The Decomposition of Surrogate Fuel Molecules During Combustion

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MULTI AGENCY COORDINATION COMMITTEE
FOR COMBUSTION RESEARCH (MACCCR)
FUELS RESEARCH REVIEW
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RATIONALE

Advances in CFD codes have led to the possibility of simulating the behavior of real fuels in real devices

Leading to new design tools

To enable this technology there is the need for an appropriate chemical kinetics database

Special problems with real fuels

*size and types of molecules*

*mixtures*
FUEL PROBLEM

Real fuels are complex mixtures of hydrocarbons

What are the mixing rules for mixtures of varying compositions
particularly important with current interest on alternative fuels

More fundamentally based approach makes mixing rules more transparent

Much current interest in surrogate mixtures
## TYPICAL SURROGATE JP-8 MIXTURE

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mole Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylcyclohexane</td>
<td>5%</td>
</tr>
<tr>
<td>cyclooctane</td>
<td>5%</td>
</tr>
<tr>
<td>Butylbenzene</td>
<td>5%</td>
</tr>
<tr>
<td>Tetralin</td>
<td>5%</td>
</tr>
<tr>
<td>Meta-xylene</td>
<td>5%</td>
</tr>
<tr>
<td>1,2,4,5-tetramethylbenzene</td>
<td>5%</td>
</tr>
<tr>
<td>1-methylnaphthalene</td>
<td>5%</td>
</tr>
<tr>
<td>Isooctane</td>
<td>5%</td>
</tr>
<tr>
<td>Decane</td>
<td>15%</td>
</tr>
<tr>
<td>Dodecane</td>
<td>20%</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>15%</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>10%</td>
</tr>
</tbody>
</table>

Investigators are convinced that combustion properties can be captured with limited number of compounds representative of groups in fuels.
Mechanism For Fuel Breakdown During Combustion

Fuel $\Rightarrow$ Fuel Radical $\Rightarrow$ Smaller Radical + 1-olefin $\Rightarrow$ 1-olefinyl radical $\Rightarrow$ olefins, diene and cyclic radicals.
PROBLEMS IN CURRENT DATABASES

Incomplete with respect to soot and cracking

- missing reactions
- wrong rate constants

Neglect of energy transfer effect

- Cannot describe reaction in Arrhenius form
- Rate constant may be pressure as well as temperature dependent
- Improper description of chemical activation processes

Most mechanisms (oxidation) are based on single component fuels.

Due to necessity for “tuning mechanisms” a mechanism for a mixture cannot be a composite of single fuel data bases
Kinetics Modules in Databases

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

Target of most models
next target in NIST program

Many models, begin with unsaturates

Current NIST Experimental and Data Evaluation Program

Widely used, problems with rich mixtures

7
SPECIAL ROLE OF UNIMOLECULAR REACTIONS

Only unimolecular and bimolecular reactions in database

Bimolecular reactions shuffle atoms

\[ \text{OH} + \text{RH} = \text{H}_2\text{O} + \text{R}^* \]

*Rate constants are the same for similar groupings*

Unimolecular reactions reduces size of molecule

*Reduces fuel to small unsaturated and radicals found in existing databases*

*Present work will focus on this category of processes*
PREMISE OF PRESENT 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.
DETERMINATION OF MECHANISMS AND RATE CONSTANTS

Need for clearly defined experimental systems
understand the role of interfering processes

Ideal conditions most easily realizable in shock tubes
well defined boundary conditions
very little possibility of surface reactions
short reaction times
Single Pulse Shock Tube and Associated Wave Processes

Pressure Temperature

500 microsecs pulse reactor
RATE CONSTANTS FOR BOND BREAKING REACTIONS FROM FUEL MOLECULES

Fuel molecule in dilute solutions

Chemical inhibitor to capture active radicals

Internal standard to determine reaction conditions
When combined with activation energies lead to present day accepted bond energies
CALCULATIONAL TRAIN

Molecular Properties (molecules and transition states)

Partition Functions

Thermodynamic properties
Equilibrium constants
Rate constants (equilibrium, thermal)

Pressure dependent rate constant
Chemical Activation processes
ESTIMATION OF THERMODYNAMIC PROPERTIES

