Detailed and Simplified Chemical Kinetics of Aviation Fuels and Surrogates

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Technical Objective
- To develop detailed and simplified chemical mechanisms for surrogate fuels and to determine thermochemical data.

Approaches
- Calculation methods based on quantum mechanical methods featuring RRKM/master equation and variable transition state techniques.
- Extensive validation wrt global properties and species concentrations.

Cases Studied
- Systems covered include cyclopentadienyl pyrolysis/oxidation, the benzene/naphthalene and toluene/1-methyl naphthalene analogies as well as n-propyl benzene.
Surrogate Fuels for Aviation Applications

- JP-4
- JP-7
- JET-A
- DF2

- TC Aromatics
- Acenaphthalenes
- C11+Naphthalenes
- Naphthalenes
- Indenes
- Indanes
- Alkyl Benzenes
- TC Paraffins
- DC Paraffins
- MC Paraffins
- Paraffins

- Indene
- 1-methyl naphthalene
- n-propyl benzene
- alkanes
- toluene
- cyclopentadiene
Topics


- Progress on the toluene/1-methyl naphthalene system – including some perhaps surprising sensitivities in the toluene auto-ignition process to issues in the hydrogen system (Gkagkas and Lindstedt 2009).

- Progress on the n-propyl benzene system and the application of an updated mechanism with new thermodynamic data derived using DFT and G3B3/G3MP2B3 composite quantum mechanical methods.

- Accurate thermodynamic data bases have been derived for 100+ chemical species relevant to the above systems.
A Semi-Automated Method for High Quality Thermodynamic Data Determination

Molecular Mechanics Minimisation and Conformational Analysis used to locate starting structure

High Accuracy Quantum Mechanics G3B3/G3MPB3 Energy Calculation

Atomization Energies, Enthalpies and Vibration Frequencies produced.

Program locTorsion used to locate all internal rotations and create input files

DFT Quantum Mechanics used to scan and analyse Internal Rotations

Program scanCalc used to harvest internal rotation data, fit $V = \frac{1}{2} \sum V_n (1 - \cos(n\theta))$ and calculate IR symmetry numbers and Moments of Inertia

Program polyScript used to harvest data from G3B3 and scanCalc log files, calculate Enthalpies of Formation and Moments of Inertia, and produce input for next stage

Statistical Mechanics Package PAC 99 used to calculate thermodynamic values from 200 K to 6000 K

7 Term JANAF Polynomials produced by regression of calculated data
The cyclopentadienyl radical forms a key part of the main reaction pathway leading from single and multiple ring aromatics to linear hydrocarbons. The motivation was outlined at the MACCCR meeting in September 2008.

Potential Energy Surfaces (PES) were calculated at the G3B3 level using Gaussian03 and compared to previous work (e.g. Zhong and Bozzelli 1998 and Kern et al. 1998).

Reaction rates were calculated with a RRKM/Master-Equation approach using ChemRate. We also evaluated POLYRATE (Truhlar and co-workers).

A detailed investigation of the C_5H_5 chemistry was performed and the impact of a substantial update featuring 21+ chemical reactions is evaluated here against experimental data from Butler (2001) and Butler and Glassman (2009).
Examples from Thermodynamic Database

**C5H4O**

<table>
<thead>
<tr>
<th>Calculated Data</th>
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<tbody>
<tr>
<td>$\Delta_f H_{298}$</td>
<td>54.750</td>
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<tr>
<td>$S_{298}$</td>
<td>291.420</td>
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<td>$C_{p298}$</td>
<td>84.202</td>
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<td>$\Delta_f H_{1000}$</td>
<td>156.309</td>
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**C5H4OH**

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<tr>
<td>$C_{p298}$</td>
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<td>$\Delta_f H_{1000}$</td>
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**C5H5OH**

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<td>$\Delta_f H_{298}$</td>
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<td>$S_{298}$</td>
<td>309.393</td>
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<td>$\Delta_f H_{1000}$</td>
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**C5H5OO**

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<td>$\Delta_f H_{298}$</td>
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<tr>
<td>$S_{298}$</td>
<td>352.445</td>
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<tr>
<td>$C_{p298}$</td>
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<td>$\Delta_f H_{1000}$</td>
<td>338.507</td>
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The Oxidation of PAH: Cyclopentadienyl Analog

Potential Energy for C$_5$H$_5$+OH Reactions
Reaction 11 – C₅H₅ + OH → C₄H₆(T) + CO

- No previous in depth study of the potential energy surface of this reaction.
- Two routes were explored for the breakdown of the C₅H₅ ring.
- Route 1 proceeded along a lower energy path and, as none of steps have a higher energy than the reactants, rates were calculated for the first step.

