Ab Initio Kinetics:
From the Schrodinger Equation to Chemical Kinetic Mechanisms

Stephen J. Klippenstein

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From Electrons to Devices

Combustion is a Classic Multi-Scale Modeling Problem

- Electrons – Electronic Schrodinger Equation; Potential Energy Surfaces
- Nuclei – Nuclear Schrodinger Equation; Rovibrational Energies
- Microscopic – TST; Microcanonical Rate Constants
- Macroscopic – Master Equation; Elementary/Phenomenological Rate Constants
- Many Different Reactions – Chemical Mechanisms
- Reactions + Fluid Dynamics – ODE Solvers; Chemkin; Ignition Delay, Flame Speeds, Species Profiles
- Devices – DNS, LES, RANS; CFD in complex geometries with chemically reacting flows; Massive Parallelism; currently 10^4 nodes; future 10^6 to 10^9 nodes.

Need: Rate constants for 1000’s of reactions

Many reactions have never been studied experimentally or theoretically
Predictive Automated Combustion Chemistry
Exascale Next Generation Fuel Simulation CODE

- Integrated Suite of Massively Parallel Computer Codes for Fuel System to Obtain Industry Transforming Improvement in Fidelity of Simulations
- Uncertainty Driven Iterative Theoretical/Computational Refinement of Mechanisms
- Parallelization via Simultaneous Characterizations of the Reactions in the Mechanism
- Couple RMG, EStokTP (MESS, KinBot, Gaussian/Molpro/NWChem, …), DRGASA, Dakota, NEK5000
- Fuels Team – Bair, Green, Jasper, Klippenstein, Lu, Wagner, Wozniak, Zador
- 0.8 Million/Yr
Outline

1. Ab Initio Electronic Structure Theory
   a) HF and Single Reference Methods
   b) Density Functional Theory
   c) Composite Methods
   d) MultiReference Electronic Structure Theory

2. Pressure Independent Rate Theory
   a) Transition State Theory
   b) Abstractions
   c) Barrierless Reactions (Radical-Radical)
   d) Radical-Molecule Reactions
   e) Dynamics

3. Pressure Dependent Kinetics & the Master Equation
   a) Single Well; Single Channel
   b) 2DME
   c) Multiple Wells; Multiple Channels
   d) Non-Thermal Effects
Acknowledgements
The research reported here has been supported by various grants from DOE-BES.
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• Code development work was supported by Mark Pederson through the Material Genome Initiative and Computational Theoretical Chemistry.
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• The Combustion EFRC provided motivation for a variety of the theoretical developments and applications.
Work on expanding these calculations to take advantage of exascale computational environments is just beginning through support from DOE-ASCR.
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Lecture 1: Introduction to Electronic Structure Theory

Stephen J. Klippenstein
Born-Oppenheimer Approximation

- Treat Electrons Separately from Nuclei
- Electron Mass \( \sim 1/2000 \) Mass of Proton
- Electrons Move Rapidly, Nuclei Move Slowly
- Adiabatic Approximation – Electrons \([\mathbf{r}, \psi_e(\mathbf{r}), E_{\text{elec}}]\) Continuously Adjust to Position of Nuclei \((\mathbf{R})\)
- Big Spacing Between Electronic Energies – Focus on Ground Energy
- Solve Electronic Schrodinger for Fixed Nuclear Position -> Potential Energy Surface; \( E_{\text{elec}} = V(\mathbf{R}) \)
- Nuclei Move Under Force = \(-dV(\mathbf{R})/d\mathbf{R}\)
- Quantized Nuclear Motion -> \( \Psi_{\text{vib rot}}(\mathbf{R}) \) and \( E_{\text{vib rot}} \)
- At Combustion Temperatures Many Rovibrational States Accessible => Classical Almost Good; Mixed Quantum & Classical
- Thermal Chemistry – Large Scale Conversion of Nuclear Positions on Ground Electronic State
- Configurations With \( \sim \) Degenerate Electronic States Are Interesting
- NonAdiabatic Dynamics, InterSystem Crossing, Transition States
Introduction to Electronic Structure Theory

1. Hartree-Fock (HF)
2. Basis Sets
3. Second-Order Moller Plesset Perturbation Theory (MP2)
4. Singles and Doubles Configuration Interaction (CISD)
5. Coupled Cluster Theory [CCSD(T); QCISD(T)]
6. Correlation Consistent Basis Sets
7. Density Functional Theory
8. High Level Schemes

- Introduction to Computational Chemistry, Frank Jensen, Wiley
- Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory; Attial Szabo and Neil S. Ostlund
Hartree-Fock (HF)

Electronic Schrodinger Equation

\[ \mathbf{H}_{\text{elec}} \Psi_{\text{elec}} = \mathcal{V} \Psi_{\text{elec}} \]

\[ \mathbf{H}_{\text{elec}} = -\sum_j \left( \frac{1}{2} \nabla_j^2 + \sum_a \frac{Z_a}{r_{ja}} \right) + \sum_{j>k} \frac{1}{r_{jk}} + \sum_{b>a} \frac{Z_a Z_b}{R_{ab}} \]

\[ \Psi_0 = \left| \phi_1(r_1) \cdots \phi_N(r_N) \right| \]

\[ V_{\text{mean}}(r_1) \sim \sum_{k \neq 1} \int d \mathbf{r}_k \phi_k^*(\mathbf{r}_k) \frac{1}{r_{1k}} \phi_k(\mathbf{r}_k) \]

\[ (h_i + V_{\text{mean}}(r_1)) \phi_j(r_1) = \varepsilon_j \phi_j(r_1) \]

\[ F \phi_i = h \phi_i + \sum_{j \text{occupied}} (J_j - K_j) \phi_i \]

\[ F \phi_i = \varepsilon_{i,j} \phi_j \]

