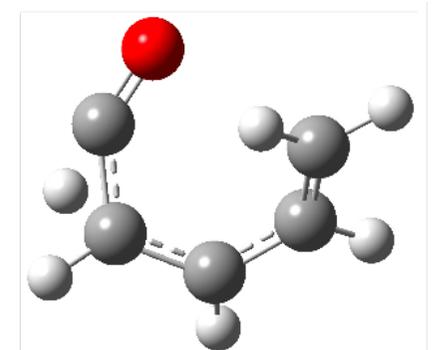


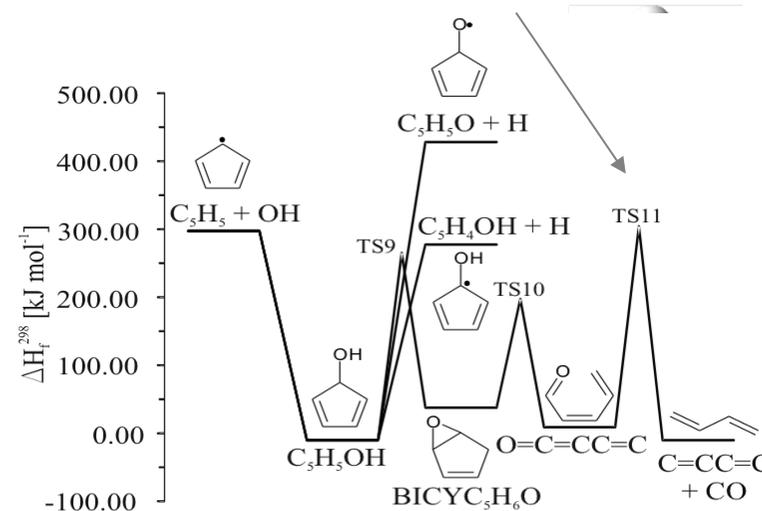
## Detailed and Simplified Chemical Kinetics of Aviation Fuels and Surrogates

Prof Peter Lindstedt (PI), Dr Valentini Markaki  
and Dr Roger Robinson (Part Time).

Supported by EOARD/AFOSR via Award  
FA8655-09-1-3089. Thanks are due to Dr  
Julian Tishkoff (AFOSR) and Dr Surya  
Surampudi (EOARD).



TS11



## Background

### Technical Objective

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

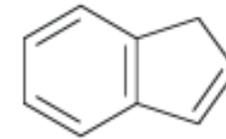
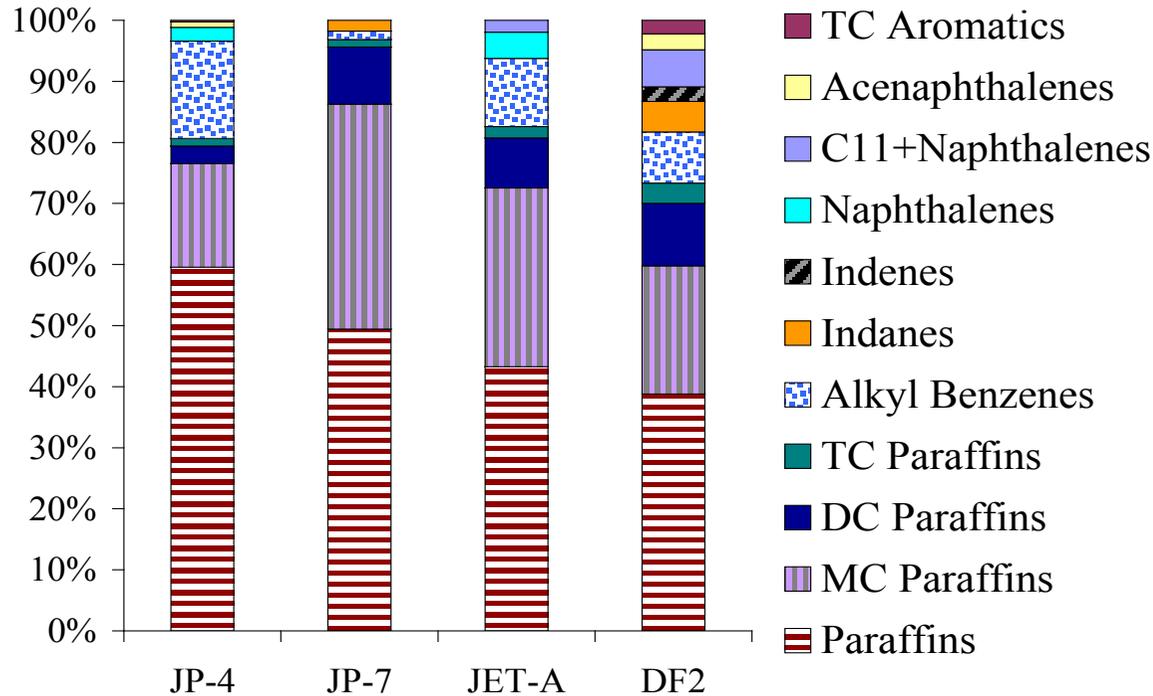
### Approaches

- ❑ Calculation methods based on quantum mechanical methods featuring RRKM/master equation and variable transition state techniques based on potential energy surfaces determined at the G4 and G4MP2 levels.
- ❑ Extensive validation with respect to global properties and species concentrations.
- ❑ Simplifications sought that permit application of developed models using computational tools for design calculations.

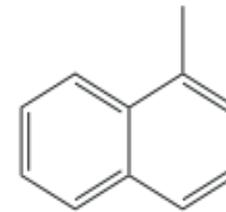
### Cases Studied

- ❑ Systems covered include **cyclopentadiene (CPD) pyrolysis/oxidation**, the benzene/naphthalene, toluene/1-methyl naphthalene analogies, n-propyl benzene and **simplifications in the modelling of ignition characteristics of alkane fuel components**.

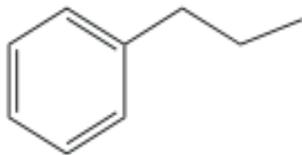
# Surrogate Fuels for Aviation Applications (Maurice)



