

Development of High-Pressure Rate Rules for Alkyl + O₂ Reactions

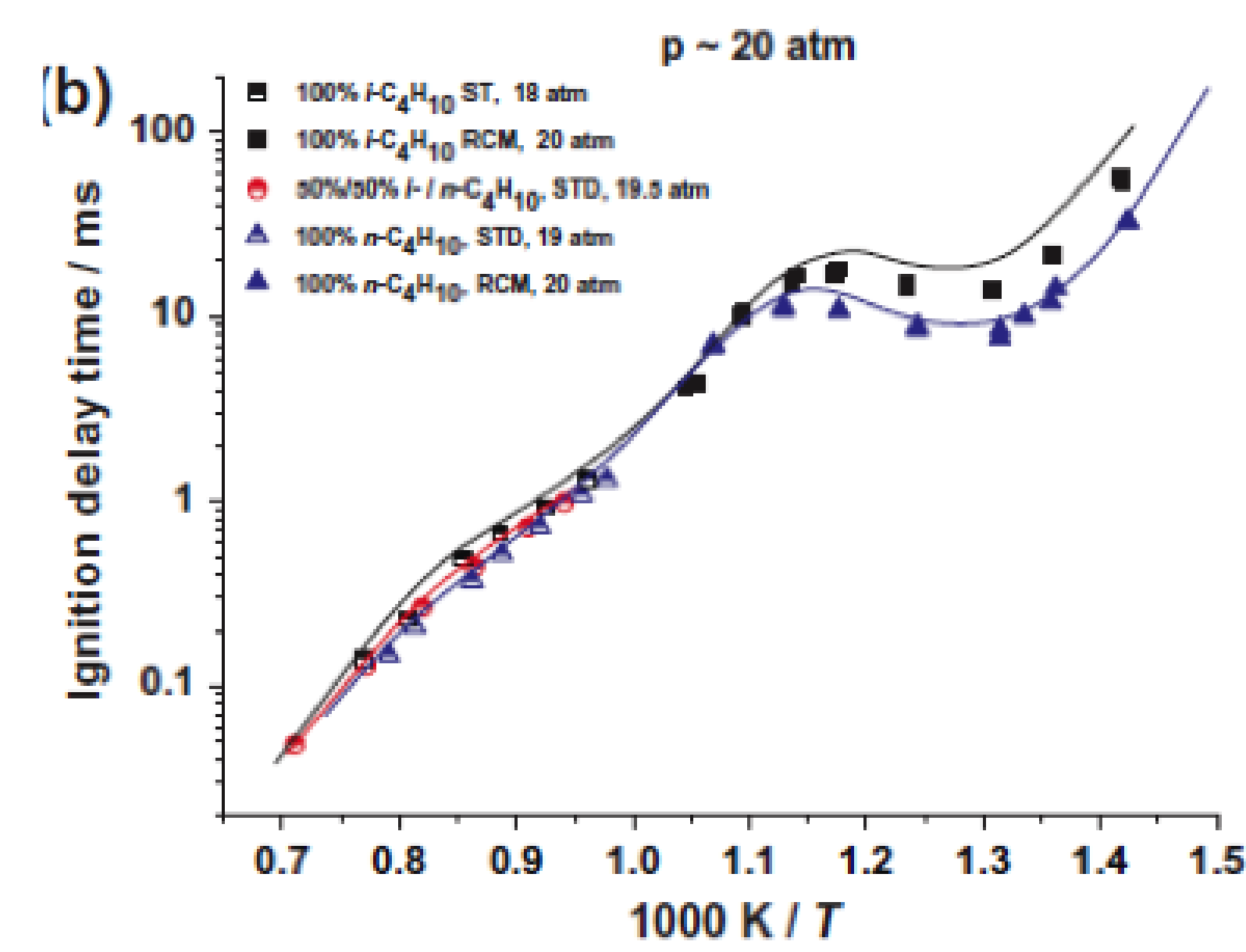
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Alternative Fuels Behave Differently Than Conventional Fuels



D. Healy et al., *Comb. Flame*, 157 (2010) 1540.

The need for increased engine performance / efficiency and new alternative fuels has proven kinetic modeling studies to be a valuable tool to assess new fuels and find optimal operating conditions.