Self-Consistent determination of \( V_{\text{mean}} \) and \( \phi_i \)

\( \phi_k \) = Spin-Orbitals - Molecular Orbitals

\( \Psi_k \) = Configuration State Functions (CSF)

Self Consistent Field (SCF); Mean Field

Iterative

Fock Operator

\( h \) = one electron; \( J \) = Coulomb

\( K \) = exchange

Hartree-Fock Equations

Spin-symmetry

Unrestricted or Restricted
LCAO-MO Expansion

Spin-Orbitals $\phi_i$ are Molecular Orbitals
Expand them in Atomic Orbitals $\chi_\mu$

$$\phi_i = \sum_\mu C_{\mu,i} \chi_\mu$$

Expand Atomic Orbitals in Gaussian Basis Sets

$$\chi_\mu (r, \theta, \phi) = N_{a,b,c} x^a y^b z^c \sum_i d_{\mu i} \exp(-\alpha_i r^2)$$

$a, b, c \Rightarrow s, p, d, \ldots; x, y, z, \text{etc.}
\alpha_i \Rightarrow 1s, 2s, 3s, \ldots$

Polarization Functions
Diffuse Functions
Pople Basis Sets

Sto-3G too small
• minimal basis set - 1 function for each electron
• 3 => each atomic orbital is a fit to 3 Gaussians

3-21G still too small
• Valence double zeta - two basis functions for each valence orbital
• 3 => number of Gaussians for core orbitals
• 2,1 => implies number of Gaussians for 1st and 2nd valence orbitals

6-31G* Smallest basis set to provide semiquantitative accuracy
• Valence double zeta
• * => polarization functions, but only on heavy atoms (C, O, N; not on H)

6-311++G**
• valence triple zeta, polarization & diffuse (+) functions on all atoms

6-311++G(3df,2pd), etc.

Polarization functions strongly affect geometry and energy
Diffuse very important for negative ions and for hydrogen bonding
Higher level schemes employ 6-31G* and larger
Beyond HF and Mean Field

Make wavefunction more general - more CSFs

\[ \Psi = \Psi_0 + \sum_{i,r} c_{ir} \Psi_i^r + \sum_{i,r} c_{ij,rs} \Psi_{ij}^{rs} + \cdots \]

\[ \Psi_{1s} = \left| \phi_s(r_1)\phi_2(r_2)\cdots\phi_N(r_N) \right| \quad \text{Singly Excited} \]

\[ \Psi_{12}^{sr} = \left| \phi_s(r_1)\phi_r(r_2)\cdots\phi_N(r_N) \right| \quad \text{Doubly Excited} \]

\[ \cdots \]

Correlation Energy = Difference From HF

Perturbation Theory

Configuration Interaction

Coupled-Cluster Theory

Single Reference vs. Multiple Reference
Second Order Perturbation Theory - MP2

Rayleigh Schrodinger Perturbation Theory
\[ E = E_0 + V_{00} + \Sigma V_{0i} V_{i0} / (E_0 - E_i) + \ldots \]

Consider sum of Fock operators as reference H

\[
E = E_{HF} + \sum_{i<j} \sum_{r<s} \frac{\langle \Psi_0 | H' | \Psi_{ij} \rangle \langle \Psi_{ij} | H' | \Psi_0 \rangle}{E_{HF} - E_{ij}}
\]

Single Reference

Effect of Single or Double excitations from ground state CSF

Size consistent - Energy of (A+B) = Energy of A + Energy of B

Nonvariational

Ground State only

MPn = oscillatory then diverges

MP3 - considers up to triple excitations

MP4 - considers up to quadruple excitations
Singles and Doubles Configuration Interaction

Consider single or double excitations from HF ground state (CISD)

\[ \Psi = \Psi_0 + \sum_{i,r} c_{ir} \Psi_i^r + \sum_{i,r} c_{ij,rs} \Psi_{ij}^{rs} \]

Not Perturbative

Excited States

Variational

Not size consistent - Energy of (A+B) ≠ Energy of A + Energy of B

Converge to exact answer with triples, quadruples, etc. => Full CI - not practical
Coupled Cluster

CCSD(T) - Gold standard - 2σ Accuracy ~1.0 kcal/mol

\[ \Psi_{CC} = \exp(T)\Psi_0 \] Include excitations to all orders via exponential

\[ T = T_1 + T_2 + T_3 + \cdots \] T_i creates excitations of order i from \( \Psi_0 \)

\[ T_2\Psi_0 = \sum_{i>j; r<s} t_{ij}^{rs} \Psi_{ij}^{rs} \]