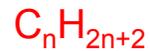
indene



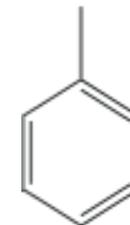
1-methyl naphthalene



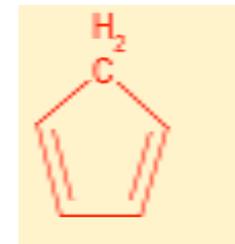
n-propyl benzene



alkanes



toluene

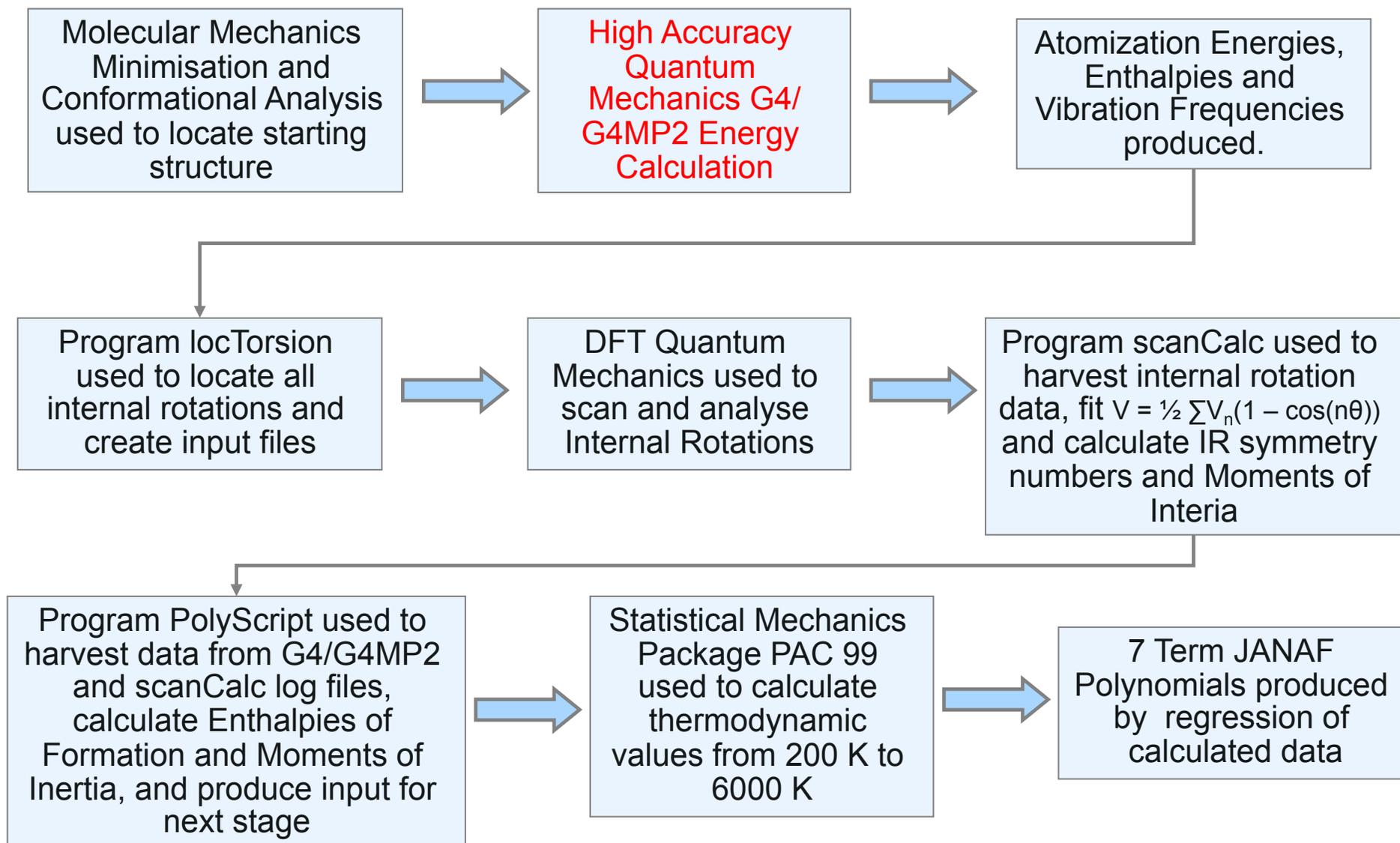


cyclopentadiene

## Topics

- ❑ Progress on the oxidation and thermal decomposition of C<sub>5</sub>-ring structures (e.g. Lindstedt, Maurice and Meyer 2001; Lindstedt and Rizos 2002; Lindstedt *et al.* 2009)
- ❑ 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.
  - ❑ 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.
- ❑ Progress on the cyclopentadienyl system as an example of use of our current choice of G4/G4MP2 methods coupled with RRKM/master equation modeling.
- ❑ Progress on simplified mechanisms for application to specific challenges. The example chosen is auto-ignition of alkanes (C<sub>7</sub>+) in the NTC region upwards.

# A Semi-Automated Method for High Quality Thermodynamic Data Determination



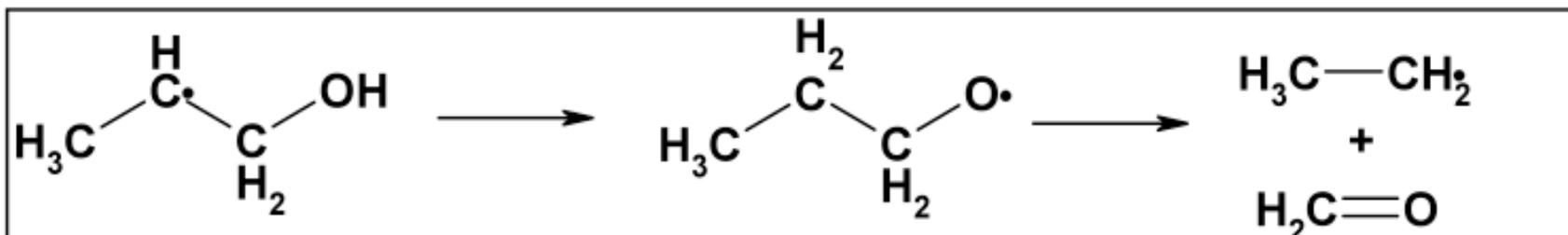
## The Cyclopentadienyl System

- ❑ 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 and G4MP2 levels 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).
- ❑ Reaction rates were calculated with a RRKM/Master-Equation approach using ChemRate (Mokrushin and co-workers). We also evaluated and use VTST methods via POLYRATE (Truhlar and co-workers).
- ❑ A detailed investigation of the CPDyl chemistry was performed and the impact of a substantial update was evaluated against CPD experimental data from Butler (2001) and Butler and Glassman (2009).

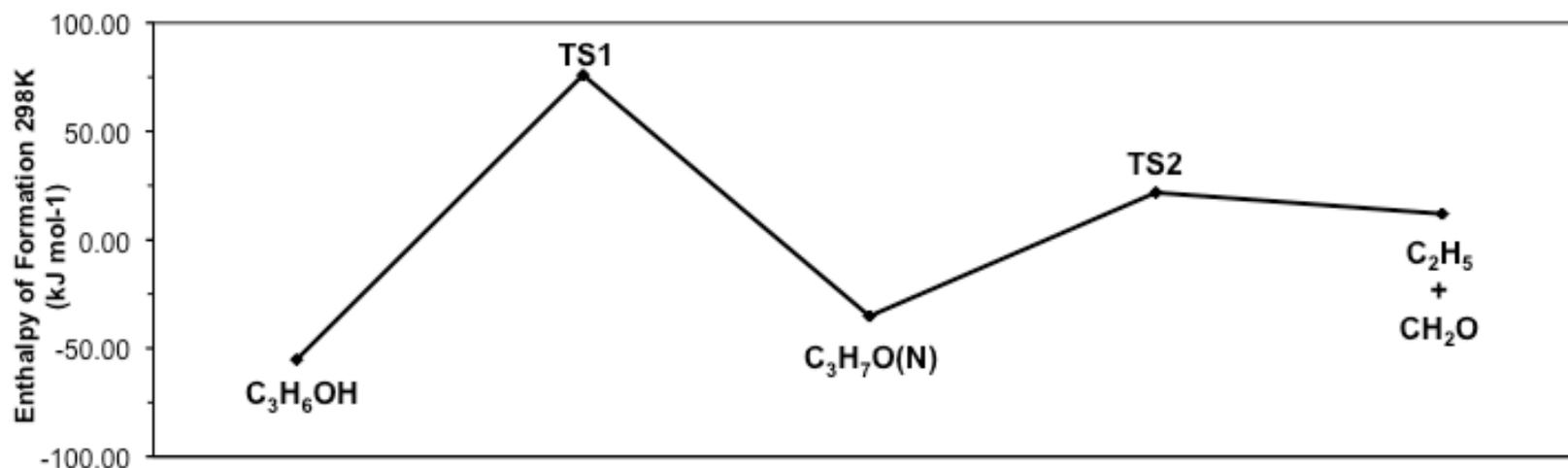
## Comments on the Current Method

- ❑ The Jahn-Teller effect for the cyclopentadienyl radical was included and treated as a pseudo rotation using the method of Katzer and Sax (2002).
- ❑ Eckart quantum tunneling corrections applied to H transfer reactions.
- ❑ Barrierless reactions require the definition of a virtual transition state defined on the basis of enthalpies and vibrational frequencies of reactants and products etc.
- ❑ The accuracy of the inherent assumptions for barrierless reactions need to be assessed on a case by case basis before implementation into chemical kinetic models. Examples are given as part of the current talk.
- ❑ The adopted approach can be expected to perform reasonably well for reactions where a transition state has been located and where the corresponding energies are accurately determined.
- ❑ An alternative fuels related example will be given.

## Illustrative Example: $\text{C}_3\text{H}_6\text{OH} \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\text{O}$

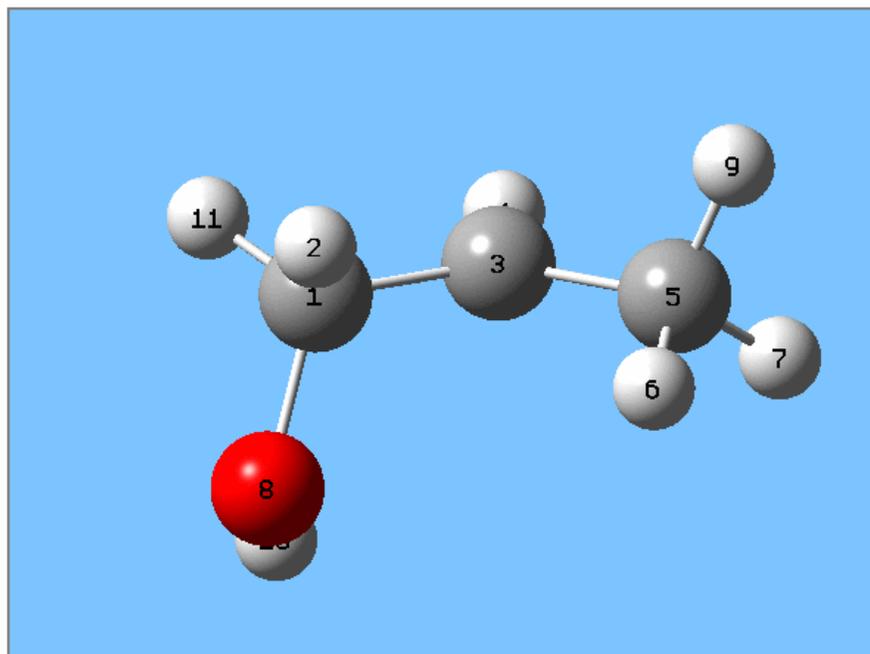


### Rate 33 – Potential Energy Surface



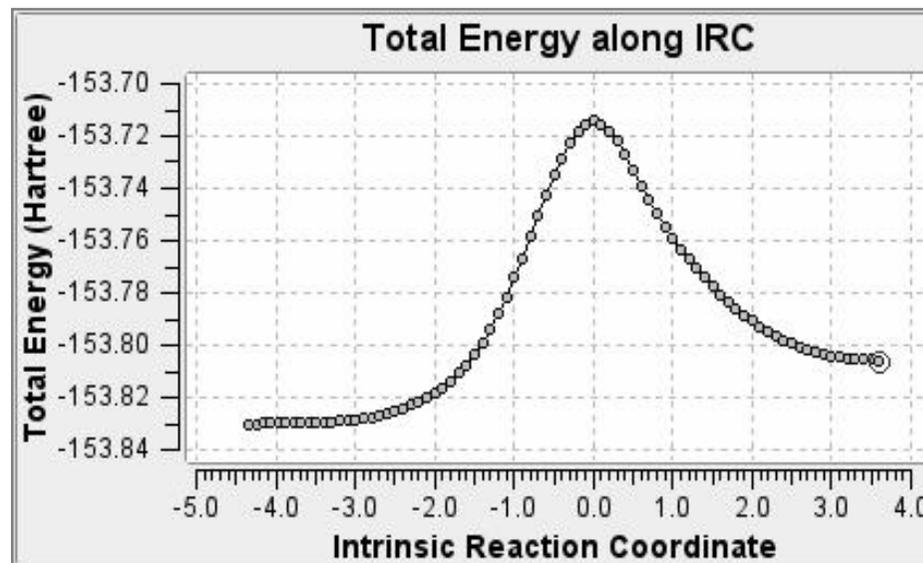
- The first transition state (TS1) assumed to be rate limiting in the multi-step process leading to the thermal decomposition.