<table>
<thead>
<tr>
<th>T</th>
<th>k</th>
<th>k</th>
<th>k</th>
<th>k</th>
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<tbody>
<tr>
<td>500</td>
<td>4.3E+12</td>
<td>1.4E+14</td>
<td>1.5E+14</td>
<td>5.4E+13</td>
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<tr>
<td>600</td>
<td>9.2E+12</td>
<td>2.4E+14</td>
<td>3.1E+14</td>
<td>1.3E+14</td>
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<tr>
<td>700</td>
<td>1.6E+13</td>
<td>2.4E+13</td>
<td>3.6E+14</td>
<td>2.4E+14</td>
</tr>
<tr>
<td>800</td>
<td>2.4E+13</td>
<td>1.8E+14</td>
<td>3.2E+14</td>
<td>4.1E+14</td>
</tr>
<tr>
<td>900</td>
<td>3.2E+13</td>
<td>1.2E+14</td>
<td>2.4E+14</td>
<td>6.1E+14</td>
</tr>
<tr>
<td>1000</td>
<td>4.1E+13</td>
<td>7.0E+13</td>
<td>1.6E+14</td>
<td>8.6E+14</td>
</tr>
<tr>
<td>1200</td>
<td>6.1E+13</td>
<td>2.1E+13</td>
<td>6.3E+13</td>
<td>1.5E+15</td>
</tr>
<tr>
<td>1400</td>
<td>7.9E+13</td>
<td>6.3E+12</td>
<td>2.3E+13</td>
<td>2.2E+15</td>
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<tr>
<td>1600</td>
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<td>8.4E+12</td>
<td>3.1E+15</td>
</tr>
<tr>
<td>1800</td>
<td>1.1E+14</td>
<td>5.9E+11</td>
<td>3.2E+12</td>
<td>4.1E+15</td>
</tr>
<tr>
<td>2000</td>
<td>1.3E+14</td>
<td>2.0E+11</td>
<td>1.2E+12</td>
<td>5.2E+15</td>
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</table>
Reaction 11 – C₅H₅ + OH → C₄H₆(T) + CO
Concentration profiles during cyclo-pentadiene oxidation in a flow reactor. $\Phi = 1.03$ (2243 ppm of fuel), $P = 1$ atm, $T = 1198$ K. Circles are measurements (Butler and Glassman 2009) and solid line is current simulation.

Concentration profiles during cyclo-pentadiene pyrolysis in a flow reactor (1044 ppm of fuel, \( P = 1 \text{ atm}, T = 1148 \text{ K} \). Circles are measurements (Butler and Glassman 2009) and solid line is current simulation.
The major naphthalene growth pathway is via cyclopentadienyl radical recombination following the two-step sequence of Lindstedt et al. (2001) passing via the formation of $\text{C}_{10}\text{H}_{9}\text{F}$. 

$$\begin{align*}
\text{C}_5\text{H}_5 + \text{C}_5\text{H}_5 &= \text{C}_{10}\text{H}_{9}\text{F} + \text{H} \quad (1) \\
\text{C}_{10}\text{H}_{9}\text{F} &= \text{C}_{10}\text{H}_8 + \text{H} \quad (2)
\end{align*}$$

For the pyrolysis cases, indene is formed predominantly via recombination of $\text{C}_5\text{H}_5$ and $\text{C}_5\text{H}_6$ with simultaneous methyl expulsion (3). The rate is based on the PES from the study by Wang et al. (2006).

$$\begin{align*}
\text{C}_5\text{H}_5 + \text{C}_5\text{H}_6 &= \text{C}_9\text{H}_8 + \text{CH}_3 \quad (3) \\
\text{C}_9\text{H}_7 + \text{H} &= \text{C}_9\text{H}_8 \quad (4)
\end{align*}$$

For the oxidation cases, indene is predominantly formed via acetylene addition to the benzyl radical (5) with $\text{C}_5\text{H}_6$ and $\text{C}_5\text{H}_5$ recombination. The rate used is that of Colket et al. (1994), which was also analysed by Lindstedt and Maurice (1996).

$$\begin{align*}
\text{C}_7\text{H}_7 + \text{C}_2\text{H}_2 &= \text{C}_9\text{H}_8 + \text{H} \quad (5)
\end{align*}$$
Major $C_9H_8$ and $C_{10}H_8$ formation channels for $C_5H_6$ oxidation in PFR (Phi = 1.6, $T = 1153$ K and initial fuel concentration = 2070 ppm).