CCSD, CCSDT, CCSDTQ, … Truncation of T Expansion

CCSD(T) = CCSD + Perturbative Triples

QCISD(T) ~ CCSD(T) with slightly fewer terms

– conceptually worse but empirically better

Size consistent; Not Variational

T1 diagnostic - Measure of Multireference Effects

<0.02 Closed Shell; <0.03 Radicals; >0.06 Catastrophe
Dunning Basis Sets

cc-pVNZ; \( N=D,T,Q,5, \ldots \)
Correlation-consistent polarized valence \( n \) zeta
systematic convergence to complete basis set (CBS) limit
extrapolate from \( T,Q \) to CBS usually accurate enough
aug-cc-pVNZ - add diffuse functions
cc-cpVNZ - to treat core correlation
cc-pV(N+d)Z - for third row atoms, e.g., S
cc-pVNZ-PP and cc-pVNZ-DK
  Effective Core Potentials - Treat Core Electrons in effective manner
  Transition Metals, etc
Frequencies – TZ or aTZ for quantitative accuracy
cc-pVNZ-F12 - explicitly correlated basis and methods
treats cusp at \( r_{12} = 0 \); use with F12 methods; CCSD(T)-F12
get nearly CBS results with TZ basis
Commerical Software Packages for Molecular Electronic Structure Theory

GAUSSIAN – Pople then Frisch
  good at lots of things, often other programs are better at any one thing
  I use for DFT geometry optimizations

MOLPRO - Werner and Knowles
  my favorite
  great for CCSD(T); CASPT2; MRCI;
  DFT no analytic second derivatives
  CCSD(T) no analytic first derivatives

QCHEM - Head-Gordon
  I suspect this is a great code, but I have no experience with it

Jaguar - Goddard
Freeware Software Packages for Molecular Electronic Structure Theory

ACES - Bartlett,
  Coupled cluster theory with analytical second derivatives
CFOUR - Stanton, Gauss
  Alternative/Successor to ACES
MRCC - Kallay
  Advanced coupled cluster theory
  Add on to MOLPRO or to CFOUR
PSI - Schaefer
  Multireference coupled cluster
COLUMBUS - Shepard (Argonne)
  Multireference CI
GAMESS - Gordon
  General purpose, DFT, CASSCF, CR-CCSD(T), IRC
NWCHEM - PNNL
  General purpose, Massively parallel
Lecture 2:

A. Density Functional Theory
B. Composite Methods

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Density Functional Theory

Great for geometry searches
Great for vibrational frequencies
Energies are more troublesome
No way to converge to correct answer but accuracy of best functionals continues to improve
Lots of functionals with something appropriate for every situation
But have to choose correct one
B3LYP still widely used – but no dispersion in B3LYP, also underestimates barriers
B2PLYP-D3 is my current favorite – based on personal evaluation of literature and modest testing in 2013
Geometries and frequencies comparable to (perhaps better than) CCSD(T)
Cost ~ equivalent to MP2
M06-2X is another good standard – sometimes better than B2PLYP-D3 but usually slightly worse; but less expensive
Density Functional Theory

Hohenberg-Kohn - Two Theorems:
1. Ground State Properties Uniquely Determined by Density
2. Defined Energy Functional in Terms of Density, with Proper Ground State Determined by Variational Minimization

Practice: Can’t Really Find Ground State Density but can Devise Useful Empirical Representations

B3LYP:
First Functional That was Clearly Useful at the Molecular Level
Popularized by Availability in Gaussian Quantum Chemistry Code
Better than HF at ~ Same Cost as HF
Usually Better than MP2 at a Fraction of the Cost
Hybrid Functional – Combination of DFT and HF.
Becke Exchange + Lee-Yang-Parr Correlation + Exact HF
J. Chem. Phys. 98, 5648, 1993. 62,000 Citations

1998 Nobel Prize – Split Between Kohn (DFT) and Pople (Classic Framework)
Jacob’s Ladder

N. Mardirossian, M. Head-Gordon, PCCP 16, 9904 (2014)
ωB97X-D; Dispersion Corrections
J. D. Chai, M. Head-Gordon
PCCP 10, 6615 (2008)
2800 Citations
Latest: ωB97X-V
M06-2X; Hybrid Meta-GGA
Y. Zhao, D. G. Truhlar
TCA 120, 215 (2008)
8400 Citations
Latest: M08-HX, MN11, MN15
B2PLYP-D3; Double Hybrid; DFT + HF exchange + MP2 Correlation
5800 Citations
Testing Density Functional Theory
L. Goerigk, S. Grimme, PCCP 13, 6670 (2011); JCTC, 7, 291 (2011)

841 Data Points
Testing Density Functional Theory

L. Goerigk, S. Grimme, PCCP 13, 6670 (2011); JCTC, 7, 291 (2011)
Testing Density Functional Theory

L. Goerigk, S. Grimme, PCCP 13, 6670 (2011); JCTC, 7, 291 (2011)
How Good Are Geometries
B2PLYPD3/TZ vs CCSD(T)/TZ

Take CCSD(T)-F12/cc-pVQZ-F12 as “perfect” energy
Whichever Geometry has the Lower Absolute CCSD(T)-F12/cc-pVQZ-F12 Energy is Better Geometry
Consider Set of Combustion Relevant CxNyOzHw Species
For 105 out of 147 Molecules B2PLYPD3 geometry is better than CCSD(T)

\[ E_{B2PLYPD3} - E_{CCSD(T)} \]
Average is -0.007 kcal/mol
Maximum is 0.19 kcal/mol
Minimum is -0.13 kcal/mol
How Good Are B2PLYPD3/TZ Frequencies?
Presume CCSD(T)/TZ Frequencies are Accurate

Evaluate
(i) \( \frac{Q_{\text{B2PLYPD3}}}{Q_{\text{CCSD(T)}}} \)
(ii) \( \exp\left(-\frac{\Delta \text{ZPE}}{k_B T}\right) \)