## Rate Limiting H Transfer

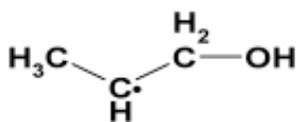


IRC Calculation - Reaction energy profile, 0.1 Ångstrom steps and energy in Hartrees.

IRC Calculation – Movie shows progress from reactants through transition state to products.



## Molecular Data (G3B3 Level Values)



Principal of moments  
of Inertia (g cm<sup>2</sup>)  
I<sub>A</sub> = 2.74 x10<sup>39</sup>  
I<sub>B</sub> = 22.17 x10<sup>39</sup>  
I<sub>C</sub> = 23.67x10<sup>39</sup>

Rotational  
moments  
of Inertia (g cm<sup>2</sup>)  
R1 = 0.14 x10<sup>39</sup>  
R2 = 2.77 x10<sup>39</sup>  
R3 = 0.50 x10<sup>39</sup>

Vibrational Frequencies(cm<sup>-1</sup>)

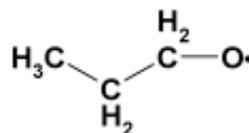
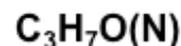
B3LYP/6-31g(d) \* 0.96

266.0	1094.4	1471.2
408.1	1180.5	2757.9
446.1	1230.2	2827.6
858.1	1306.0	2842.1
905.5	1381.6	2926.7
985.6	1423.9	2981.3
1027.7	1445.1	3069.9
1077.1	1455.5	3603.4

Vibrations Modelled as  
Hindered Internal Rotors

68.3    105.3    257.4

	Rotor 1	Rotor 2	Rotor 3
V1	303.65	38.13	6.91
V2	217.73	148.55	-7.09
V3	480.85	27.98	144.39
V4	4.63	59.80	2.46
V5	-1.12	-10.68	-7.48
V6	-1.28	-13.98	26.18



Principal of moments  
of Inertia (g cm<sup>2</sup>)  
I<sub>A</sub> = 5.52 x10<sup>39</sup>  
I<sub>B</sub> = 16.08 x10<sup>39</sup>  
I<sub>C</sub> = 19.07 x10<sup>39</sup>

Rotational  
moments  
of Inertia (g cm<sup>2</sup>)  
R1 = 2.58 x10<sup>39</sup>  
R2 = 0.51 x10<sup>39</sup>

Vibrational Frequencies(cm<sup>-1</sup>)

B3LYP/6-31g(d) \* 0.96

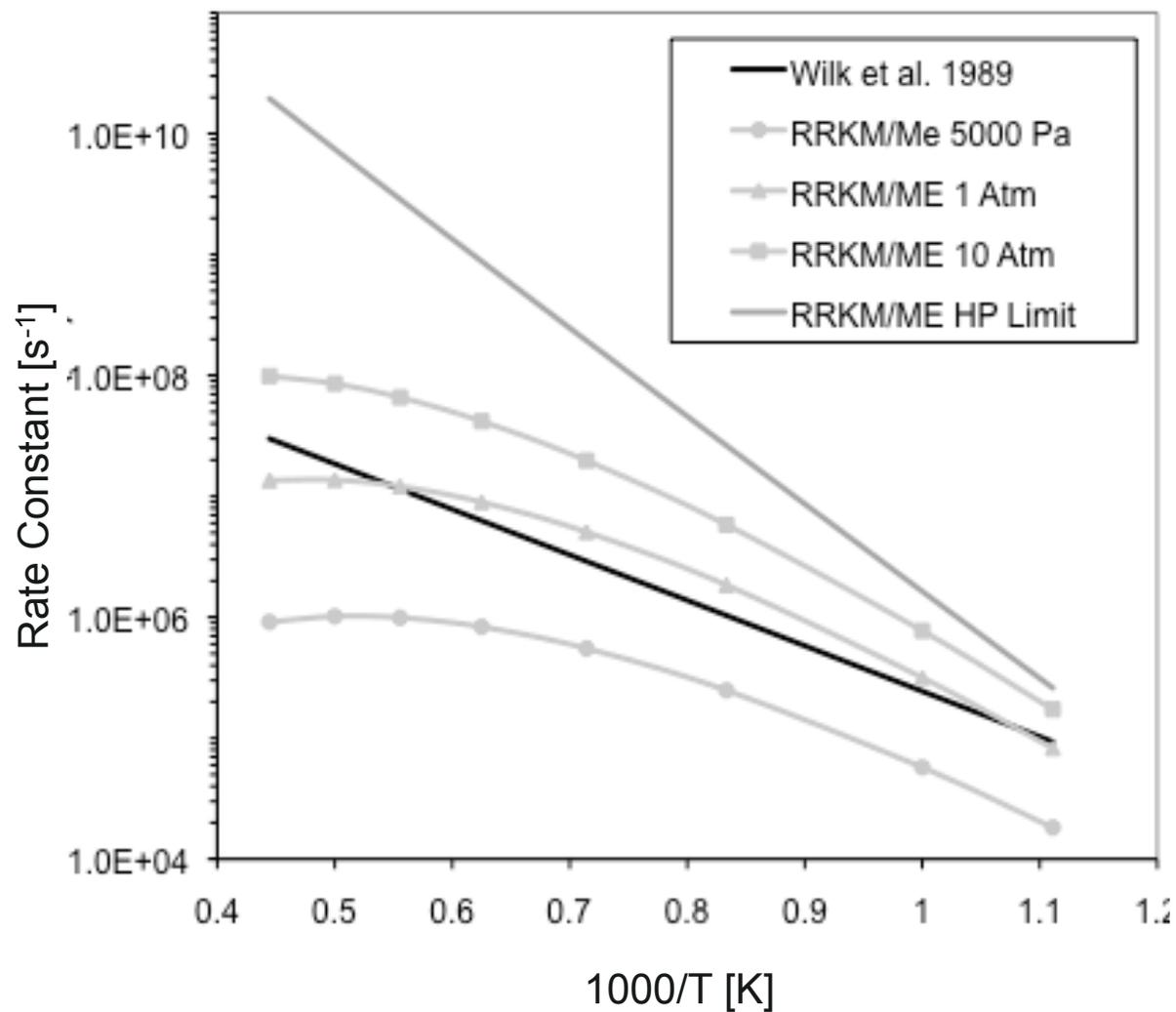
295.9	1178	2769
472.3	1248	2827
563.9	1299	2920
766.5	1331	2927
836.5	1345	2954
954.2	1386	2990
959.9	1453	3008
1054	1468	
1066	1478	

Vibrations Modelled as  
Hindered Internal Rotors

140.6    222.90

	Rotor 1	Rotor 2
Max kJ mol <sup>-1</sup>	13.30	12.03
V1	-8.59	-6.46
V2	78.73	-9.22
V3	1036.24	1002.61
V4	-3.22	10.17
V5	38.30	7.64
V6	-54.12	-20.84

## Rate Determinations for $\text{C}_3\text{H}_6\text{OH} \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2\text{O}$