Research is geared toward verifying rate constants in key reaction pathways for low temperature hydrocarbon oxidation mechanisms.

Obstacles to Overcome

- Thousands of species involved in each combustion
- Tens-of-thousands of reaction pathways available
- Limited experimental data available
- High-level calculations restricted to small molecules

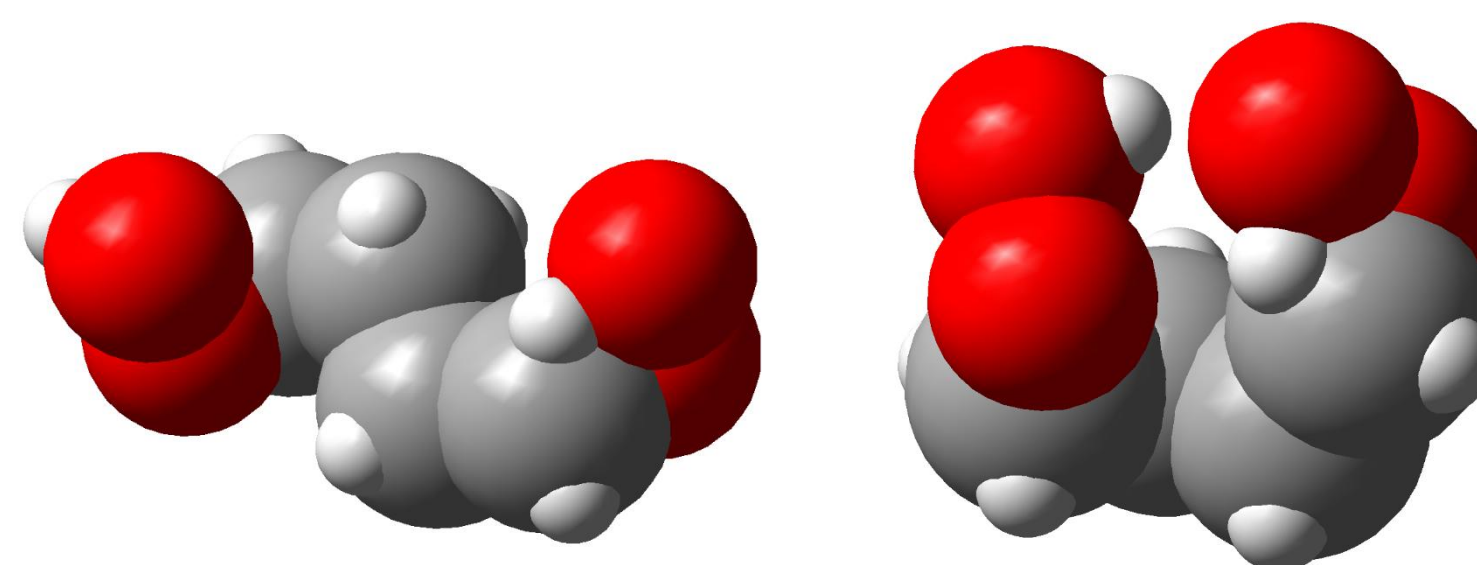
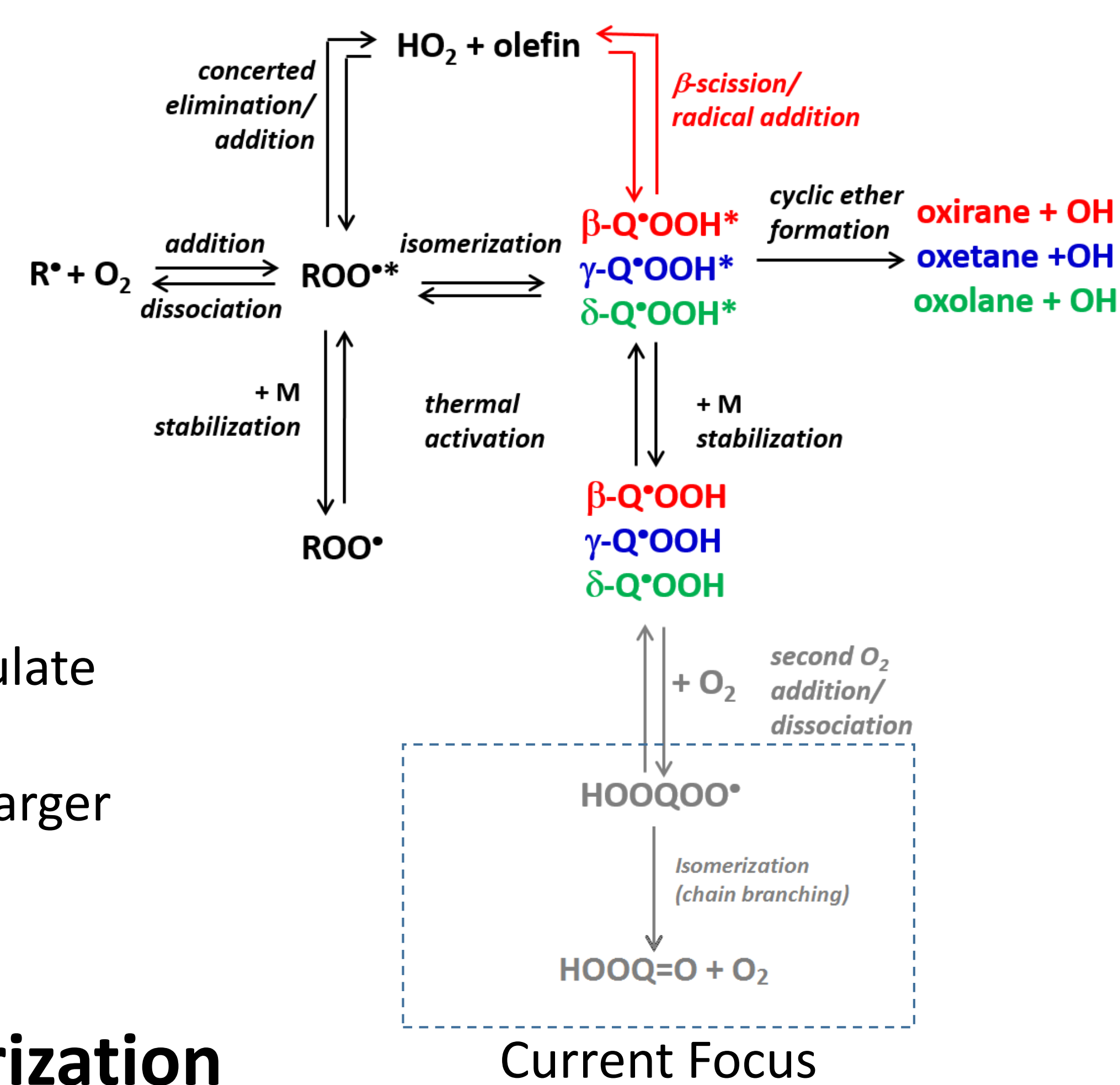
Overall Strategy

