The Oxidation of Fuel Radicals

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\[ \cdot + O_2 \rightarrow O-O^* \]

ISOMERIZATION PATHWAYS

Multi Agency Coordination Committee for Combustion  
Research [MACCCR]  
Fuel Research Review  
Los Angeles, California  
September 16, 2009
Kinetics Modules in Databases

- GRIMECH - methane (light hydrocarbon) combustion
- Pyrolysis of fuels
- Oxidation of larger fuels
- Soot formation

Target of most models
Focus of current NIST work

Widely used
Problems with rich mixtures

Recent NIST experimental and data evaluation program

Many models, begin with unsaturates
PREMISE OF WORK

There are simple correlations between structure of fuel molecules and their rate constants for decomposition and isomerization.

These correlations can be uncovered from an examination of the literature, suitable experiments, and theoretical treatments.

FOR A HOMOLOGOUS SERIES DATA BASE FOR EVERY LARGE FUEL MOLECULE CONTAINS AS A SUBSET THE DATABASE FOR SMALLER FUEL MOLECULES.
DETERMINING MECHANISMS AND RATES OF DECOMPOSITION OF FUEL RADICALS

Generate fuel radicals through decomposition of appropriate precursors; alkyl iodide, branched hydrocarbons

Carry out studies in single pulse shock tube

dilute mixtures

short residence times

presence of inhibitors to isolate reaction

obtain direct measure of branching ratios

thermal cracking patterns

Convert to high pressure rate expressions

Extension to cover all combustion conditions

Solution of the master equation to take into account energy transfer effects
SINGLE PULSE SHOCK TUBE AND ASSOCIATED WAVE PROCESSES
RADICALS STUDIED

C H₃CH₂CH₂CH₂CH₂CH₂*
CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂*
CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂*
CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂ CH₂CH₂*
CH₂=CHCH₂CH₂CH₂*
CH₂=CHCHCH₂CH₂CH₂*
CYCLOHEXYL
CYCLOPENTYL
CH₃CH(CH₃)CH₂CH₂CH₂CH₂*
CH₃CH(CH₃)CH₂CH₂CH₂CH₂CH₂*
MECHANISM AND BRANCHING RATIOS FOR THE DECOMPOSITION OF OCTYL RADICALS

4 isomers undergoing 6 beta bond scissions and 6 reversible isomerizations
MECHANISM AND BRANCHING RATIOS FOR REACTIONS INITIATED WITH 5-METHYL HEXYL RADICALS

Figure 1. Alkene yields from the decomposition of 5-methylhexyl radicals. Symbols are experimental data: ◆ = ethene; ○ = isobutene; ■ = propene; □ = 3-methylbutene; ▲ = cis-2-hexene; △ = trans-2-hexene; ◇ = 1-hexene. The values for 1-hexene have been divided by two for clarity. The lines represent fits from the RRKM/Master Equation model described in the text.
MASTER EQUATION SOLVER: PROGRAM TO DETERMINE MOLECULAR DISTRIBUTION FUNCTION
FALL-OFF BEHAVIOR FOR THE REACTION N-ALKYL = ETHYLENE + 1-(N-2)OLEFIN FOR N=4 TO 8 AT 1 BAR

Fall-off does not monotonically increase due to low reaction threshold

Fall off effects decreases only slowly with molecular size

Fall off effects are insensitive to molecular size near high pressure limit
### High Pressure Rate Expressions for Octyl Radical Decomposition and Isomerization

<table>
<thead>
<tr>
<th>A: Reaction</th>
<th>Log A</th>
<th>n</th>
<th>E/R</th>
<th>Log (k [1000])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-octyl = ethene + 1-hexyl</td>
<td>11.96</td>
<td>.31</td>
<td>13708</td>
<td>6.93</td>
</tr>
<tr>
<td>2-octyl = propene + 1-pentyl</td>
<td>10.78</td>
<td>.84</td>
<td>14001</td>
<td>7.24</td>
</tr>
<tr>
<td>3-octyl = 1-butene + 1-butyl</td>
<td>13.31</td>
<td>.04</td>
<td>14340</td>
<td>7.21</td>
</tr>
<tr>
<td>3-octyl = 1-heptene + methyl</td>
<td>9.98</td>
<td>1.08</td>
<td>14790</td>
<td>6.78</td>
</tr>
<tr>
<td>4-octyl = 1-pentene + 1-propyl</td>
<td>11.74</td>
<td>.55</td>
<td>14134</td>
<td>7.26</td>
</tr>
<tr>
<td>4-octyl = 1-hexene + ethyl</td>
<td>9.83</td>
<td>1.11</td>
<td>13600</td>
<td>7.25</td>
</tr>
<tr>
<td>1-octyl = 4-octyl (1-4-H trans)</td>
<td>.71</td>
<td>3.23</td>
<td>8479</td>
<td>6.72</td>
</tr>
<tr>
<td>1-octyl = 4-octyl (1-5-H trans)</td>
<td>1.36</td>
<td>2.82</td>
<td>5413</td>
<td>7.46</td>
</tr>
<tr>
<td>1-octyl = 3-octyl</td>
<td>.47</td>
<td>3.08</td>
<td>5544</td>
<td>7.29</td>
</tr>
<tr>
<td>4-octyl = 1-octyl 1-4-H trans</td>
<td>-.38</td>
<td>3.57</td>
<td>9532</td>
<td>6.20</td>
</tr>
<tr>
<td>4-octyl = 1-octyl 1-5-H trans</td>
<td>.27</td>
<td>3.16</td>
<td>6466</td>
<td>6.94</td>
</tr>
<tr>
<td>3-octyl = 1-octyl</td>
<td>.52</td>
<td>3.11</td>
<td>6579</td>
<td>6.99</td>
</tr>
<tr>
<td>2-octyl = 3-octyl</td>
<td>.27</td>
<td>3.27</td>
<td>6642</td>
<td>7.20</td>
</tr>
<tr>
<td>2-octyl = 4-octyl</td>
<td>.15</td>
<td>3.32</td>
<td>8125</td>
<td>6.60</td>
</tr>
<tr>
<td>3-octyl = 2-octyl</td>
<td>1.33</td>
<td>2.96</td>
<td>6625</td>
<td>7.34</td>
</tr>
<tr>
<td>4-octyl = 2-octyl</td>
<td>.071</td>
<td>3.32</td>
<td>8128</td>
<td>6.52</td>
</tr>
</tbody>
</table>

