On the Chemical Kinetics of an Unsaturated C7 Ester: Methyl 3 Hexenoate Ignition and Speciation Studies

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Motivation

Growing support for renewable fuels that also potentially reduce harmful combustion emissions and yield higher efficiencies.

Methyl and ethyl esters are primary components of biodiesel compounds.

For example, biodiesel composition for rapeseed methyl ester (RME) and soy methyl ester (SME) [1]:

<table>
<thead>
<tr>
<th>Ester</th>
<th>C=C</th>
<th>% of RME</th>
<th>% of SME</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl palmitate</td>
<td>0</td>
<td>4.3</td>
<td>6-10</td>
</tr>
<tr>
<td>methyl stearate</td>
<td>0</td>
<td>1.3</td>
<td>2-5</td>
</tr>
<tr>
<td>methyl oleate</td>
<td>1</td>
<td>59.9</td>
<td>20-30</td>
</tr>
<tr>
<td>methyl linoleate</td>
<td>2</td>
<td>21.1</td>
<td>50-60</td>
</tr>
<tr>
<td>methyl linolenate</td>
<td>3</td>
<td>13.2</td>
<td>5-11</td>
</tr>
</tbody>
</table>

In general, large esters are difficult to study, consequently published data are scarce.

However, there are some studies; including (C₇) methyl hexanoate [2,3], (C₈) methyl heptanoate [4], (C₁₁) methyl decanoate [5], (C₁₇) methyl palmitate [6], and (C₁₉) methyl oleate [7].

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Recent experimental and computational work has focused on C₅ and smaller esters (saturated C₅) methyl butanoate [2,8-17] and (unsaturated C₅) methyl crotonate [10,11,12].

Previous UM RCF Studies and Program Objectives

Iso-octane [18]
- RCF, $\Phi = 0.2-1.98$, inert:$O_2 = 1.38-5.89$, $P = 8.7-16.6$ atm, $T = 903-1020K$
- $\tau_{ign} = 2.8 \times 10^{-3} \times P^{1.25} \times \Phi^{-0.79} \times \chi(O_2)^{-1.14} \times \exp(27300/R_{[\text{cal/mol/K}]T})$

Methyl butanoate [8]
- RCF, $\Phi = 0.3-0.4$, inert:$O_2 = 3.76$, $P = 4.7-19.6$ atm, $T = 935-1117K$
- $\tau_{ign} = 3.2 \times 10^{-3} \times P^{1.21} \times \Phi^{-0.77} \times \chi(O_2)^{-1.62} \times \exp(30300/R_{[\text{cal/mol/K}]T})$

Methyl crotonate [19]
- RCF, $\Phi = 0.3$, inert:$O_2 = 3.76$, $P = 10.5$ atm, $T = 951-1066K$
- $\tau_{ign} = 5.6 \times 10^{-7} \times \exp(33200/R_{[\text{cal/mol/K}]T})$

Goals
- Better understanding of combustion chemistry through ignition and speciation studies
- Provide new data enabling biodiesel use in advanced engine strategies

Approach
- Utilize the University of Michigan Rapid Compression Facility (UM RCF) to conduct ignition and speciation studies
- Compare fuel combustion metrics of ignition delay times, activation energies, intermediate species and reaction pathways

End of compression pressures from 0.25 to 50 atm by varying:
  - Compression ratio
  - Nosecone design
  - Fill pressure

Transparent end wall and optical ports provide access for additional diagnostic capabilities including laser absorption and extinction. Modular test section allows rapid exchange of components. FAST gas and soot sampling systems.
Test Section Characteristics

- $V \approx 200 \text{ cm}^3$
- $V: A_s \approx 0.8-1.1$
- $T_{\text{Axis}} \approx \pm 5\%$ of $T_{\text{Isen}}$
- 65% of $V$ at $\pm 10\%$ of $T_{\text{Axis}}$
- Thermal boundary layer $\leq 5 \text{ mm}$ after 30 ms
- Long test times, $>90\%$ of $P_{\text{max}}$ after 30 ms

Transport effects? Gas motion? Temperature gradients?
Minimized by uniformity, allowing isolation of chemical kinetics.

