Detailed and Simplified Chemical Kinetics of Aviation Fuels and Surrogates

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Objectives

- Seek to improve upon current reaction class-based estimation methods.
- Seek to identify specific issues that require more detailed studies using higher accuracy methods and/or experimentation.

Approach

- The application of computational methods that can provide chemical kinetic data of sufficient accuracy to guide the development of detailed chemical kinetic mechanisms at a decent rate of progress.
- Extensive validation.
- Example of the impact of consistent use of thermodynamic data.
- Some comparisons of results obtained using different \textit{ab initio} methods for the determination of rate data from the same PES. The example chosen relates to biofuels.
- Progress on the n-propyl benzene [nPB] system
- Some comments on C$_5$-ring structures and the cyclopentadiene system.
The error for the composite G4 method (Curtiss et al. 2007), as measured against a hydrocarbon test set, is estimated to be 0.48 kcal/mol with a RMS deviation of 0.70 kcal/mol.

G4MP2 is a second order perturbation theory version of G4 with a somewhat reduced accuracy of 0.63 kcal/mol for the same test set.

Thermodynamic data bases have been substantially updated for more than 200 species of relevance to current projects.

Jahn-Teller effects are added in cases such as cyclopentadiene (e.g. Robinson and Linstedt 2011).

The method appears robust, though larger molecules (say C_{14}+) can be non-trivial and result in significant computational effort.
- Fuel rich laminar ($\phi = 2.4$) premixed flat acetylene flame (Westmoreland and co-workers).
- Polyenes may have an impact on soot mass growth.
- No reasonable change in rate parameters resolved the issue with the $C_6H_2$ profile.
- Thermodynamic data was obtained from reputable computations.
Impact of Thermodynamics

- A re-evaluation of the thermodynamics using calculations at the G4MP2 level produced the outcome shown.
- The agreement is notably improved and suggests that consistent use of data at this level provides reasonable agreement for the current case.
- Acetylene flames are likely to come to the fore again due to new synchrotron data and the importance of soot.
Data for Rate Processes

- **Potential Energy Surfaces** at the G4/G4MP2 level in order to reduce uncertainties somewhat from G3/G3B3 used in the past.


- Calculations of high pressure limit rate data using Transition State Theory (TST) and Canonical Variation Theory (CVT) with VRC-VTST computations carried out and the Canonical Unified Statistical (CUS) model was applied in some cases (Truhlar and co-workers 2010).

- **Multiple well systems** are also studied using a RRKM/MW technique or the Inverse Laplace Transform (ILT) method of Robertson et al. (2010).
The studied reactions were delineated using four classes:

- bimolecular exchange reactions;
- dissociation reactions with a clear transition state;
- barrierless dissociation reactions;
- multiwell reactions.

Different methods were used and compared mainly on the basis of the same G4 or G4MP2 derived energy data.
Enthalpies anchored at 298 K.

Transition state properties for barrierless reactions were estimated using the enthalpy of formation and frequencies of both reactants and products (c.f. VRC-VTST).

The applied rotational data was evaluated from the external rotors of the active component and Benson correction parameters including the vibrational frequency of the bond to be broken.

Hindered internal rotors typically scanned at the B3LYP/6-31g(d) level (issues related to barrier height).

The contribution of hindered internal rotors taken into account considering the overall energy barrier to rotation, symmetry number and the internal moment of inertia.

Eckart quantum tunnelling corrections were applied to reactions involving hydrogen transfers with large imaginary frequencies, barrier widths obtained from IRC calculations.
- Energies anchored at 0 K.
- Internal (not hindered) rotors currently treated through vibrational data and one-dimensional tunnelling considered through an asymmetric Eckart barrier (Miller 1979).
- Full multiwell treatment of reactions with multiple steps on more complex PESs were computed using this methodology.
TST/SCT used for bimolecular exchange reactions and VRC-VTST for barrierless dissociation reactions.

Data from the PES for each step of the process was required and the GAUSSRATE interface was used to provide direct dynamics calculations of energies, gradients and Hessians on the reaction path.