Use *ab initio* computational methods to calculate rate constants for smaller species, and then generalize the results on a per-site basis for larger species.

Building the Starting Material:

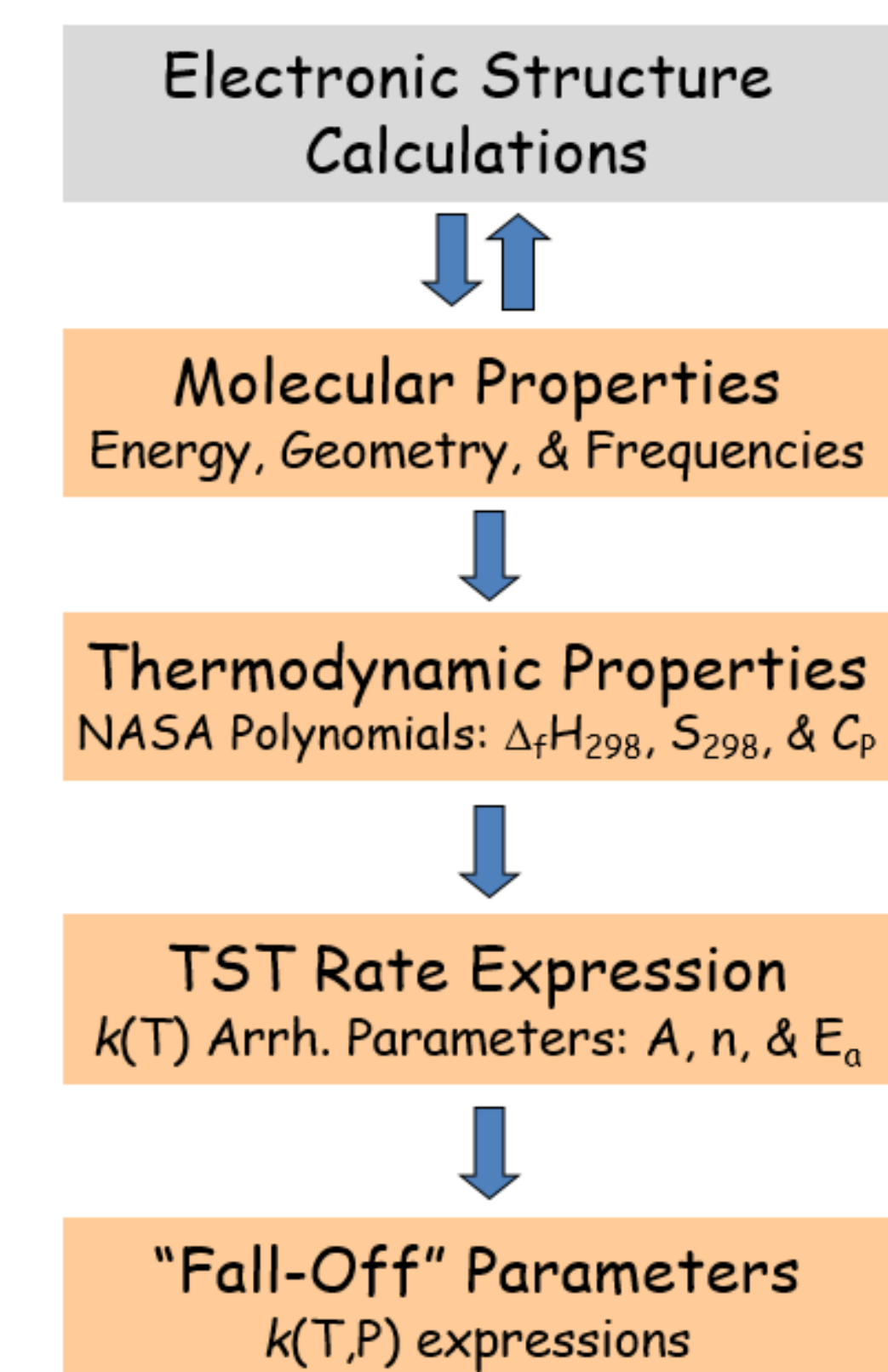
Second Addition of O₂ and Isomerization

- Initial build is not always the *correct* geometry
- Incorrect geometries lead to inaccurate thermodynamic properties
- Without a good foundation, subsequent calculations aren't any good!



Difference in CBS-QB3 Free Energy: 0.263554 kcal/mol

Computational Methodology



CBS-QB3 as implemented in Gaussian provides:

- DFT geometry / frequencies
- Multistep energy calculations

Customized Software:

- Statistical mechanics
- Hindered-Rotor potential energy scan
- Canonical Transition State Theory

Outputs either validate or add to thermodynamic/kinetic databases to provide fit data