Some Differences Because CCSD(T)/TZ is not Converged wrt Basis

Largest Differences are for Torsions, which doesn’t matter at high T
Protocol – Model Chemistry

Start with B3LYP geometry optimization and vibrational analysis
(except for small barrier processes - B3LYP underestimates barrier heights and so often says there is no barrier when one does exist.)
Repeat with better functional for final geometry optimizations and vibrational frequencies
Then proceed to composite method for final energy evaluation

Code for Automating This Sequence
EStokTP  Cavallotti
Soon to be on tcg.cse.anl.gov/papr
Accurate Electronic Structure

Basis Set

Complete Basis Set (CBS)
- aug-cc-pVQZ
- cc-pVQZ
- 6-311++G(3df,2pd) aug-cc-pVTZ
- cc-pVTZ
- 6-311++G(d,p) aug-cc-pVDZ
- cc-pVDZ
- cc-pCVDZ

Method
- HF
- MP2
- CASSCF
- CISD
- CASPT2
- CCSD(T)
- CCSDT(Q)
- MRCI
- Active Space
- Full CI
- Quantum Monte Carlo
- DFT
- AM1

Full CI with CBS

Make Separability Assumptions
CCSD(T)/TZ ~ CCSD(T)/DZ + MP2/TZ-MP2/DZ
“High Level” Composite Schemes Efficient

G1, G2, G3, G3MP2, G3B3, G3X, G4 - Pople
QCISD(T)/small; MP2 and MP4 large; Pople bases
small = 6-31G*

CBS-QB3, CBS-APNO - Petersson
like Gn but smaller basis sets = cheaper
QB3 small ~ 6-31+G*; APNO small = (14s9p4d2f)/[6s6p3d2f]

BAC - Melius
Bond Additivity Correction
corrections related to known errors for specific bond types

BAC-CCSD(T) – Goldsmith

Such schemes are valuable for many heavy atoms (e.g., more than 7)
Accuracy limited to about 1 kcal/mol – termed chemical accuracy
New methods achieve accuracy approaching 0.1 kcal/mol – subchemical accuracy
But orders of magnitude more expensive
Subchemical Accuracy

Many Schemes  Focal Point (Allen); Heat (Stanton); Wn (Martin); …

ANL0 Scheme
•  Up to 34 electrons ~ 5 Heavy Atoms
•  Days of CPU for 1 Energy

CCSD(T)/TZ Optimizations and Frequencies
•  High Accuracy Harmonic Partition Function (~10%)

CCSD(T)/CBS - CCSD(T)/AQZ’,A5Z’ (~ 1 kcal/mol 2σ)

Corrections
1. Higher Order Electronic Excitations - CCSDT(Q)/DZ
2. Core-Valence – All Electron; CCSD(T)/CBS
3. Anharmonic - Spectroscopic Pert; B3LYP/cc-pVTZ
4. Relativistic – DKH; CI/TZ
5. DBOC - HF/cc-pVTZ
Combustion Thermochemistry Database

All C/N/O/H Species <= 34 electrons (370 Species)

Heat of Formation Error Distribution

- ATcT (Ruscic) 150 values as Ref.

2σ Thermal Errors

BAC-CBS


QCISD(T)/CBS(TZ,QZ) //
B3LYP/6-311++G(d,p)

BAC kcal/mol
- C-H -0.03
- C-C -0.36
- C=C -0.96
- C≡C -1.41
- O-H 0.21
- C-O 0.09
- C=O 0.11
- O-O -0.58

2σ = 0.58 kcal/mol
Basis Set Comments

Anions Need Diffuse Functions; Zwitterions Do Too

Basis Set Superposition Error
• More basis functions for monomer to use when calculating $E$ in presence of other monomer
• For long-range interactions I find that augmented functions actually give worse interaction energies
• CBS schemes treat BSSE
• Alternative is Counterpoise Corrections

DFT less sensitive to Basis sets
• not trying to converge $E$ so no real point in large basis set
• some functionals designed for specific basis sets
• some sensitivity for low frequencies

Low Frequency Convergence Requirements
• Int=ultrafine (in Gaussian)
• For numerical displacements [e.g., CCSD(T) with MOLPRO] require tighter convergence thresholds than code norms
• Anharmonic frequencies require $3^{rd}$ and $4^{th}$ derivatives – often problematic
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Lecture 3: MultiReference Electronic Structure Theory

Stephen J. Klippenstein
Outline

1. Motivation
2. Complete Active Space (CAS) Wavefunction
3. Second Order Perturbation Theory with CAS Reference (CASPT2)
4. Multi-Reference Configuration Interaction (MRCI)
5. Multi-Reference Coupled Cluster Theory [MR-CCSD(T)]
CH₄ Bond Dissociation Curves - Single Reference

Harding, SJK, Jasper, PCCP, 9, 4055 (2007)
Multiconfiguration Self-Consistent Field (MCSCF)

MCSCF - CI with optimization of both coefficients and molecular orbitals

\[ \Psi = \Psi_0 + \sum_{i,r} c_{ir} \Psi_i^r + \sum_{i,r} c_{ij,rs} \Psi_{ij}^{rs} \]

\[ \Psi_0 = |\phi_1(r_1) \cdots \phi_N(r_N)| \]

\[ \phi_i = \sum_{\mu} C_{\mu,i} \chi_\mu \]