ALKANES

follow Pitzer on frequencies from addition of CH$_2$ into alkane structure
rotational constants from standard bond lengths and angles
barriers to internal rotation 3.4 kcal
small adjustment of skeletal bends to reproduce entropies in standard tables

ALKYL RADICALS

follow Benson: remove three frequencies characteristic of H motion
barrier of internal rotations adjacent to radical site lowered to zero
Energies characteristic of primary and secondary C-H bond: difference of 2.5 kcal/mol

Use bond energies of 412 kJ/mol for secondary C-H bond, 420 kJ/mol for primary C-H bond and 50 kJ/mol for allyl resonance energy
RATE CONSTANTS FOR DODECANE DECOMPOSITION

per C\textsubscript{n}-C\textsubscript{n} bond for n=2 to 10

per C-C\textsubscript{11} bond

100 BAR     10 BAR     1 BAR

100 BAR     10 BAR     1 BAR
RATE CONSTANTS FOR HEPTANE DECOMPOSITION

- Log [K] vs. 1000/T for different pressures (100 bar, 10 bar, 1 bar) and per Cn-Cn bond for n = 2 to 5.
- Log [K] vs. 1000/T for different pressures (100 bar, 10 bar, 1 bar) and per C-C6 bond.
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
ESTIMATING RATE EXPRESSIONS FOR UNIMOLECULAR REACTIONS OF FUEL RADICALS

Begin with experimental measurements

*direct studies*

*rate constants for reverse reaction*

*chemical activation studies*

Many reactions, few reaction types

*beta bond scissions*

*localized*

*Isomerizations: Hydrogen transfer*

*involves entire molecule*

*Cyclizations*

Convert to *high pressure rate expressions*

Expend to cover all relevant pressures as well as temperatures
RADICALS STUDIED (initial reactant)

Includes all isomerization products

- \( \text{C H}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \)
- \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \)
- \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \)
- \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \)
- \( \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2^* \)
- \( \text{CH}_2=\text{CHCHCH}_2\text{CH}_2\text{CH}_2^* \)
- CYCLOHEXYL
- CYCLOPENTYL
- \( \text{CH}_3\text{CH(CH}_3\text{)CH}_2\text{CH}_2\text{CH}_2^* \)
- \( \text{CH}_3\text{CH(CH}_3\text{)CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \)

From 1-olefin fuels and products from alkyl radical decomposition

From cyclic fuels and 1-olefinyl radical isomerization

Effects of methyl substitution (Fischer-Tropsch fuels)
MECHANISMS AND BRANCHING RATIOS FOR THE DECOMPOSITION OF HEXYL RADICALS

\[\begin{align*}
2\text{-C}_6\text{H}_{13} & \rightarrow \text{C}_3\text{H}_6 & \rightarrow & \text{C}_2\text{H}_4 \\
1\text{-C}_6\text{H}_{13} & \rightarrow \text{C}_3\text{H}_7 & \rightarrow & \text{CH}_3 \\
3\text{-C}_6\text{H}_{13} & \rightarrow \text{C}_2\text{H}_4 & \rightarrow & \text{CH}_3 \\
1\text{-C}_4\text{H}_9 & \rightarrow \text{C}_2\text{H}_5 & \rightarrow & \text{C}_2\text{H}_4 \\
1\text{-C}_5\text{H}_{10} & \rightarrow \text{C}_2\text{H}_5 & \rightarrow & \text{C}_2\text{H}_4 \\
1\text{-C}_4\text{H}_8 & \rightarrow \text{C}_2\text{H}_4 & \rightarrow & \text{H} \\
\end{align*}\]
MECHANISM AND BRANCHING RATIOS FOR THE DECOMPOSITION OF OCTYL RADICALS

4 isomers undergoing 6 beta bond scissions and 6 reversible isomerizations
SUMMARY OF LITERATURE DATA PERTINENT TO THE UNIMOLECULAR REACTIONS OF FUEL RADICALS

- Beta bond scissions
- 1-5 H-atom transfer isomerization
DETERMINATION OF RATE EXPRESSIONS FROM THERMAL CRACKING PATTERNS

Begin with smallest fuel radicals – beta bond scissions from direct experimental results from decomposition and reverse addition process at lower temperatures

Use data on isomerization involving smaller radicals as guide to prediction for same process involving larger radicals.