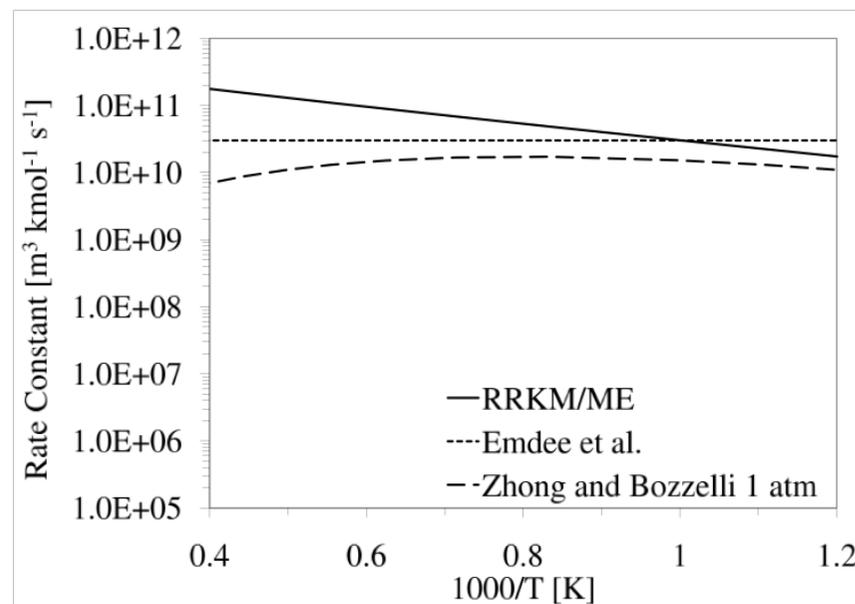
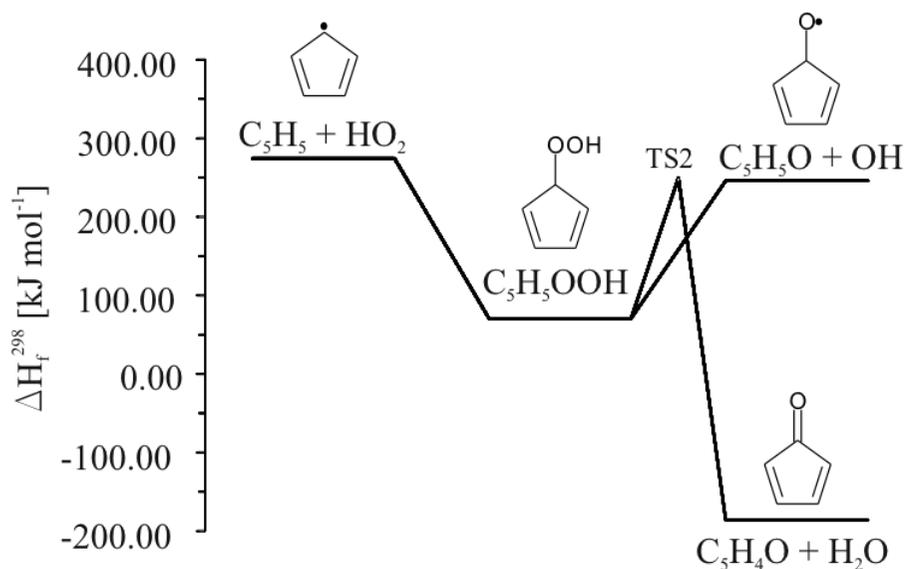


## The Cyclopentadienyl System

Reaction Number	Reactant 1	Reactant 2	Product 1	Product 2
1	C5H5	O2	C5H5O	O
2	C5H5	O2	C5H5OO	
3	C5H5	HO2	C5H4O	H2O
4	C5H5	HO2	C5H5O	OH
5	C5H5	O	C4H5(T)	CO
6	C5H5	O	C5H4O	H
7	C5H5	O	C5H5O	
8	C5H5	OH	C5H4OH	H
9	C5H5	OH	C5H5OH	
10	C5H5	OH	C5H5O	H
11	C5H5	OH	C4H6(T)	CO
12	C5H5O		C4H5(T)	CO

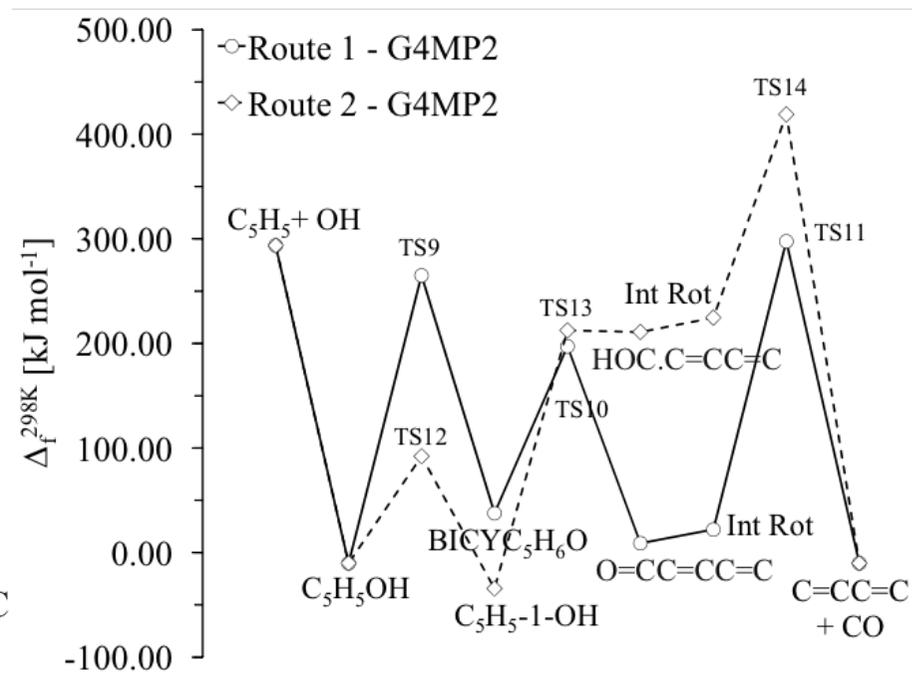
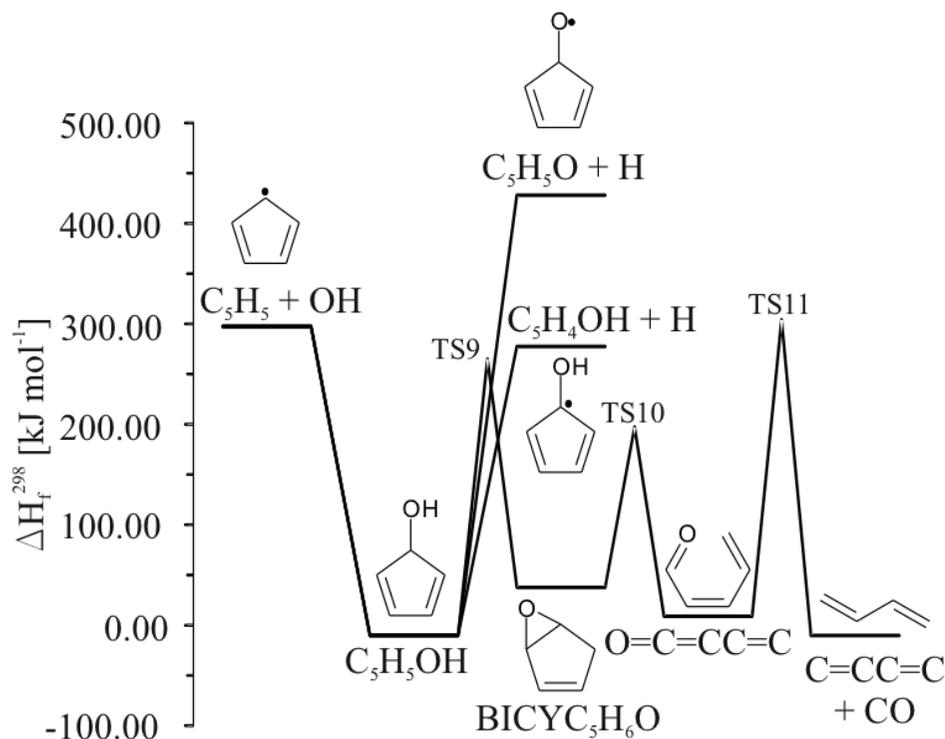
- Rate data for two channels to be highlighted.

## The Oxidation of CPDyl via HO<sub>2</sub>



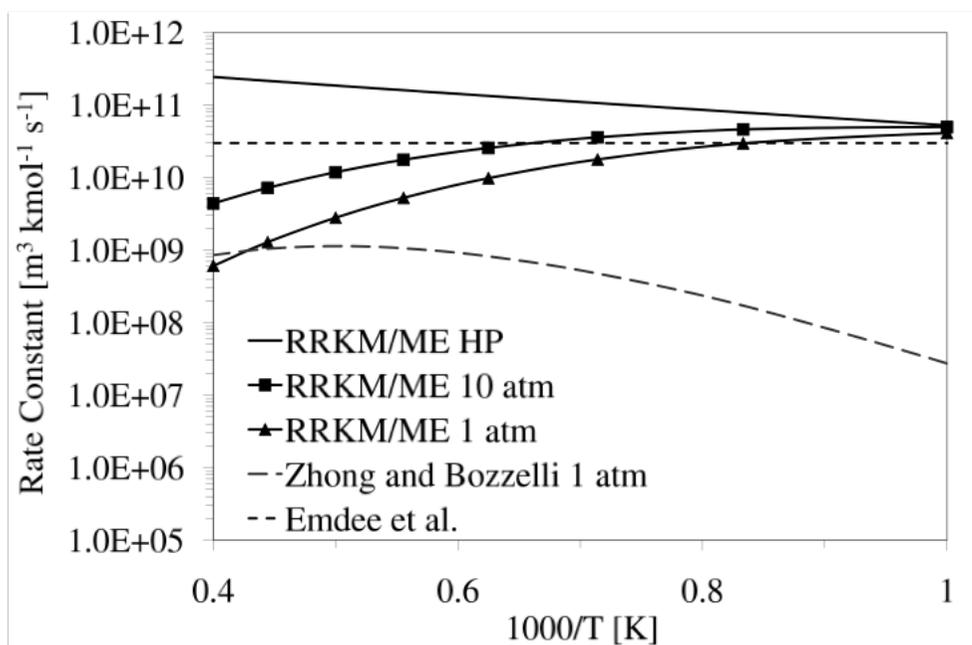
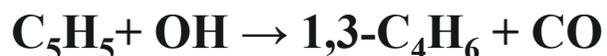
- ❑ A calculation of the branching ratio for proceeding from the initial adduct (C<sub>5</sub>H<sub>5</sub>OOH) suggests that the route via TS2 is insignificant (3-4 orders of magnitude).
- ❑ The RRKM/ME value shown is the HP limit. Pressure fall-off can be estimated via the virtual transition state.
- ❑ The reaction is key for the dynamics of CPD oxidation around 1200 K.