Optimize both \( C_{\mu i} \) and \( c_{ir} \), …

Don’t consider all single and double excitations too timeconsuming and not necessary

Choose limited set of excitations based on chemistry
Complete Active Space  CASSCF

CASSCF
Partition electrons/orbitals into active and inactive spaces
Include all excitations within active space and none within inactive space
Occupation numbers tell which orbitals need multireference description
Choose on basis of deviation of occupation numbers from 0 or 2
HOMOs and LUMOs (Highest Occupied & Lowest Unoccupied)
Bond Breaking - $\sigma,\sigma^*$ or two radical orbitals - (2e,2o)
More generally - include all bonds whose chemistry changes
$\pi$ bonds should almost always be included

State Averaged - to treat degenerate states

Not Black Box - Calculation will often choose different orbitals in different regions of space

 Orbital Rotations often helpful
Stretch bonds to get correct active orbitals then shrink back down to correct geometry

Full Valence  Maximum ~ 14e,14o
Second Order Perturbation Theory with CAS Reference (CASPT2)

CASSCF has no dispersion energy
Do perturbation theory from CAS reference
Essentially size consistent
Problems with degeneracies; Use shift
Very useful for weakly interacting systems and for geometries
Not very accurate energies for significant chemical changes
Frequencies are OK
MOLPRO - two forms
  RS2 - has analytic derivatives but no contraction
  RS2C - contracted but no analytic derivatives
    contraction very useful for larger active spaces
    makes little difference for small active spaces
  Parallel molpro implies RS2C frequency analysis can be rapid
For 2e,2o case, CPU roughly same as MP2
Energies for Geometries with Multireference Wavefunctions

Traditional:
Find active space that treats chemistry of reactants, transition state, and products
Often hard to do and energies not especially accurate

Alternative:
Find active space for particular multireference geometry
Evaluate singlet-triplet splitting with CASPT2 or CAS+1+2+QC
Evaluate energy of triplet state relative to reactants and products with QCISD(T)
Multi-Reference Configuration Interaction from CAS Reference (MRCI)

CAS+1+2 - Include all single and double excitations from CAS reference space
CAS+1+2+QC - Davidson correction for higher order excitations

MRCI is not size consistent
Comparison of CASPT2 and MRCI useful
When similar then they are probably both reliable
When different there is something to think about
Can try to bring into agreement by expanding active space
Often method that predicts lower barrier appears to be correct
CH$_4$ Bond Dissociation Curves - Multi-Reference

Harding, SJK, Jasper, PCCP, 9, 4055 (2007)

Blue - CASSCF
Purple - CASPT2
Red - CAS+1+2+QC
Black - Full CI
CH$_4$ Bond Dissociation Curves - DFT and Basis Set

Harding, SJK, Jasper, PCCP, 9, 4055 (2007)

Solid - 6-31G*
Dotted - adz
Dashed - atz
Dot-dash - aqz

Blue - MPW1K
Purple - B3LYP
Gray - CASPT2
Black - Full CI
C$_2$H$_6$ Bond Dissociation Curves

Harding, SJK, Jasper, PCCP, 9, 4055 (2007)

Blue - MPW1K

Purple - B3LYP

Orange - MP2

Green - CASSCF

Red

Solid - CCSD(T)
Dashed - QCISD(T)

Gray

Solid - CASPT2
Dashed - CAS+1+2+QC
Percent Deviation in $C_2H_6$ Bond Dissociation Curves

Use Spin-splitting based Davidson corrected MRCI without internal contraction as reference

Spin-Splitting (SS) Approach

$E = ^3\text{CCSD}(T) + \text{Singlet} - \text{Triplet}$ with Multireference Method
Radical + O\(_2\) Interaction Curves

\[ C_2H_5 + O_2 \]

\[ C_2H_3 + O_2 \]


SJK, PCI, 36, 77 (2017).
Higher Order
Coupled Cluster Theory

CCSDT, CCSDTQ, CCSDTQP, …

Great for when multireference effects are significant but not overwhelming

Approximate treatment of higher excitations in coupled-cluster theory. II. Extension to general single-determinant reference functions and improved approaches for the canonical Hartree-Fock case


MRCC program by Kallay
CH$_4$ Bond Dissociation Curves

![Graph showing bond dissociation curves for CH$_4$ with different methods and data points labeled as CCSD(T), CCSDT, CCSDT(Q), CCSDTQ, PT2, Davidson, Pople, and Cl.](image)
Spin-Flip Coupled Cluster Theory

Golubeva, Nemukhin, SJK, Harding, Krylov, JPCA, 111, 13264 (2007)

Figure 12. Ethane, aug-cc-pVTZ. Errors of selected methods against MR-CISD+Q for the region relevant to kinetics modeling. All curves are shifted such that the energies at 5.2918 Å are equal to zero.
Renormalized Coupled Cluster Theory
CR-CCSD(T)

CH$_3$ + H (Basis=6-311G**)
Multi-Reference Coupled Cluster Theory [MR-CCSD(T)]

MRCI and CASPT2 not accurate enough for some problems
Too much multireference character for CCSD(T) to be accurate
Need more than single and doubles excitations
MR-CCSD(T) combines the best of both MRCI and CCSD(T)
Active research topic
Formalism is complicated
State-Specific MR-CCSD(T) limited to a few configurations but quite appealing

Triple excitations in state-specific multireference coupled cluster theory: Application of Mk-MRCCSDT and Mk-MRCCSDT-n methods to model systems