Typical M3H Ignition Data

Frame rate = 26,000 fps
Exposure = 38 μs

\[ P_{\text{eff}} = 10.7 \text{ atm} \]
\[ T_{\text{eff}} = 1040 \text{ K} \]
\[ \Phi = 0.3 \]
Inert:O\textsubscript{2} = 3.76
\[ \tau_{\text{ign}} = 3.9 \text{ ms} \]
Summary of M3H Ignition Data

- M3H ignition
- M3H ignition and gas sampling
- Best fit linear regression
- Iso-octane [18]
- Methyl butanoate [8]
- Methyl crotonate [19]

\[ P = 9.5-11.6 \text{ atm} \]
\[ T = 892-1102 \text{ K} \]
\[ \Phi = 0.3 \]
\[ \chi(O_2) = 20.9\% \]
\[ \text{Inert:O}_2 = 3.76 \]
\[ \tau_{ign} = 1.4-35.9 \text{ ms} \]

\[ \tau_{ign} = 5.1 \times 10^{-6} \exp \left[ \frac{27930}{R_{cal} [\text{K-mol}] T} \right] \]

UM RCF – Speciation Studies

Driver Section

Hydraulic Globe Valve Assembly

Convergent Section

Optical Port (x3)

Extension Section

Pressure Transducer (Kistler 6041AX4)

Test Section

Festo MHE3 Valve (x4)

Driven Section

Sampling Port

U-rings

Pressure Transducer (Kistler 4045A2)

Sabot

Valve to Vacuum

Nosecone
Typical M3H Sampling Data

\[ P_{\text{eff}} = 10.3 \text{ atm} \]
\[ T_{\text{eff}} = 944 \text{ K} \]
\[ \Phi = 0.3 \]
\[ \text{Inert:O}_2 = 3.76 \]
\[ \tau_{\text{ign}} = 14.2 \text{ ms} \]
Results of Gas Chromatography

Species detected, but not quantified: propene, butyraldehyde

Species below detectable limits: carbon monoxide, acetylene, ethanol, 3-buten-1-ol
Time Histories of Stable Intermediate Species Present During M3H Ignition (experimental data) and MH Ignition (modeling results)

Methane

Methanol

Acetaldehyde

Ethane

Ethene

1-Butene

\[ \square \text{ = methyl 3 hexenoate sampling data} \]

\[ \text{— = methyl hexanoate mechanism [3]} \]

Chemkin simulation:

Adiabatic, 0-D, constant volume @ 945 K, 10.5 atm

Fuel = 0.68 %

O\(_2\) = 20.80 %

N\(_2\) = 75.68 %

CO\(_2\) = 2.84 %

Conclusions and Current Work

Summary and Conclusions

First ignition and speciation data for methyl 3 hexenoate
Ignition delay time and species measurements exhibit low scatter
M3h exhibits faster reactivity compared to longer alkane, smaller saturated and unsaturated esters
NTC behavior was not observed in m3h for conditions studied, although not unexpected
Large quantities (>200 ppm) of ethene are formed quickly (t/τ_{ign} <30%) during m3h ignition; whereas 1-butene remains below 100 ppm throughout the ignition delay period; contrary to the reaction pathways predicted for the saturated counterpart to m3h, methyl hexanoate
These data are important to create an accurate understanding of combustion chemistry of even larger unsaturated esters

Current work

Further identification and calibration of intermediate species
The ignition and speciation data guide our development of a m3h reaction mechanism
We would like to acknowledge the generous financial support of the U.S. Department of Energy Basic Energy Sciences Program and the U.S. Department of Energy via the University of Michigan Consortium on Efficient and Clean High-Pressure, Lean Burn (HPLB) Engines.