## Potential Energy for $C_5H_5+OH$ Reactions

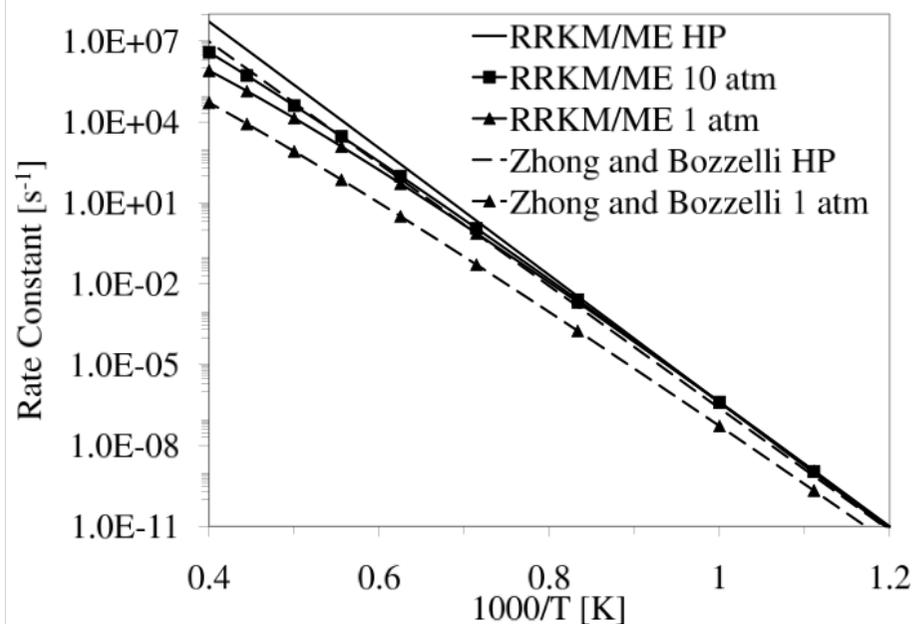
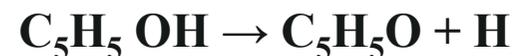


- ❑ No previous in depth study of the PES of the reaction  $C_5H_5 + OH \rightarrow C_4H_6(T) + CO$ .

## Examples of $C_5H_5+OH$ Reactions

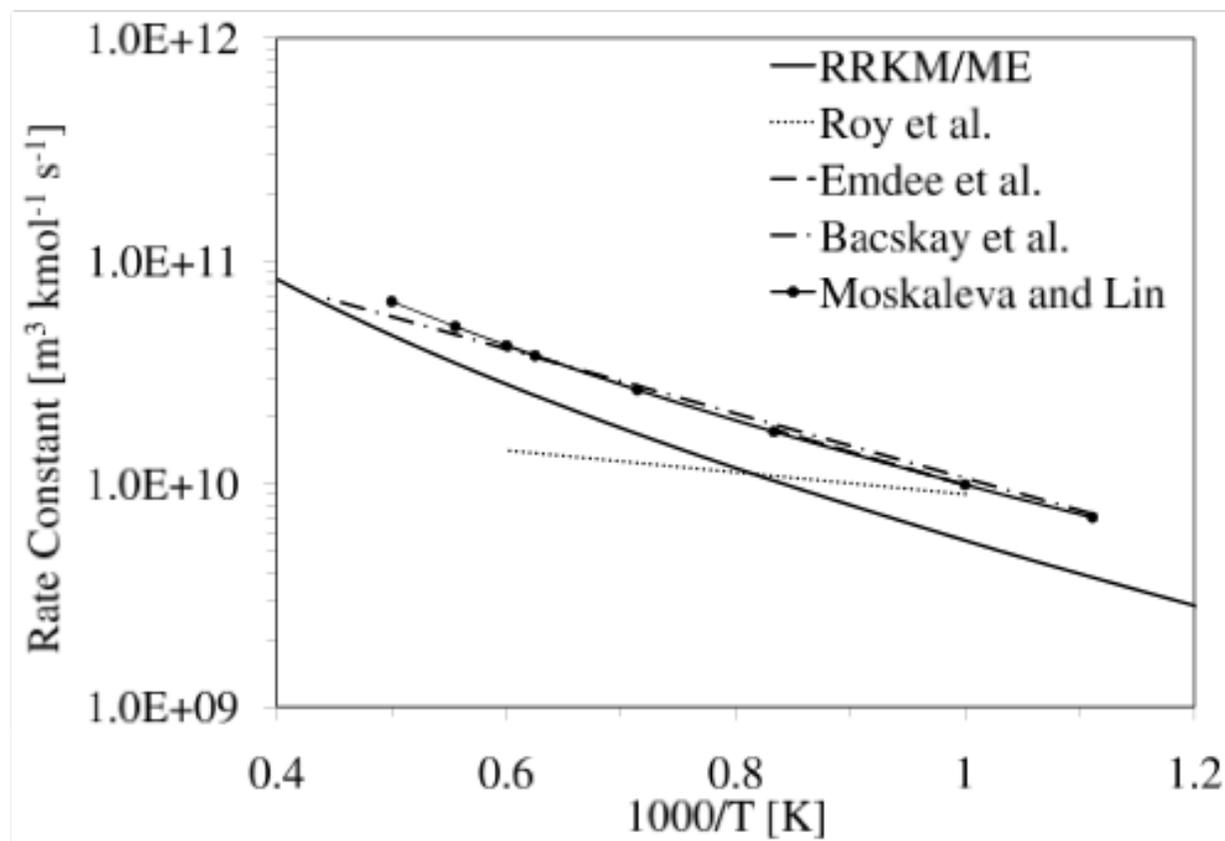


- The reaction turns out to be the most important channel leading to  $1,3-C_4H_6$  and oxidation steps leading to  $1,3-C_4H_5$  have a dominant influence on  $C_4H_4$ .



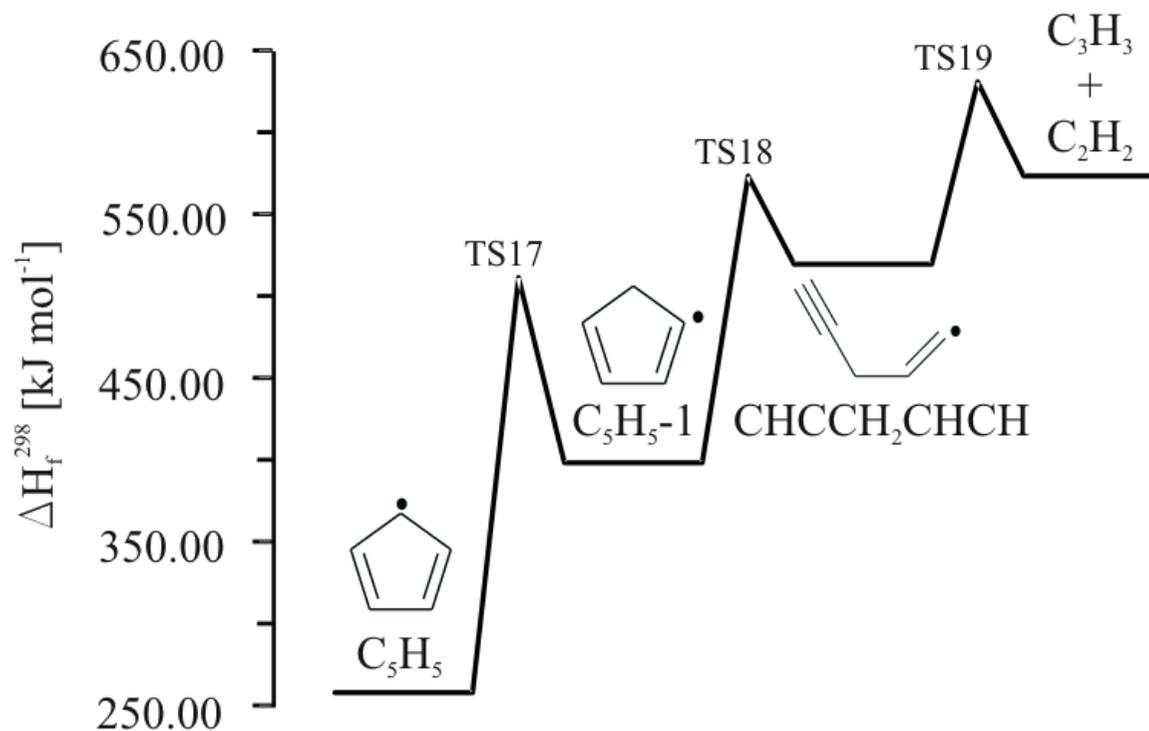
- The reaction is comparatively slow – The Zhong and Bozzelli HP limit close to the current 10 atm value.

## Sample Reaction $\text{C}_5\text{H}_6 + \text{H} \rightarrow \text{C}_5\text{H}_5 + \text{H}_2$



- The above reaction has an initial transition state so the current RRKM/ME determination is probably reasonable.