Radical-Radical Abstractions

\[ \text{C}_2\text{H}_5 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_4 \]

Multi-Reference Summary

Must use multi-reference approach for any singlet diradical or other low spin polyradical

CASPT2 is a great approach for geometry optimization and frequency analysis

MOLPRO has a very nice set of CASPT2 routines

CASPT2 is a great approach for weakly interacting species - e.g., long-range radical-radical interactions

MRCI+Q is sometimes but not always better than CASPT2

Use singlet triplet splitting trick when you can

Common mistakes:

1. Use of CCSD(T) for singlet diradicals when T1 diagnostic is large
2. Use of CAS for geometry optimizations – it’s just not accurate enough
3. Assumption that CASPT2 and/or MRCI+Q energies are highly accurate
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Work on expanding these calculations to take advantage of exascale computational environments is just beginning through support from DOE-ASCR.
Pressure Independent Rate Theory

Stephen J. Klippenstein
Outline

Pressure Independent Rate Theory
  a) Transition State Theory (TST) – Formalism
  b) Ab Initio TST
    1. EStokTP; Carlo Cavallotti; Automated for
       » Abstraction
       » Addition
       » Isomerization
       » …
    2. Barrierless Reactions
    3. Multiple Transition States
  c) Role for Dynamics
Lecture 4: Transition State Theory

1. Motivation
2. Dynamical Derivation and the Variational Principle
3. Partition Functions, Numbers of States, and Density of States
4. Conventional Transition State Theory
5. Accuracy
Motivation

Chemical Models Need Rate Coefficients for 1000’s of Reactions

Experiments
• Too time consuming
• Often can’t perform experiments at T,P of interest
• Can’t isolate species of interest

Theory
• Empirical Models
  – Correlations and extensions of related experiments
  – Greater accuracy desirable
• Classical Trajectories
  – Need global potential energy surface
  – No quantum effects
  – Timescale ~ 1 ns or shorter
• Quantum Dynamics
  – Too computationally intensive
  – 4 – 5 Atom Systems
• Transition State Theory (TST)
  – Compromise of Efficiency and Accuracy
What is TST?

Eyring, Polanyi - independently 1935; Wigner – Dynamical 1936

**Review Articles**

The Current Status of Transition State Theory
Donald G. Truhlar, Bruce C. Garrett, and Stephen J. Klippenstein

**RRKM Theory and Its Implementation**

**Modeling the Kinetics of Bimolecular Reactions**

**Predictive Theory for Hydrogen Atom-Hydrocarbon Radical Association Kinetics**
Lawrence B. Harding, Yuri Georgievskii, and Stephen J. Klippenstein

**Predictive Theory for the Association Kinetics of Two Alkyl Radicals**
Stephen J. Klippenstein, Yuri Georgievskii, and Lawrence B. Harding

**Ab Initio Methods for Reactive Potential Surfaces**
Lawrence B. Harding, Stephen J. Klippenstein, and Ahren W. Jasper
\[ k = \int dq dp P(q,p) \delta(s - s^\pm) \chi(q,p) \frac{p_s}{m} \]

**Trajectory Expression for the Rate Constant**

\[ P(q,p) \] probability of specific \( q,p \)

**Statistical Assumption**

\[ P(q,p) = \frac{\exp[-\beta H(q,p)]}{\int dq dp \exp(-\beta H)} \]

**Canonical**

\[ P(q,p) = \frac{\delta(E - H)}{\int dq dp \delta(E - H)} \]

**Microcanonical J-Resolved**

\[ P(q,p) = \frac{\delta(E - H) \delta(J - J_T)}{\int dq dp \delta(E - H) \delta(J - J_T)} \]

- \( s = s^\pm \) defines dividing surface
- \( p_s/m \) = velocity through \( s^\pm \)
- \( \chi \) = reactivity function
  - 1 if trajectory is reactive
  - 0 otherwise

**Key advantage of TST is that it is a local theory**

Transition State Assumption and the Variational Principle

Transition State Assumption

- Assume all trajectories with positive velocity through dividing surface are reactive
- Replace $\chi$ with $\Theta (p_s/m) – \text{step function}$
- $\Theta (p_s/m) \geq \chi$
- $k_{TST} \geq k_{\text{Trajectory}}$; Variational Principle

Variational Transition State Theory

- Consider family of TS dividing surfaces
- Best Dividing Surface is one that provides minimum estimate for $k$
Transition State Theory (TST)

**Canonical**

\[ k(T) = \frac{k_B T}{h} \frac{Q^\pm}{Q_{\text{reac}}} \exp(-E^\pm / k_B T) \]

\[ Q_{\text{Quan}} = \sum_i \exp(-\beta E_i) \]

\[ Q_{\text{class}} = \int \frac{dq dp}{\hbar^n} \exp(-\beta H) \]

**Microcanonical**

\[ k(E) = \frac{N^\pm(E)}{h\rho_{\text{reac}}(E)} \]

\[ N_{\text{Quan}}(E) = \sum_i \Theta(E - E_i) \]

\[ N_{\text{class}}(E) = \int dq dp \Theta(E - H)/\hbar^n \]

\[ N_{\text{class}}(E) \alpha B(m_i) \int dq (E - V)^{n/2} \]

\[ Q_{\text{class}} \alpha C(T,m_i) \int dq \exp(-\beta V) \]

\[ \rho(E) = \partial N / \partial E \]