VRC-VTST calculations were carried out in a similar manner. Single-faceted dividing surfaces were used with the pivot points defined at the two bonding atoms.

The reaction coordinate (s) was varied between approximately 1.2 and 6 Å depending on the reaction studied.
Example of a more complex PES with possible stabilisation occurring at the intermediate well.

Work on the $C_3H_7O$ potential has been performed by Zador et al. (2009) in the context of the $C_3H_6 + OH$ reaction.
The agreement between the 10 atm rate and the estimation of Wilk et al. (1989) is rather good at combustion temperatures.

Pressure fall-off is significant.

It is not uncommon for the latter to be a source of concern.

Sample Reaction: \( \text{C}_3\text{H}_6\text{OH} \rightarrow \text{C}_2\text{H}_5\text{CH}_2\text{O} \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\text{O} \)
Laminar Burning Velocities for n-Propanol [MESMER Data]
Low Pressure Flat Flame I – Fuel Rich n-Propanol Mixture

- n-Propanol/Oxygen/Argon flame from Li et al. (2008) with $\Phi = 1.8$, 40 % Ar, 4000 Pa.
- The mechanism including multiple well data results in better agreement.
- The improvement is particularly obvious for propionaldehyde.
- The experimental method cannot distinguish between ketene and other mass 42 species.
- The RRKM/ME approach remains useful.
- More details can be provided.
Bimolecular exchange reactions involved in the initial breakdown of n-propyl-benzene featuring a hydrogen exchange with common radical and molecular species (H, OH, O, O$_2$ and CH$_3$).

Geometries for reactants, transition states, complexes and products optimised at the B3LYP/6-31G(2df,p) level. Energies calculated at the G4 and G4MP2 composite level.

For the RRKM(/ME) calculations, energies, vibrational data and moments of inertia were taken from G4/G4MP2 calculations.

Hindered rotors investigated at the B3LYP/6-31G(d) level and corrections included.

TST/SCT with energies, first derivatives, gradients and Hessians computed at the B3LYP/6-31G(d) level with higher level calculations currently taking place.
Standard reactant - transition state - product channels were found for reactions involving H and CH$_3$ radicals.

For reactions involving OH radicals, van der Waals stabilised complexes were found on both reactant and product sides of the transition state.

Product side complexes were ignored for non-CUS based computations.

Radical complexes on both product and reactant sides also identified for reactions involving O (work is still in progress).
The nPB System

![Diagram showing the reaction process]

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reactant 1</th>
<th>Reactant 2</th>
<th>Product 1</th>
<th>Product 2</th>
<th>Energy Reactants (kJ mol⁻¹)</th>
<th>Energy TS (kJ mol⁻¹)</th>
<th>Energy Products (kJ mol⁻¹)</th>
<th>Activation Energy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₉H₁₂</td>
<td>H</td>
<td>C₉H₁₁-1</td>
<td>H₂</td>
<td>225.75</td>
<td>244.89</td>
<td>194.14</td>
<td>19.14</td>
</tr>
<tr>
<td>2</td>
<td>C₉H₁₂</td>
<td>H</td>
<td>C₉H₁₁-2</td>
<td>H₂</td>
<td>225.75</td>
<td>234.34</td>
<td>184.40</td>
<td>8.59</td>
</tr>
<tr>
<td>3</td>
<td>C₉H₁₂</td>
<td>H</td>
<td>C₉H₁₁-3</td>
<td>H₂</td>
<td>225.75</td>
<td>228.43</td>
<td>150.33</td>
<td>2.68</td>
</tr>
</tbody>
</table>
\[ [1,2,3] \text{C}_9\text{H}_{12} + \text{H} = \text{C}_9\text{H}_{11-1/-2/-3} + \text{H}_2 \]