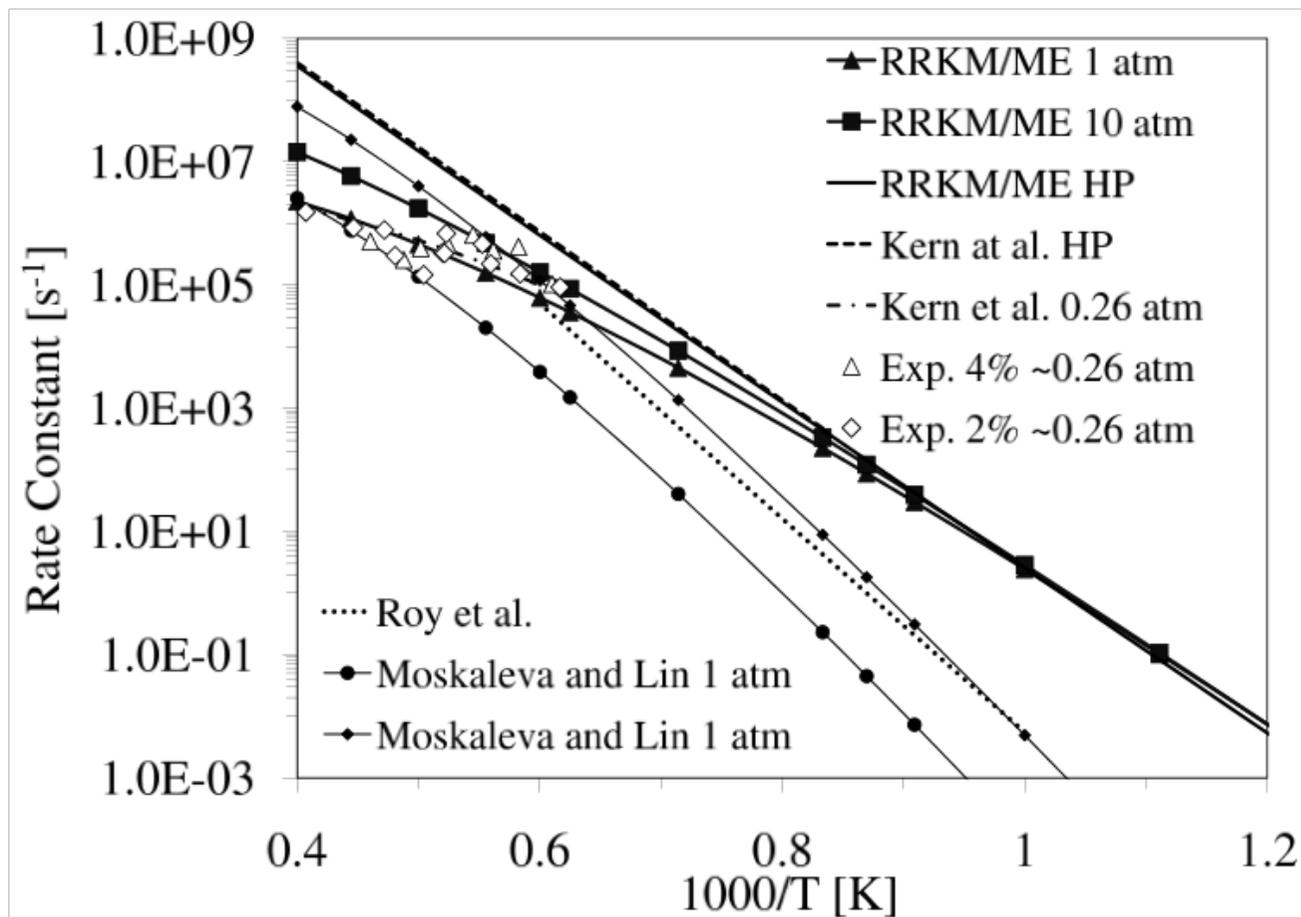
## Sample Reaction $C_5H_5 \rightarrow C_3H_3 + C_2H_2$



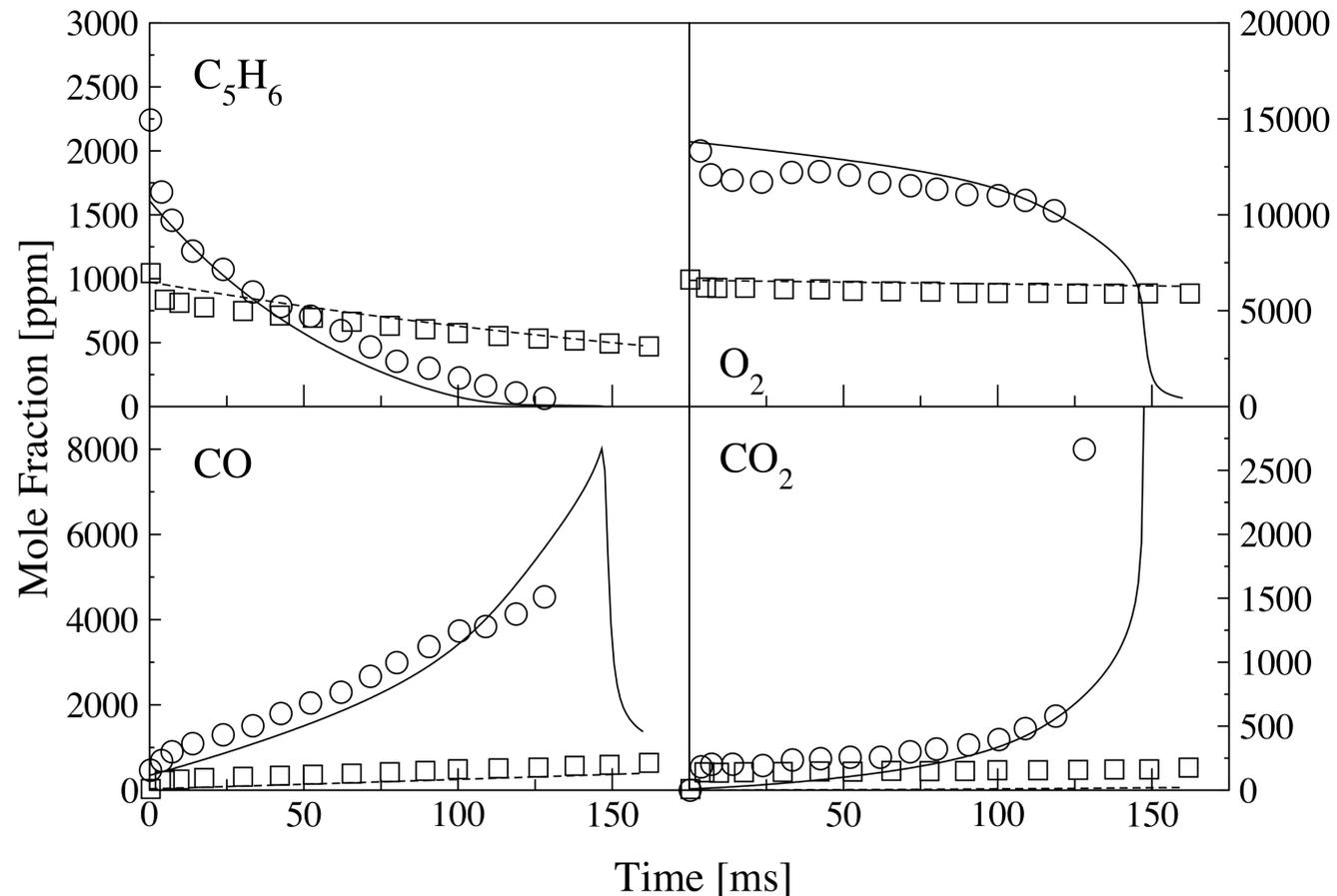
- ❑ The above reaction has an initial transition state (TS17) that has been identified as rate determining by Moskaleva and Lin (2000) amongst others.
- ❑ Reaction identified as of key importance in combustion applications. Energies determined at the G4 level.

## Sample Reaction $C_5H_5 \rightarrow C_3H_3 + C_2H_2$

- The two Moskaleva and Lin (2000) values refer to forward and reverse rates.
- The G4 level value for the rate determining barrier is 22 kJ/mol lower than estimated by Moskaleva and Lin (2000).