**Microcanonical - J Resolved**

\[ k(E,J) = \frac{N^\pm(E,J)}{[h\rho_{\text{reac}}(E,J)]} \]
Thermodynamic Formulation of TST

Equilibrium Constant = ratio of Partition Functions

\[ K_{eq} = \frac{Q_{\text{products}}}{Q_{\text{reactants}}} = \exp \left( - \frac{\Delta G}{k_B T} \right) \]

\[ k(T) = \frac{k_B T}{h} \frac{Q^\pm}{Q_{\text{reactants}}} \exp \left( - \frac{E^\pm}{k_B T} \right) \]

\[ k(T) = \frac{k_B T}{h} \exp \left( - \frac{\Delta G^\pm}{k_B T} \right) \]

\[ k(T) = \frac{k_B T}{h} \exp \left( - \frac{\Delta H^\pm}{k_B T} \right) \exp \left( \Delta S^\pm \right) \]

Variational $\Rightarrow$

Maximize $\Delta G^\pm$

Maximize $\Delta H^\pm$

Minimize $\Delta S^\pm$
Ab Initio Transition State Theory

\[
k(T) = \frac{k_B T}{h} \frac{Q^\pm}{Q_{\text{reac}}} \exp\left(-\frac{E^\pm}{k_B T}\right)
\]

Implementation requires an evaluation of the partition function for both the reactants and the transition state. Determine these from information on structure, energy, and rovibrational properties of reactants and transition state. Use ab initio electronic structure theory to determine these properties.

\[\Rightarrow \text{Ab Initio Transition State Theory}\]

How accurate is ab initio transition state theory?

- Depends on how it is implemented.

How efficient is it?

- Depends on how it is implemented.

Typically can get about a factor of two accuracy with a day or less of CPU, at least for combustion temperatures.
Conventional Transition State Theory

- **Fixed Transition State Location**
  - Saddle point on potential Energy Surface

- **Rigid Fragments**
  - \( E_{\text{rot}} (J,K) = B J(J+1) + (A-B) K^2 \)
  - \( A,B \) are rotational constants
  - \( J,K \) are rotational quantum numbers

- **Harmonic Vibrations**
  - \( V(q_i) = k_i q_i^2 / 2 \)
  - \( E_{\text{vib}} (v_i) = h \omega_i (v_i + \frac{1}{2}) \)
  - \( \omega_i = \text{harmonic vibrational frequency} \sim (k_i/m_i)^{1/2} \)
  - \( v_i \) is the quantum number for vibrational mode \( i \)
Canonical Partition Functions

Rigid Rotor Harmonic Oscillator (RRHO)

\[ Q = Q_{trans} Q_{rot} Q_{vib} Q_{elec} \]

\[ Q_{trans} = \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \]

\[ Q_{rot} = \frac{\pi^{1/2}}{\sigma} \left( \frac{8\pi^2 I_a k_B T}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_b k_B T}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_c k_B T}{h^2} \right)^{1/2} \]

\[ Q_{vib}^{\text{quan}} = \prod_{i=1}^{n} \frac{\exp(-\hbar \nu_i / 2k_B T)}{1 - \exp(-\hbar \nu_i / k_B T)} \]

\[ Q_{vib}^{\text{class}} = \prod_{i=1}^{n} \frac{k_B T}{\hbar \nu_i} \]

\[ Q_{elec} = \sum_{i=1}^{n} g_i \exp\left(-\frac{E_i}{k_B T}\right) \]

Statistical Mechanics, D. A. McQuarrie, Harper & Row
Number of States

\[ N(E,J) = \sum_{i,K} \Theta(E - E_{vib_i} - E_{rot_{J,K}}) \]

\[ N(E) = \sum_{J} N(E,J)(2J + 1) \]

\[ N(E) = \int d\varepsilon N_{vib}(E - \varepsilon) \rho_{rot}(\varepsilon) \]

\[ \rho_{rot}(E) = \frac{\partial N_{rot}(E)}{\partial E} = \frac{2}{\sigma} \left( \frac{E}{B^2C} \right)^{1/2} \]

Beyer-Swinehart for \( N_{vib} \)

\( \omega_j = \) vibrational frequency for mode \( j \)

1. \( N_{vib}(i) = 1, \) for all \( i \)
2. For \( j = 1,n \)
3. For \( i = \omega_j,m \)
4. \( N_{vib}(i) = N_{vib}(i) + N_{vib}(i-\omega_j) \)
5. End \( i \) loop
6. End \( j \) loop

Reaction Path Degeneracies

Multiply partition function by

\[
\frac{m}{\sigma}
\]

\(m\) = number of optical isomers
\(\sigma\) = rotational symmetry number for given configuration

Do for both reactants and transition state

Yields correction to rate constant that is equal to the reaction path degeneracy

\[
\frac{m^\pm \sigma}{m\sigma^\pm}
\]
Beyond Conventional RRHO TST
Variational Transition State Theory

Follow reaction path - Imaginary mode at saddle point

W. L. Hase
D. G. Truhlar
W. H. Miller

Project vibrational frequencies along reaction path
Evaluate TS partition function along reaction path
Find minimum

- Canonical - $\kappa(T) = \min \left\{ \int dE \int dJ \, P(E,J) \, k(E,J,R) ; \, R \right\}$
- Microcanonical - $\kappa(T) = \int dE \, P(E) \, \min \left\{ \int dJ \, P(J) \, k(E,J,R) ; \, R \right\}$
- E, J Resolved - $\kappa(T) = \int dE \int dJ \, P(E,J) \, \min \left\{ k(E,J,R) ; R \right\}$