Example of Rate Rule Development

Canonical Transition-State Theory provides high-pressure rate coefficients

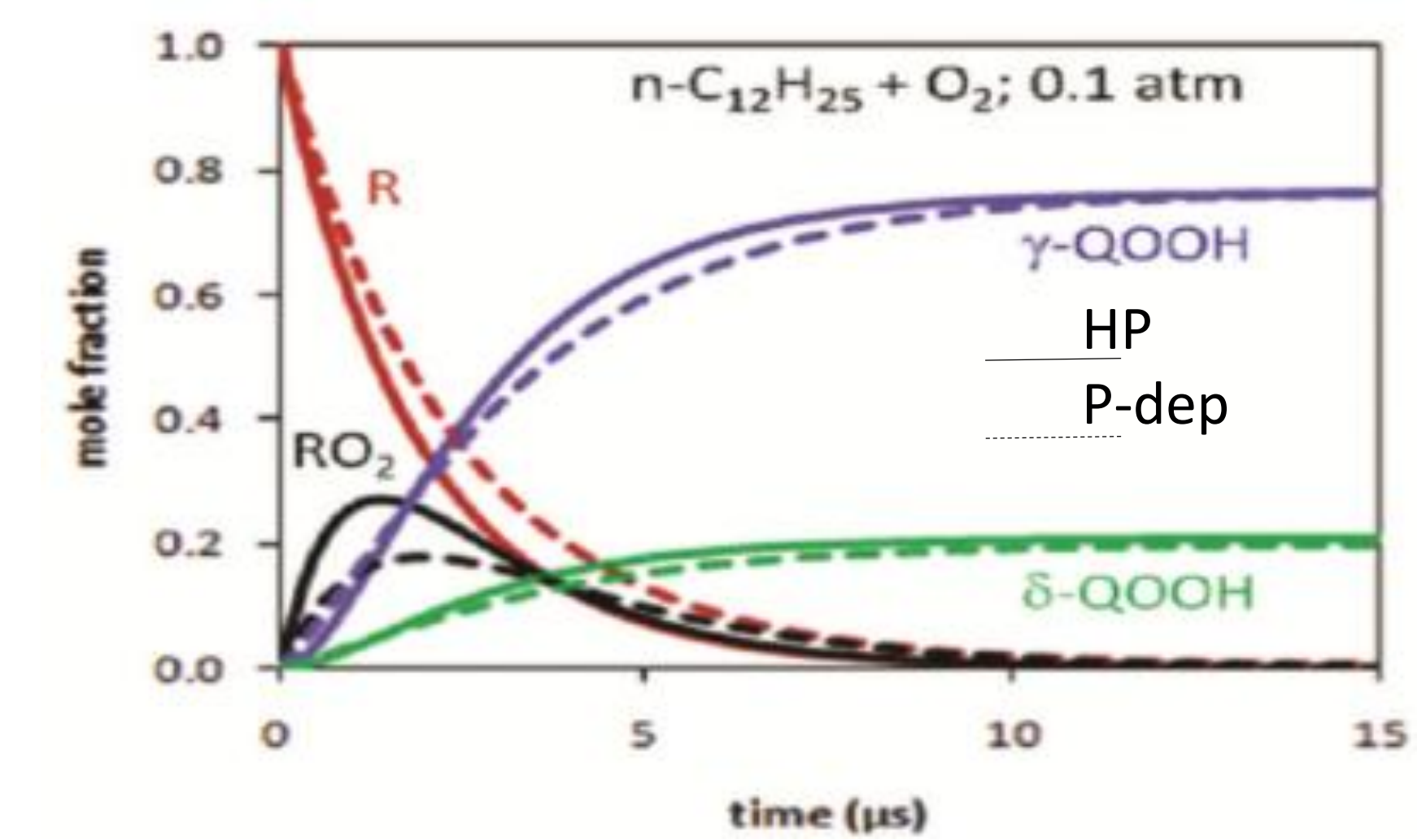
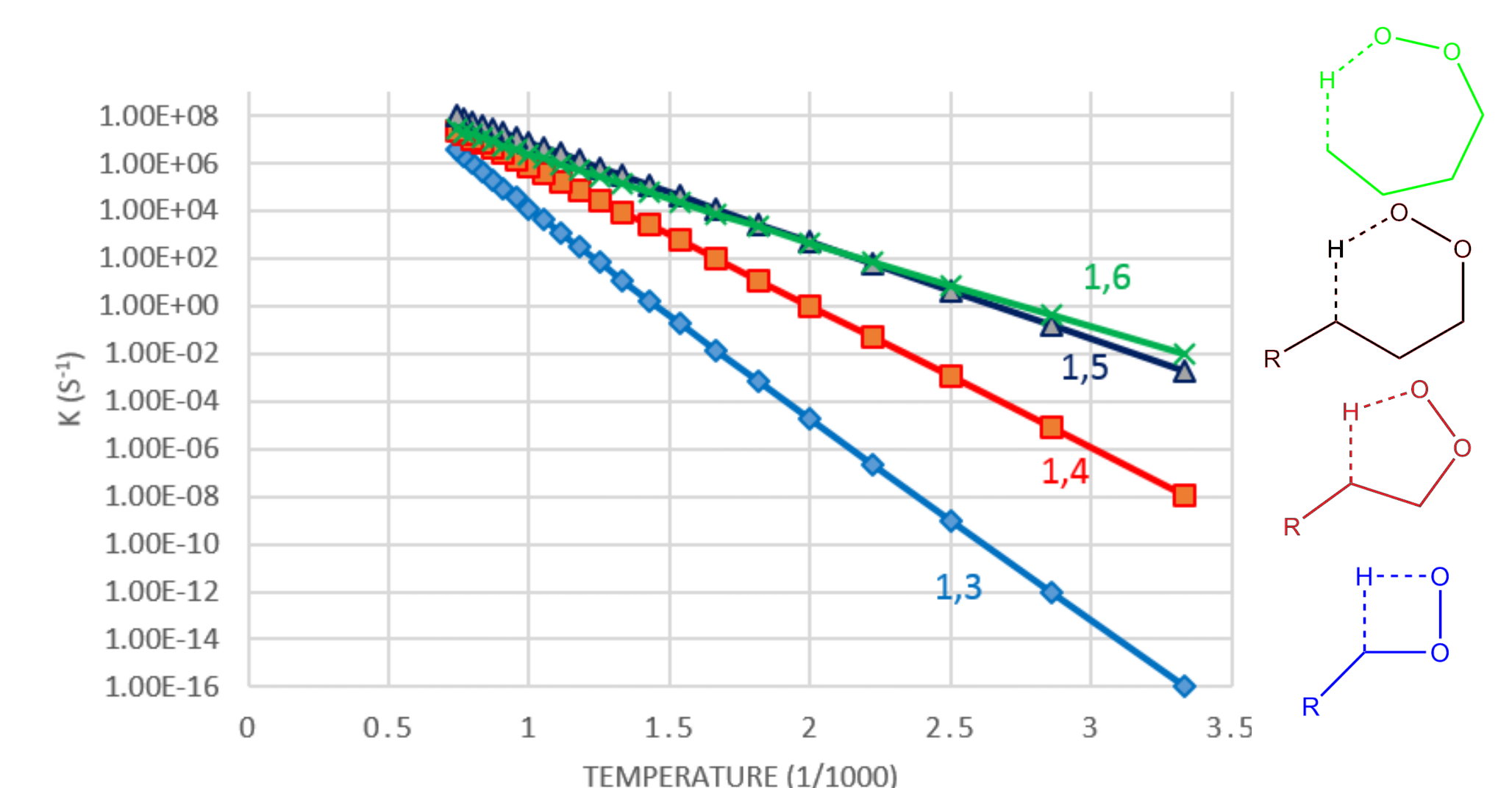
Rate constants are calculated over temperature range from 300 K – 1500K and fit into modified Arrhenius expression

High-P rate constants used in QRRK/MSC analysis to obtain T- and P-dependent rate constants.

Conc.-time profiles calculated using high-P and P-dependent mechanism

Results suggest that the direct use of HP rate rules is sufficient to describe reactions under most conditions relevant to combustion/ignition engine problems

Future research efforts are directed toward refining data by improving thermodynamic profiles for reactants and transition states



Villano et al., *J. Phys. Chem. A* 115 (2011) 13425.

Villano et al., *J. Phys. Chem. A* 115 (2012) 5068.

Villano et al., *J. Phys. Chem. A* 115 (2011) 13425.

