Experiments and Modeling of the Autoignition of Methyl-Cyclohexane at High Pressure

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Introduction

• Cycloalkanes and alkyl-cycloalkanes are well known as components of many transportation fuels
• Methyl-cyclohexane (MCH) has been suggested as a candidate to model the cycloalkane and alkyl-cycloalkane content of real fuels
• Low Temperature Combustion (LTC) is important to the operation of advanced engine concepts
• Therefore, detailed kinetic models may be required to predict combustion phasing, heat release rates, and especially engine-out emissions
Cyclohexanes are prevalent in transportation fuels

Chemical classes in diesel

Chemical classes in gasoline

Slide courtesy Dr. Bill Pitz, LLNL, from paper 1B12
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Motivation

• Previous work* comparing MCH ignition delays to a model from 2007† showed significant over-prediction of both first stage and overall ignition delay

• Our objective is to update and extend the model to better predict existing and new experimental conditions

*Mittal & Sung, *Combustion and Flame*, 2009, **156**, 1852-1855
†Pitz et al., *Proc. Combust. Inst.*, 2007, **31**, 267–275
Experimental Methods

- Experiments to measure the ignition delay of methyl-cyclohexane (MCH) are performed in a heated Rapid Compression Machine (RCM)
- Homogeneous gas-phase mixtures of fuel and oxidizer are compressed and the piston is held in place at Top Dead Center (TDC), creating a constant volume reactor
- The compression ratio of the RCM, and the initial pressure and initial temperature of the mixture are varied to vary the pressure and temperature at TDC
- The pressure and temperature at TDC are referred to by subscript “C” – i.e. $P_C$ & $T_C$ respectively
Experimental Methods

- The end of compression (when the piston reaches TDC) is defined as the maximum of the pressure prior to the ignition.
- The ignition delays are the times from the end of compression to the local maxima of the time derivative of the pressure.
- During the ignition delay, the reactants are losing energy by heat transfer to the relatively colder reactor walls.
- Because we have a constant volume, closed reactor, the heat loss produces pressure drop.
- We characterize this pressure drop by replacing oxygen with nitrogen in the mixture to eliminate the explosion but retain a similar heat loss profile to the reactive experiments.
- \( T_C \) is taken as the temperature at TDC of a non-reactive simulation.
Experimental Conditions

• Experiments are conducted for three mixtures, whose diluent compositions contain varying amounts of N\textsubscript{2} and Ar to maintain a similar specific heat ratio for all of the mixtures

| Mix # | \(\phi\) | MCH | O\textsubscript{2} | N\textsubscript{2} | Ar |
|-------|--------|-----|-----------------|-----------------|----|
| 1     | 1.0    | 1   | 10.5            | 12.25           | 71.75 |
| 2     | 0.5    | 1   | 21.0            | 0.00            | 73.50 |
| 3     | 1.5    | 1   | 7.0             | 16.35           | 71.15 |

• The equivalence ratio is adjusted by varying the initial oxygen mole fraction at constant fuel mole fraction

• MCH ignition delays were previously measured in our RCM at \(P_C = 15.1\) and \(25.5\) bar*

• New experimental ignition delays are measured in this work at \(P_C = 50\) bar

• The temperature range for the three pressure conditions is similar from 690 – 910 K

*Mittal & Sung, *Combustion and Flame*, 2009, *156*, 1852-1855
Experimental Results

- Ignition delays in the NTC region for Mix #2 ($\phi = 0.5$) are not reported because substantial reactivity occurred during the compression stroke for $T_C > 740$ K.
- Mix #2 does not have two-stage ignition in the temperature range investigated here.
Experimental Results

- Reactivity during the compression stroke prevents reporting complete resolution of the NTC region for Mix #1 ($\phi = 1.0$)

- Two-stage ignition is reported for one experimental condition for Mix #1
Experimental Results

- Mix #2 is the most reactive because it has the highest initial O\textsubscript{2} concentration.
- The NTC region for Mix #3 (\(\phi = 1.5\)) approximately extends from 775 K to 840 K.
- Two stage ignition was measured for Mix #3 for temperatures from 740 K to 800 K.
Updates to MCH mechanism

- New C1-C4 base chemistry from NUIG
- New aromatics base chemistry from NUIG-LLNL
  - Based on work by Metcalfe et al. and Mehl et al.
- Cyclohexane submodel is more recent LLNL version*
- Unsaturated ring intermediate products resolved with much more fidelity (previously lumped)
- MCH abstraction reactions:
  - MCH + OH rates from ANL experiments†
  - Others using latest LLNL reaction rate rules
- RO₂ isomerization rate constants
  - from Fernandes et al‡ for cases involving cyclohexane ring
  - new ab initio rate constant computed for case involving methyl group (*this work*)

*Silke et al., J. Phys. Chem. A., 2007, 111, 3761-3775
†Sivaramakrishnan and Michael, Combust. Flame, 2009, 156, 1126-1134
‡Fernandes et al., Phys. Chem. Chem. Phys. 2009, 11, 1320–1327
Comparison with Modeling – Overall Ignition Delays

- The model has improved significantly since 2007!
- Experimental ignition delays in the high temperature region are predicted well
- Low temperature ignition delays are generally underpredicted, especially for the $\phi = 1.5$ case
• First stage ignition delays are under-predicted for all equivalence ratios and pressures, but are within factor of 2 of the experimental data.

• First stage ignition is also predicted for conditions where it was not found experimentally at 50 bar and all three equivalence ratios.
Sensitivity Analysis

- Sensitivity analysis of the overall ignition delay shows that the important reactions are the initial H-abstractions from the fuel, the direct reaction of peroxyl radicals to form HO$_2$ and methylcyclohexene, and isomerizations of the peroxyl radicals.

- Similar analysis for first stage ignition shows that the same reactions are important.

![Graph showing percent sensitivity of various reactions](image-url)
Path analysis shows the model exhibits the expected decomposition pathways, including formation of methylcyclohexenes, QOOH and ROOH species.
Conclusions

• New experimental data has been collected for MCH in a heated RCM at conditions of $P_C = 50$ bar, $\phi = 0.5, 1.0, 1.5$, and $T_C = 690 - 910K$

• The 2007 model for MCH combustion by Pitz et al. has been updated with improved rate rules and new reaction classes

• The new model is able to predict overall ignition delays to within a factor of 2 for most conditions

• First stage ignition delays are under-predicted for all conditions, but are nevertheless within a factor of 2 of the experiments

• First stage ignition is predicted for conditions at high pressure that do not have first stage ignition experimentally
Thank you!

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MCH CONV Simulations

MCH CONV Ignition Delays

MCH CONV Pressure Traces