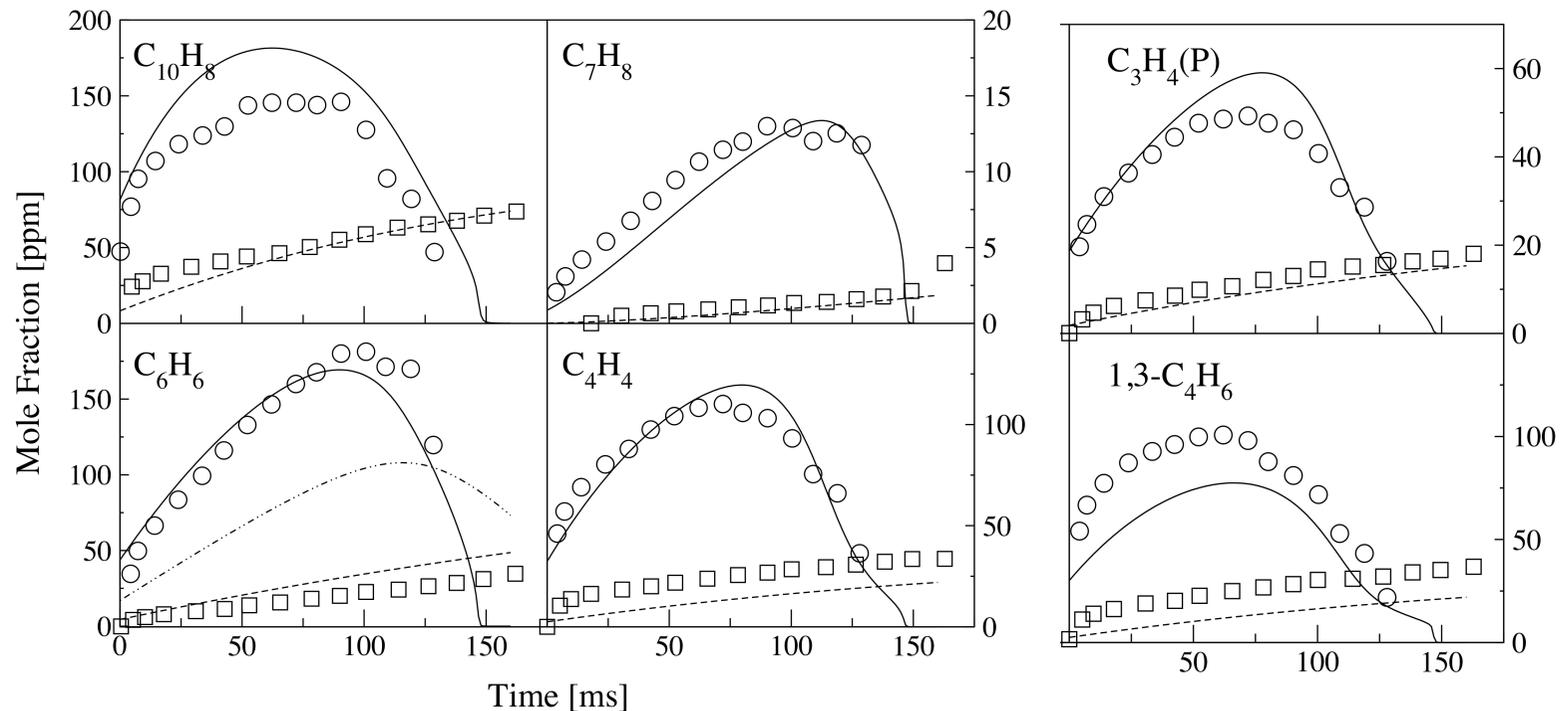


## CPD Oxidation



- Concentration profiles during CPD oxidation in a flow reactor.  $\Phi = 1.03$  (2243 ppm of fuel,  $P = 1$  atm,  $T = 1198$  K) and  $\Phi = 1.03$  (1051 ppm of fuel,  $P = 1$  atm,  $T = 1148$  K) (Butler and Glassman 2009) and the lines is current simulation.

## CPD Oxidation



- Conditions as per previous slide. The formation of C<sub>4</sub>H<sub>4</sub> and 1,3-C<sub>4</sub>H<sub>6</sub> is almost completely dominated by oxidation reactions and the current rates have been applied.
- Symbols are measurements (Butler and Glassman 2009) and lines computations. The dot-dashed line obtained with the Moskaleva and Lin (2000) reverse rate.

## The Prospects for Targeted Simplifications

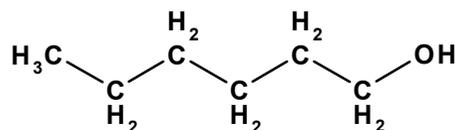
- ❑ In some cases significant reduction can be achieved by automated methods in other cases it is necessary to introduce conceptual ideas in order to achieve the desired level of simplification.
- ❑ Such simplifications are dependent upon the availability of detailed chemical kinetic data for estimation of rate parameters and on the use of experimental and/or computational results obtained in the regime of interest for validation purposes.
- ❑ The NTC region is a particular issue and simplified sub-models arguably of particular value.
- ❑ The issue is here addressed through the introduction of a characteristic reactive site approach combined with systematic reduction with results presented for n-heptane.

## The n-Heptane System

- Thermodynamic data was produced using the G3B3 method for C<sub>7</sub> based species including heptanol, derivatives and radicals. Examples given below.

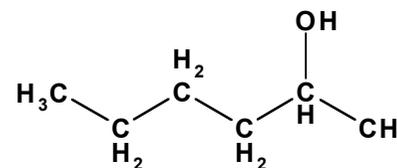
**1-Heptanol**

$$\Delta_f H_{298} = -339.25 \text{ kJ/mol}$$



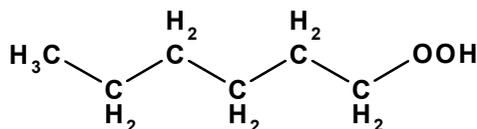
**2-Heptanol**

$$\Delta_f H_{298} = -357.49 \text{ kJ/mol}$$



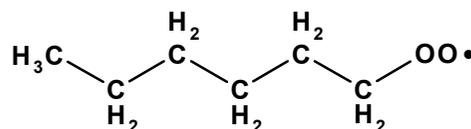
**Heptane-1-hydroperoxide**

$$\Delta_f H_{298} = -266.60 \text{ kJ/mol}$$



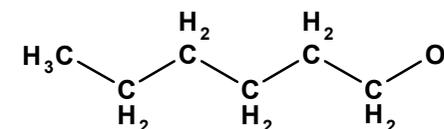
**Heptane-1-peroxide**

$$\Delta_f H_{298} = -127.50 \text{ kJ/mol}$$



**Heptanal Radical**

$$\Delta_f H_{298} = -122.24 \text{ kJ/mol}$$



## Low to Medium Temperature n-Heptane Mechanisms

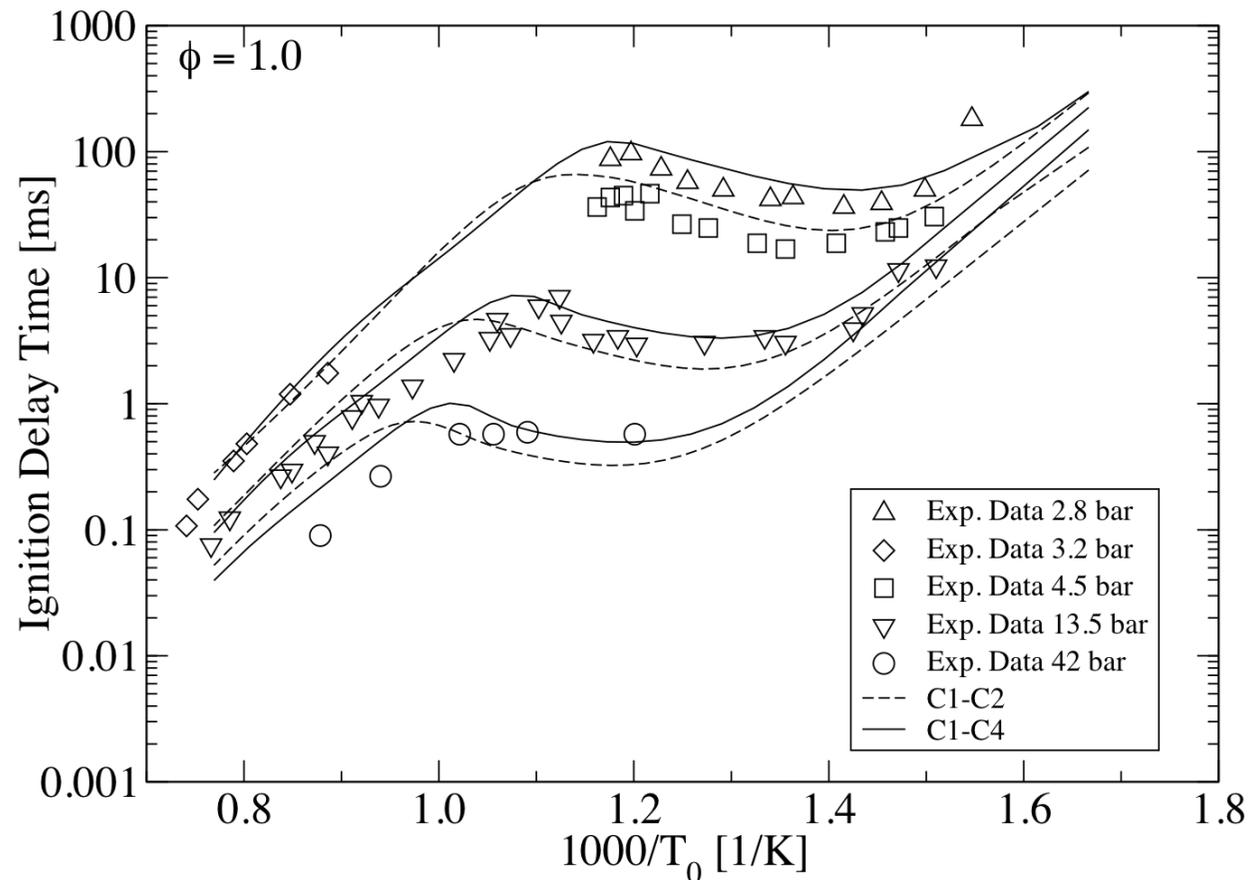
- ❑ Simplified chemical kinetic mechanisms describing the auto-ignition characteristics of n-heptane have been formulated with rate parameters based on work by established groups (e.g. Westbrook and co-workers).
- ❑ The temperature regime  $700 < T \text{ (K)} < 1200 \text{ K}$  was considered along with pressures in the range  $3 < P \text{ (atm)} < 50$ .
- ❑ The mechanism is of particular relevance to technologies where auto-ignition plays a potentially significant part.
- ❑ The reduced low temperature mechanism was based on the extraction of 9 characteristic steps featuring 6 additional species from a comprehensive mechanism featuring 1000+ species.
- ❑ The corresponding skeletal mechanism comprises around 100 chemical species.