1-butyl does not isomerize

1-pentyl can only undergo 1-4 hydrogen transfer

1-hexyl can undergo 1-4, 1-5 isomerizations

1-heptyl can undergo 1-4, 1-5, 1-6, 2-5 isomrizations

KEY CONCLUSIONS: SIMILAR TYPE OF ISOMERIZATIONS HAVE EQUIVALENT RATE EXPRESSIONS

ISOMERIZATIONS INVOLVING 6-MEMBER TRANSITION STATE ARE SO FAST THAT LARGER TRANSITION STATE BECOMES UNIMPORTANT IN LARGE MOLECULES
## HIGH PRESSURE RATE EXPRESSIONS FOR UNIMOLECULAR REACTIONS INVOLVING HEPTYL RADICALS

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Log A</th>
<th>N</th>
<th>Activation energy E/R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-C₇H₁₅ = C₂H₄ + 1-C₅H₁₁</td>
<td>11.90</td>
<td>.33</td>
<td>13694</td>
</tr>
<tr>
<td>2-C₇H₁₅ = C₃H₆ + 1-C₄H₉</td>
<td>11.70</td>
<td>.56</td>
<td>14138</td>
</tr>
<tr>
<td>3-C₇H₁₅ = 1-C₄H₈ + 1-C₃H₇</td>
<td>12.47</td>
<td>.31</td>
<td>14221</td>
</tr>
<tr>
<td>3-C₇H₁₅ = 1-C₆H₁₂ + CH₃</td>
<td>11.04</td>
<td>.75</td>
<td>14797</td>
</tr>
<tr>
<td>4-C₇H₁₅ = 1-C₄H₁₀ + C₂H₅</td>
<td>12.77</td>
<td>.31</td>
<td>14221</td>
</tr>
<tr>
<td>3-C₇H₁₅ = 1-C₇H₁₅</td>
<td>2.87</td>
<td>2.43</td>
<td>6441</td>
</tr>
<tr>
<td>4-C₇H₁₅ = 1-C₇H₁₅</td>
<td>2.10</td>
<td>2.88</td>
<td>9884</td>
</tr>
<tr>
<td>2-C₇H₁₅ = 1-C₇H₁₅</td>
<td>1.52</td>
<td>2.81</td>
<td>7561</td>
</tr>
<tr>
<td>3-C₇H₁₅ = 2-C₇H₁₅</td>
<td>2.30</td>
<td>2.83</td>
<td>9048</td>
</tr>
<tr>
<td>1-C₇H₁₅ = 3-C₇H₁₅</td>
<td>2.83</td>
<td>2.39</td>
<td>5237</td>
</tr>
<tr>
<td>1-C₇H₁₅ = 4-C₇H₁₅</td>
<td>2.07</td>
<td>2.85</td>
<td>8680</td>
</tr>
<tr>
<td>1-C₇H₁₅ = 2-C₇H₁₅</td>
<td>2.39</td>
<td>2.51</td>
<td>6292</td>
</tr>
<tr>
<td>2-C₇H₁₅ = 3-C₇H₁₅</td>
<td>1.39</td>
<td>3.09</td>
<td>9113</td>
</tr>
</tbody>
</table>
DEPARTURE FROM HIGH PRESSURE BEHAVIOR FOR BETA-BOUND SCISSION REACTIONS OF HEPTYL RADICALS

starting radical
1-heptyl: red
2-heptyl: dark green
3-heptyl: blue
4-heptyl: black

Reaction
1-heptyl = C₇H₄ + nC₅H₇: solid
2-heptyl = C₃H₆ + nC₄H₉ long dash
3-heptyl = 1-C₄H₈ + nC₃H₇ short dash
3-heptyl = 1-C₆H₁₂ + CH₃ dot
4-heptyl = 1-C₅H₁₀ + C₂H₅ dash dot dot dash
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.
SUMMARY

Unimolecular rate constants on the cracking of larger fuel compounds and radicals have been determined on the basis of past work and present experiments.

It is now possible to describe the pyrolytic decomposition of fuel molecules individually or in mixtures.

Form basis for studying mechanisms and rate constants for oxidation processes.

Need for systematic exploration of chemically activated decomposition in oxidative and soot formation processes.