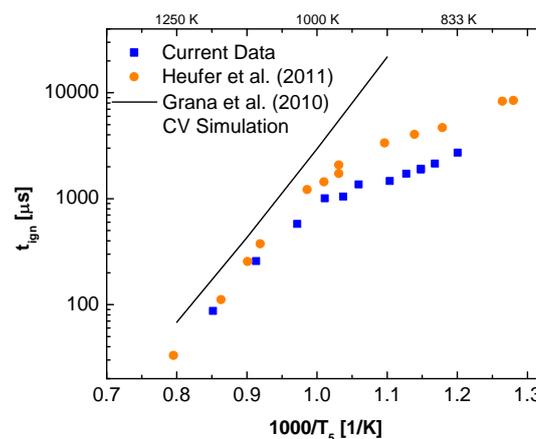


Figure 7: 1-butanol in stoichiometric air, $P = 20$ atm. The two data sets are not experimentally comparable at low temperatures (see text)

4. Conclusions

The ignition delay times for the isomers of butanol were measured behind reflected shock waves at a variety of conditions. Agreement was found with data from previous researchers for 1-butanol, but disagreement was observed for the other three isomers. The ignition delay time increases for the isomers at most conditions in the following order: 1-butanol, 2-butanol and i-butanol similar, t-butanol. It was observed that ignition time decreases significantly with increasing pressure, but remains mostly unchanged for changing equivalence ratio. A constant-volume, constant-internal-energy simulation using a mechanism developed by Grana et al. (2010) [6] agrees within a factor of two with the ignition delay times of 1-butanol. However, there is poorer agreement for the other three isomers.

Acknowledgments

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