**Equilibrium constant of formation log [kₐ]**

- **Octyl-1**: \(-38.931-1.031\times10^{3}/T+4.904\times10⁶/T²-2.601\times10⁹/T³+4.473\times10^{1¹}/T⁴\)
- **Octyl-2**: \(-39.196-1.941\times10^{2}/T+4.736\times10⁶/T²-2.554\times10⁹/T³+4.403\times10¹¹/T⁴\)
- **Octyl-3**: \(-39.098-5.633\times10^{3}/T+4.912\times10⁶/T²-2.608\times10⁹/T³+4.485\times10¹¹/T⁴\)
OXIDATION OF FUEL RADICALS: PAST WORK

No direct studies leading to high pressure unimolecular rate expressions
Products from flame and cool flames sampling

*Oxygenated organics*

*Unsaturated organics*

*Cyclic ethers*

*Thermal rate constants used in models; no consideration of chemical activation processes*

OH and HO$_2$ from smaller fuel molecules and modeling

*Sandia (Taatjes)*

Ab-initio calculations

*Green et al*

*Merle et al*

*Bozzellie et al*

*Sandia (Klippenstein)*
STRATEGY FOR STUDYING RADICAL OXIDATION

Generate radicals as in pyrolysis experiments

Dilute concentrations of radicals
Vast excess of chemical inhibitor

Add sufficient amount of oxygen molecules to change reaction direction from pyrolysis to oxidation

Determine cracking patterns as function of oxygen concentration

Reproduce oxidative cracking pattern through solution of the master equation for chemical activation process
SUMMARY OF EXPERIMENTAL RESULTS

n-Butyl Iodide (100 ppm) decomposition with various concentrations of oxygen

cyan = ethylene
Red = 1-butene
Blue = propene
Green = tetrahydrofuran

Circle = 150, 9.15%
Square = 150, 4.04%
Triangle = 150, 1.51%
White (blue) = 300, 10.35%
Hexagon = 600, 10.15%
Rate Constants from Chemical Activation Processes

Radical + O₂, <=> RadicalOO* => Variety of products

\[
\text{RadicalOO} \quad \text{M} \quad \text{RadicalOO}
\]

\[
k = k_{ca} \times \text{branching\_ratio}
\]

\[
\text{branching\_ratio} = \frac{(\text{decomposition})_i \text{ or } (\text{stabilization})_i}{\sum \text{all channels}}
\]
Branching Ratios for Products from n-Propyl Peroxy Radical Decomposition

- 500 K, 0.1 bar

- 500 K, 100 bar
TREATMENT OF DATA

Product (ethylene, propene, 1-butene) = \( k_{\text{uni,BI}}(\text{butyl-I}) + k_{\text{uni,P}}(\text{butyl}) \)
\[ + k_{\text{ox,P}}(\text{butyl}) \times O_2 \]

tetrahydrofuran (THF) = \( k_{\text{ox,T}}(\text{butyl}) \times O_2 \)

Product/THF = \( ( k_{\text{uni,BI}}(\text{butyl-I}) + k_{\text{uni,P}}(\text{butyl}))/k_{\text{ox,T}}(\text{butyl}) \times O_2 \)
\[ + \]

\[
\frac{k_{\text{ox,P}}}{k_{\text{ox,T}}}
\]
Oxidative Decomposition of n-Butyl Radical

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \text{★} + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OOH} \]

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OOH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2 + \text{HO}_2 \]

\[ \text{C}_2\text{H}_4 + \text{HO}_2 \rightarrow \text{CH}_2\text{O} + \text{OH} \]