## Low to Medium Temperature n-Heptane Mechanisms

### Test Cases for n-Heptane

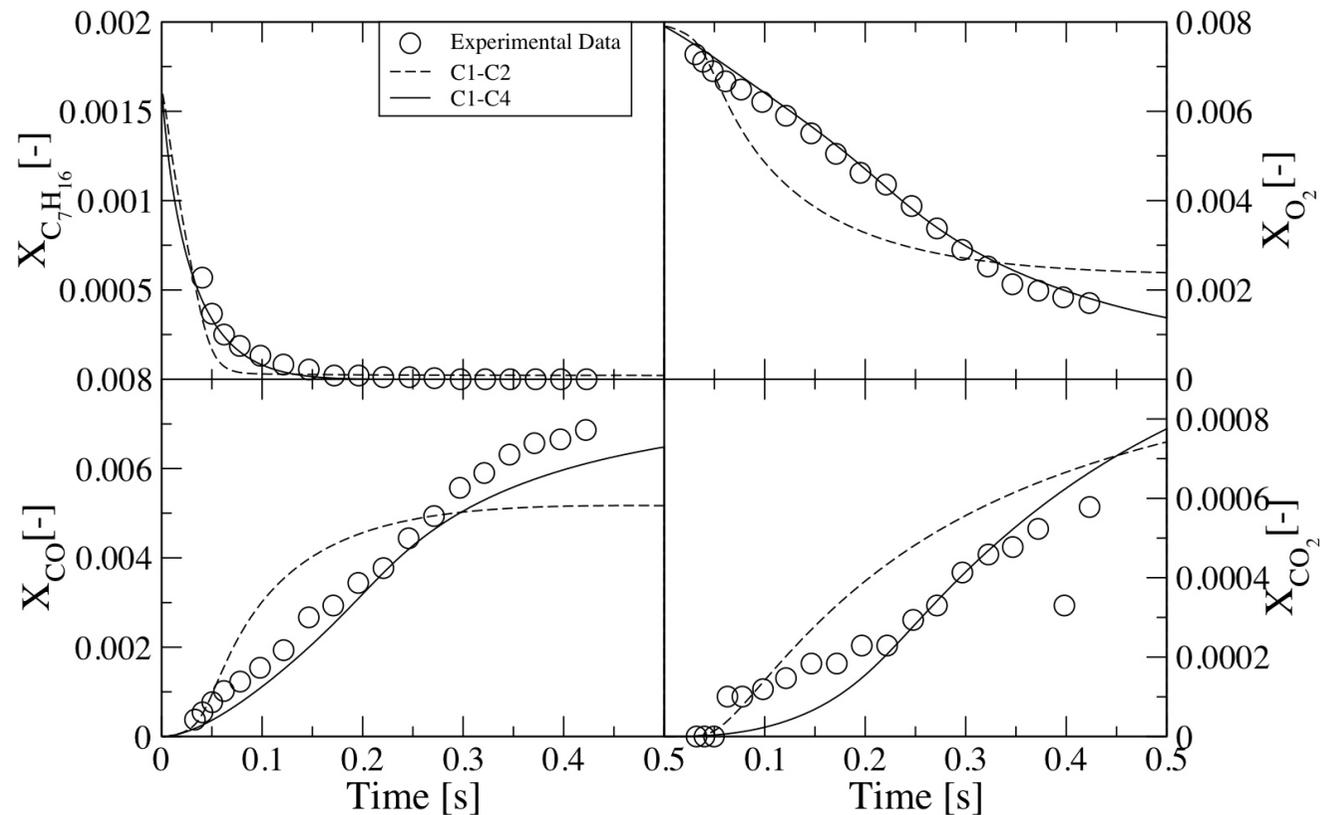
- ❑ Shock tube data from Ciezki and Adomeit (1993) with  $\Phi = 0.5 - 2.0$  in air,  $T = 625 - 1250$  K and  $P = 3.2 - 42$  bar among others.
- ❑ Flow reactor data from Held et al. (1997) with a lean PFR at  $\Phi = 0.79$ ,  $T = 940$  K and  $P = 1$  atm and a rich PFR at  $\Phi = 2.27$ ,  $T = 1085$  K and  $P = 1$  atm.

## Low to Medium Temperature n-Heptane Mechanisms



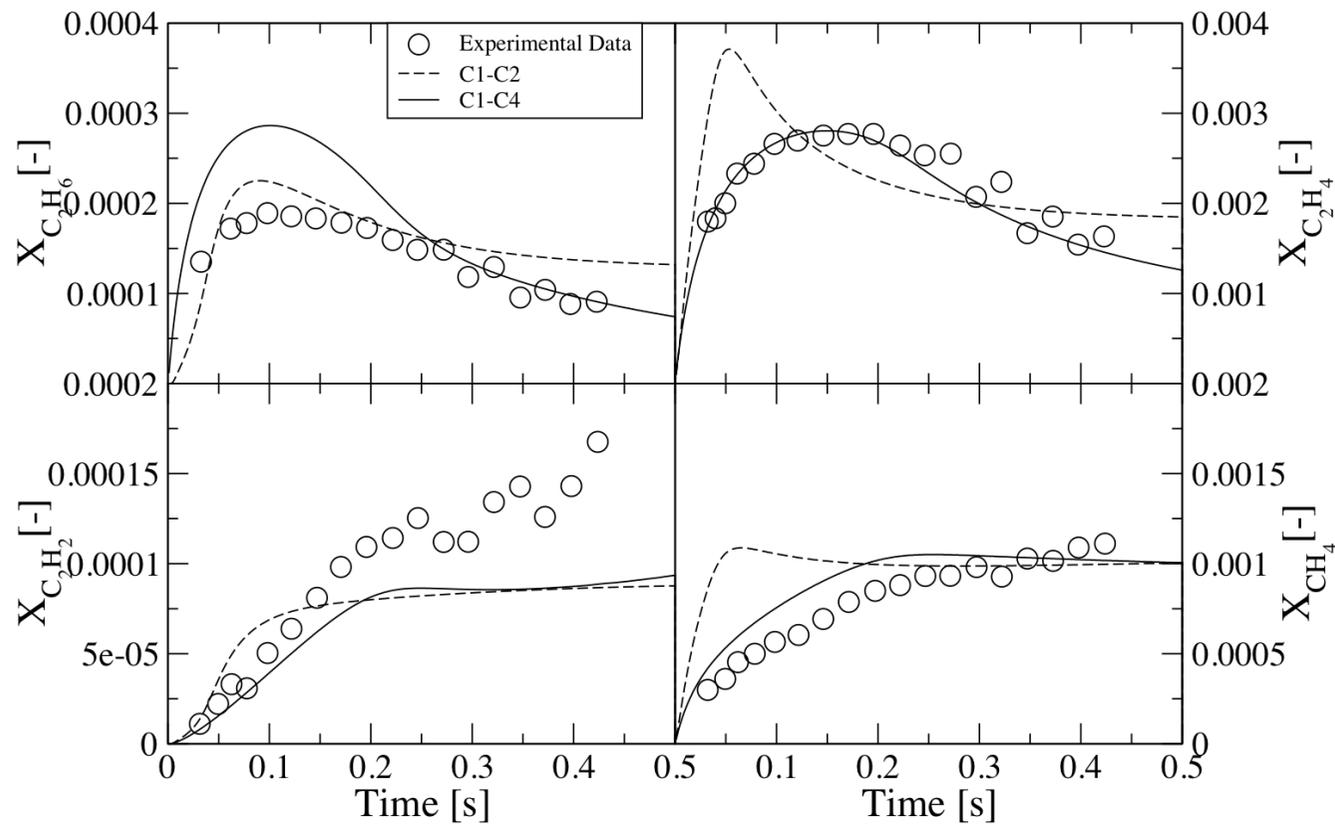
- Ignition delay times obtained with simplified chemistry for n-heptane coupled with C<sub>1</sub>-C<sub>2</sub> and C<sub>1</sub>-C<sub>4</sub> sub-mechanisms for a stoichiometric mixture.

## Low to Medium Temperature n-Heptane Mechanisms



- Flow reactor data from Held *et al.* (1997) for a rich PFR at  $\Phi = 2.27$ ,  $T = 1085$  K and  $P = 1$  atm.

## Low to Medium Temperature n-Heptane Mechanisms



- Flow reactor data from Held *et al.* (1997) for a rich PFR at  $\Phi = 2.27$ ,  $T = 1085$  K and  $P = 1$  atm.

## Summary

- ❑ 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.
- ❑ Thermodynamic data bases have been substantially updated for a wide range of compounds, currently 100+ species, and a semi-automatic technique has been formulated, evaluated and updated to include G4/G4MP2 based methods.
- ❑ Particular attention has been given to the critical cyclopentadiene system and a key oxidation reactions studied. The method has also been assessed with respect to pyrolysis reactions.
- ❑ 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.
- ❑ In particular, use will be made of experimental data and the developed alkane chemistry in the context of simplified approaches for the NTC region.