Theoretical Chemical Kinetics
and
Combustion Modeling

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Scope of Research

- Theoretical Chemical Kinetics
  - reactions over multiple, interconnected potential wells
  - dissociation of weakly bound free radicals
  - collisional energy transfer in highly excited molecules (collaboration with Ahren Jasper)

- Combustion of Bio-derived Fuels (collaboration with Judit Zádor)

- The Formation of Aromatic Compounds, Polycyclic Aromatic Compounds, and Soot in Flames of Aliphatic Fuels
Theoretical Methods

1. Potential Energy Surfaces
   **Pathways** – H transfers, ring formation, etc.
     – manual transition-state searches
     – B3LYP/6-311++G(d,p) geometries and vib. freq.
   **Energies** – rQCISD(T)/dz,tz or rQCISD(T)/tz,qz extrapolated to $\infty$
     – “multireference correction” if T1 diagnostic exceeds ~ 0.02
     – uncertainties <~ 1 kcal/mol for minima
     – <~ 2 kcal/mol for saddlepoints

2. Microscopic Kinetics – Transition-State/RRKM Theory
   **Barriers** – rigid-rotor / harmonic-oscillator (+ hindered rotors for torsional modes) conventional TST
   **Barrierless** – Variable Reaction Coordinate TST

3. Collisional Energy Transfer – single-exponential-down model

4. Macroscopic Kinetics
   **Master Equation** – determine phenomenological rate coefficients
Electronic Structure Methods – Comparison with Lynch and Truhlar (2001)

Nth Smallest Error

Absolute Error / kcal mol⁻¹

UB3LYP // UB3LYP
uMP2 // uMP2
rQCISD(T) // uB3LYP
rMP2 // uMP2
rCCSD(T) // uB3LYP
rQCISD(T) // uMP2

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Collisional Energy Transfer in Unimolecular Reactions

- Ultimate goal is to place ME input for $P(E,J;E',J')$ on equal footing with that for $k(E,J)$
- Start with single-channel dissociations ($\text{CH}_4$) and use Miller-Klippenstein-Raffy solution to the 2-d ME to calculate rate constants $k(T,p)$
- Need only $<\Delta E_d>$ at dissociation limit averaged over rotations
- Direct classical trajectories using MP2/ aug’-cc-pVDZ potentials
CH$_4$-He Intermolecular Potential

![Graphs showing energy vs. R$_{CH_4}$ for different potentials: MP2/aug-cc-pVDZ, exp/6, LJ-A, and LJ-B.](image)
Energy Transfer Parameters for 8 Different Colliders

\[ \langle \Delta E_d \rangle, \text{cm}^{-1} \]

\[ \langle \Delta E^2 \rangle^{1/2}, \text{cm}^{-1} \]

\( T, \text{K} \)
Influence of Anharmonicity at Low Pressures

$M = \text{Ar}$

$k_0$, cm$^3$ molecule$^{-1}$ s$^{-1}$

$T$, K

$p$, atm

1. Present
2. Scaled
3. JPCRD (2005)
4. Hartig (1971)

$10^6 k$, s$^{-1}$

1073 K, 1098 K, 1123 K, 1148 K

JPCRD, Present, Scaled
n-propanol H abstractions
i-propanol H abstractions
Evans-Polanyi Plot
n-isomer Radicals: Dissociation and Isomerization

![Graph showing energy changes for various reactions involving radicals.](image)
i-isomer Radicals: Dissociation and Isomerization

\[
\begin{align*}
\text{0.0 propene + OH} & \quad E = -1.9 \\
\text{vdW} & \quad E = -2.2 \\
\text{-2.2 propen-2-ol + H} & \quad E = -2.2 \\
\text{-9.0 vinyl alcohol + CH}_3 & \quad E = -9.0 \\
\text{-13.9 acetone + H} & \quad E = -13.9 \\
\text{-19.0 acetaldehyde + CH}_3 & \quad E = -19.0
\end{align*}
\]
n-propanol + HO₂
Dissociation of \( \beta_i \text{ Radical} \)

propene + OH
vinyl alcohol + CH\(_3\)

Dunlop and Tully (1993)
750 Torr He
$i$-propanol + OH

This work, Dunlop and Tully, Galano et al.