- Abstraction from terminal site (top left), second site (top right) and adjacent to ring (right).
- Estimations by Dagaut et al. based on \( n \)-propyl.
\[ \text{C}_9\text{H}_{12} + \text{CH}_3 = \text{C}_9\text{H}_{11}-2 + \text{CH}_4 \]
[4] \( \text{C}_9\text{H}_{12} + \text{CH}_3 = \text{C}_9\text{H}_{11}-1 + \text{CH}_4 \)
[8] $\text{C}_9\text{H}_{12} + \text{OH} = \text{C}_9\text{H}_{11}\text{-2} + \text{H}_2\text{O}$
[8] $\text{C}_9\text{H}_{12} + \text{OH} = \text{C}_9\text{H}_{11-2} + \text{H}_2\text{O}$

Rate Constant [m$^3$ kmol$^{-1}$ s$^{-1}$] vs $1000/T$ [K]

- CUS
- TST/SCT
- Dagaut et al.
[9] \( C_9H_{12} + OH = C_9H_{11-3} + H_2O \)
[9] \( \text{C}_9\text{H}_{12} + \text{OH} = \text{C}_9\text{H}_{11}-3 + \text{H}_2\text{O} \)
[15] C₉H₁₂ + O₂ = C₉H₁₁⁻³ + HO₂

![Graph showing rate constant vs 1000/T in Kelvin.](image-url)
The cyclopentadienyl (CPDyl) radical forms a key part of the main reaction pathway leading from single and multiple ring aromatics to linear hydrocarbons.

Potential Energy Surfaces (PES) were calculated at the G4 level using Gaussian09 and compared to previous work (e.g. Emdee et al. 1992; Zhong and Bozzelli 1998; Tokmakov et al. 2004; Harding et al. 2007).

A substantial update of the CPD chemistry has been made (Robinson and Lindstedt 2011) and the impact evaluated against experimental data from Butler (2001) and Butler and Glassman (2009).

Some of the PES are rather complex with multiple wells and selected cases were subsequently investigated using multiwell techniques (MESMER).
Thermal Decomposition of CPDyl

Potential energy diagram with energies determined at the G4 level for the thermal decomposition of the cyclopentadienyl radical (CPDyl).

\[ \Delta H_f^{298} \text{[kJ mol}^{-1}] \]

- TS17
- TS18
- TS19

\[ \text{C}_3\text{H}_5 \quad \text{C}_5\text{H}_5^{-1} \quad \text{CHCCH}_2\text{CHCH} \quad \text{C}_3\text{H}_3\quad + \quad \text{C}_2\text{H}_2 \]
Thermal Decomposition of CPDyl

Rate Constant [s\(^{-1}\)]

1000/T [K]

- RRKM/ME HP
- RRKM/MW 1 atm
- RRKM/MW 10 atm
- Kern et al. HP
- Roy et al.
- Moskaleva et al. 1 atm
- Keifer 4% ~0.26 atm
- Keifer 2% ~0.26 atm
Concentration profiles during CPD oxidation in a flow reactor. Φ = 1.03 (2243 ppm fuel, T = 1198 K) and Φ = 1.03 (1051 ppm fuel, T = 1148 K).
Concentration profiles during CPD oxidation in a flow reactor. $\Phi = 1.03$ (2243 ppm fuel, $T = 1198$ K) and $\Phi = 1.03$ (1051 ppm fuel, $T = 1148$ K).
Further CPD Related Data

- Burning velocities for CPD (private communication Egolfopoulos 2011) – preliminary modelling result.
- CPD and CPDyl concentrations in the acetylene flame of Westmoreland and co-workers.
Summary/Current Work

- Critical reaction paths in the oxidation of aromatic surrogate fuel components have been analyzed and rates of reaction determined via \textit{ab initio} methods.
- Particular attention has been given to the critical cyclopentadiene system and a key oxidation reactions studied.
- Work has commenced on the initiation reactions in the n-propyl benzene system and this is expected to conclude over the next few months.
- Decomposition reactions in the nPB system will also be studied in order to determine rates and fall-off.
- Selected complex PES in the CPDyl system will be explored further using multiwell methods.
- Uncertainties in barrier heights and the corresponding impact on rate parameters are being evaluated using a wider subset of available methods (e.g. G4MP2, G4, B3LYP/6-31G(d), M062X/6-311G(2df,p) and CCSD(T)/aug-cc-pVQZ; c.f. Zheng and Truhlar 2010).