Conditions used were obtained from Butler (2001).

The Oxidation of Indene via HO$_2$ and O$_2$
PES for $C_9H_7 + O_2 = C_7H_6O + HCCO$
Concentration profiles during 1-methyl naphthalene oxidation in a jet-stirred reactor. In the subsequent graphs the circles are measurements (Mati et al. 2007) and the solid line the current simulation.

Previous studies of 1-methyl naphthalene include those of Shaddix (1993), Pitsch (1996), Potter (2004), Mati et al. (2007).

<table>
<thead>
<tr>
<th>$\Phi$</th>
<th>$P$ (atm)</th>
<th>$T$ (K)</th>
<th>$X_{O_2}$</th>
<th>$X_{C_{11}H_{10}}$</th>
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<tbody>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>1097-1290</td>
<td>0.0270</td>
<td>0.001</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>1094-1400</td>
<td>0.0135</td>
<td>0.001</td>
</tr>
<tr>
<td>1.5</td>
<td>1.0</td>
<td>1147-1440</td>
<td>0.0090</td>
<td>0.001</td>
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</table>
1-Methyl Naphthalene Oxidation

Concentration profiles during 1-methyl naphthalene oxidation in a jet-stirred reactor. $\Phi = 1.0$, $P = 1$ atm, $1100 < T [K] < 1400$. Circles are measurements (Mati et al. 2007) and solid line is current simulation.

**1-Methyl Naphthalene Oxidation**

<table>
<thead>
<tr>
<th>$\Phi$</th>
<th>$P$ (atm)</th>
<th>$T$ (K)</th>
<th>$[O_2]$ ppm</th>
<th>$[C_{11}H_{10}]$ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>1069</td>
<td>0.0270</td>
<td>0.001</td>
</tr>
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<td>1.5</td>
<td>1.0</td>
<td>1066</td>
<td>0.0135</td>
<td>0.001</td>
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<tr>
<td>1.5</td>
<td>1.0</td>
<td>1198</td>
<td>0.0090</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Concentration profiles during 1-methyl naphthalene oxidation in a flow reactor. In subsequent graphs the circles are measurements (Shaddix et al. 1997) and the solid line the current simulation.
1-Methyl Naphthalene Oxidation

Concentration profiles during 1-methyl naphthalene oxidation in a flow reactor. The circles are measurements (Shaddix et al. 1997) and the solid line the current simulation.
Sensitivity analysis of the time resolved OH radical concentrations in Toluene/Oxygen/Argon mixtures in shock tube with 0.1% toluene, 0.9% oxygen, $T = 1689$ K and $P = 1.79$ atm.

Circles are measurements (Vasudevan et al. 2005).

The solid line is our current model, the dashed line the same model with the rate of Baulch et al. (2005) for $O + H_2 \rightarrow OH + O$.

The dashed dotted line is our current model with the $C_5H_5 + C_2H_2 \rightarrow C_7H_7$ channel removed.
Differences in reaction rates at 1045 K. The temperature was selected as characteristic in the turbulent flame ignition studies pursued by Gkagkas and Lindstedt (2009).

The mechanism of Li et al. (2004) used the rate from Sutherland et al. (1986), which also formed the CEC recommendation of Baulch et al. (1992,1994), and Sun et al. (2007), used the more recent CEC suggestion of Baulch et al. (2005).
Background: Hydrogen Chemistry

- Logarithmic sensitivities of the liftoff height to changes in reaction rate parameters.
- Reaction 2 has the unfortunate combination of sensitivity and uncertainty.
- Analysis performed at 1045 K and atmospheric pressure.
- There is a need for a careful determination of rates in this difficult regime.
Time resolved OH concentrations of H$_2$/O$_2$/Ar mixtures in shock tubes obtained with detailed and systematically reduced chemical mechanisms. Symbols are measurements [43] and lines are calculations. Initial conditions are: (a) H$_2$=5.0%, O$_2$=0.493% at 0.675 atm and 1980 K (b) H$_2$=1.10%,O$_2$=0.208% at 1.98 atm and 2898 K.
Critical reaction paths in the oxidation of aromatic surrogate fuel components have been analyzed and more accurate rates of reaction determined via ab initio methods.

Good progress made on several system, including several of relevance to substituted aromatics.

Thermodynamic data bases have been substantially updated for a wide range of compounds, currently 100+ species, and a semi-automatic technique has been formulated and evaluated.

Alkanes and other components currently addressed via large working groups (e.g. AFRL Energy IPT (PI: Egolfopoulos, USC) and a MURI (PI: Dryer, Princeton) and the current work is complementary.