Pyrolytic Decomposition of n-Butyl Radical

(through n-Butyl Iodide)

\[ \text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2 + \text{HI} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \text{★} \]

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \text{★} + \text{C}_2\text{H}_4 \rightarrow \text{CH}_3\text{CH}_2 + \text{C}_2\text{H}_4 \]

\[ \text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \]
MASS BALANCE

- no oxygen 150 torr initial pressure
- 9.15% oxygen 150 torr initial pressure
- 10.15% oxygen 600 torr initial pressure
- 10.35% oxygen 300 torr initial pressure

all mixtures containing 100 ppm n-butyl-I and 1% mesitylene
ETHYLENE/THF RATIOS AS A FUNCTION OF TEMPERATURE AND OXYGEN CONCENTRATION
1-BUTENE/THF RATIOS AS A FUNCTION OF TEMPERATURE AND OXYGEN CONCENTRATION

Log [1-C₄H₈/THF] vs 1000/T

- 150, 9.16%
- 150, 1.54%
- 150, 4.04%
- 300, 10.35%
- 600, 10.15%

Physical and Chemical Properties Division
PROPENE/THF RATIOS AS A FUNCTION OF TEMPERATURE AND OXYGEN CONCENTRATION

\[ \log \left[ \frac{C_3H_6}{THF} \right] = 2.92 - \frac{2120}{T} = 0.64 \] (930K)

Log \[ C_3H_6/THF \] = 2.92 -2120/T= .64 (930K)
Ethylene/THF Yields as a Function of $1/O_2$: Extrapolation to Infinite Oxygen Concentration

Log $[C_2H_4/(2xTHF)] = 7.35 - 6000/T = 1.1$ at 930 K
1-BUTENE/THF Yields as a Function of 1/O₂: Extrapolation to Infinite Oxygen Concentration

\[
\text{Log } [1-\text{C}_4\text{H}_8/\text{THF}] = 4.717 - \frac{3422}{T}
\]
OLEFIN VS TETRAHYDROFURAN YIELDS

![Graph showing the relationship between Log [olefin/THF] and 1000/T [K] for different olefins. The graph includes lines for C2H4, C3H6, and 1-C4H8.]
MECHANISTIC INFERENCES

Ethylene and propene are formed from beta bond scissions after H-transfer isomerization

1-Butene is formed prior to isomerization

No formation of larger aldehydes

Contribution from oxirane (3) and oxetane (4) channels are negligible
## NEXT STEPS

Derive high pressure rate expressions

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Basis for deriving rate expressions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_3\text{H}_6\text{O}^* + \text{O}_2 \rightarrow \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}^* )</td>
<td>Merle et al and data on ( \text{R+O}_2 )</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}^* \rightarrow \text{C}_3\text{H}_6\text{H}_2\text{CH}_2 + \text{H}_2\text{O}_2 )</td>
<td>From 1-butene/THF</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}^* \rightarrow \text{C}_3\text{H}_6\text{H}_2\text{C}^*\text{H}_2\text{C}_2\text{H}_2\text{O}_2 )</td>
<td>From branching of ethylene/1-butene: propene</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}_2 \rightarrow \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}^* )</td>
<td>Detailed balance</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}_2 \rightarrow \text{C}_3\text{H}_6\text{H}_2\text{CH}_2 + \text{C}_3\text{H}_6\text{H}_2\text{O}_2 )</td>
<td>From beta bond scission</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}^* \rightarrow \text{C}_3\text{H}_6\text{H}_2\text{C}^*\text{H}_2\text{C}_2\text{H}_2\text{O}_2 )</td>
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<td>( \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}_2 \rightarrow \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}_2^* )</td>
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</tr>
<tr>
<td>( \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}_2 \rightarrow \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}_2^* )</td>
<td>From propene/THF</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}_2 \rightarrow \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}_2^* )</td>
<td>Fast</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}_2 \rightarrow \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}_2^* )</td>
<td>Fast</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}_2 \rightarrow \text{C}_3\text{H}_6\text{H}_2\text{C}_2\text{H}_2\text{O}_2^* )</td>
<td>From ethylene/THF, check with calculation of Wijaya et al</td>
</tr>
</tbody>
</table>
TASKS AND PROBLEMS

Molecular properties of oxygenates: hydroperoxides and peroxy radicals depend on ab initio calculations

Fit results through solution of master equation using CHEMRATE

Expand data to cover all relevant combustion conditions differentiate between chemical activation and thermal processing

Larger radicals: n-pentyl

Lower temperatures: smaller oxygen loading

Use nitrites
SUMMARY

A new method for determining the mechanisms and rate constants for the oxidation of alkyl radicals has been developed.

Results have been demonstrated for n-butyl radicals generated from n-butyl-iodide pyrolysis in varying concentrations of oxygen and excesses of a chemical inhibitor.

Ethylene is the main product, smaller amounts of 1-butene, propene and THF are also detected.

Results for limiting oxygen concentrations have been determined.
ACKNOWLEDGEMENT

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