Barrierless reactions are more complicated

- Harmonic not very meaningful
- SJK, Harding, Georgievskii
Beyond Conventional RRHO TST
Tunneling Corrections (Γ)

Most Important - Calculate Imaginary Frequency Accurately

One Dimensional

Wigner - Perturbative Expansion

\[ Γ = 1 - \left( \frac{h ν}{k_B T} \right)^2 /24 \]

Eckart - Asymmetric form parametrized by reactant, product and saddle point energies and imaginary frequency

Analytic form for Γ

Multidimensional and Corner Cutting - Truhlar

Small Curvature (SCT)
Large Curvature (LCT)

Optimized Multidimensional Tunneling (OMT)

Polyrate – Freeware

http://comp.chem.umn.edu/polyrate/

Ring Polymer Molecular Dynamics - Manolopoulos
Variational transition state theory with multi-dimensional tunneling

For example, see reviews:
Beyond Conventional RRHO TST

Moments of Inertia - Coupling of external and internal momenta


Torsional Modes - Hindered Rotors

\[ Q \sim \int \! d\phi \exp\left[-\frac{V(\phi)}{k_B T}\right] \]

Sometimes Consider Torsional Dependence of Moments of Inertia But Coupling of Internal and External Rotations Means this is Not Necessarily Better

Pitzer-Gwinn \[ Q_{\text{quantum,HR}} = Q_{\text{quantum,HO}} \ast \frac{Q_{\text{class,HR}}}{Q_{\text{class,HO}}} \]

Torsional Modes are Not Separable from Remaining Modes – Project Torsions from Hessian

Intramolecular Hydrogen Migration in Alkylperoxy and Hydroperoxyalkylperoxy Radicals: Accurate Treatment of Hindered Rotors


An extended hindered rotor model with incorporation of Coriolis and vibration-rotational coupling for calculating partition functions and derived quantities

Beyond Conventional RRHO TST
Multidimensional Torsions

Generally There are Many Coupled Torsions
Commonly Assume Product of Independent 1D Torsions is OK
Accurate to Within About a Factor of 2 (or better for Simple Cases) if Done Well

How should we calculate multi-dimensional potential energy surfaces for an accurate
reproduction of partition functions?


MESS (Master Equation System Solver) – Georgievskii – tcg.cse.anl.gov/papr
Multidimensional Quantized Torsions with Coupling to External Rotation
Also Includes Vibrational Adiabaticity for Orthogonal Modes
Requires Multidimensional PES - Works for up to Three or Four Modes
Multidimensional Classical Simpler - PES Still Problematic for More than 4 Modes

MSTor – Truhlar - https://comp.chem.umn.edu/mstor/
Approximate Quantized Multidimensional Torsions – Based on Multiple Interpolations
(for Quantum Effects, For Mode Couplings, etc.) of Expansions about the full Set of
Torsional Minima

Umbrella Modes and Torsions are Coupled for Radicals – Ignored
Not Clear How to Treat Ring Mode Anharmonicities
Beyond Conventional RRHO TST Anharmonicities

Separable - With Beyer Swinehart

NonSeparable

Spectroscopic Perturbation Theory (SPT)

Relate power series expansion of E in quantum numbers $v_i$ to 2nd, 3rd and 4th order derivatives of potential $E = \omega_i(v_i+1/2) - x_i (v_i+1/2)^2$


SCTST (SPT for both reactants and TS)

Problems due to resonances and due to turnovers in $E(v_i)$

H. Woolley, J Res NBS, 56, 2655 (1956) – Direct evaluation of effect on Q

VibSCF; VibCI - MULTIMODE - Bowman

http://www.chemistry.emory.edu/faculty/bowman/multimode/

Monte Carlo + Pitzer Gwinn

\[ Q = dq_1 \ldots dq_n \exp[-\beta V(q_1,\ldots q_n)] \]

\[ Q_{\text{quantum,HR}} = Q_{\text{quantum,HO}} \ast Q_{\text{class,HR}} / Q_{\text{class,HO}} \]


Path Integrals

Ab Initio Transition State Theory—Errors from Electronic Structure and State Counting Should be Comparable

Electronic Structure

- Full-CI
- CCSD(T)
- MRCI
- CASPT2
- DFT
- MP2
- HF

CBS: cc-pVQZ
cc-pVTZ
cc-pVDZ
6-31G*
3-21G
Sto-3G

Quantum Scattering Theory
- Full CI / CBS Potential

Quantum Dynamics
- Conventional RRHO-TST
- VTST
- VRC-TST
- Tunneling Anharmonic
- Path Integrals Multiple TS’s

Kinetic Methodology
- Classical Trajectories
- Semiclassical Dynamics
Kinetic Accuracy

Kinetic Accuracy ~ Factor of 2
- Energy to chemical accuracy
- Transition State Theory
- RRHO Energy Levels
- 1D Torsions
- Eckart Tunneling
- 1000 K and Higher

Subkinetic Accuracy ~ 20% Accuracy
- Many factors
- Multidimensional Tunneling; Variational Effects
- Anharmonicities; Transition State Recrossing
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• The majority of the work was supported through the Gas Phase Chemical Physics program with Wade Sisk as the program monitor
• Code development work was supported by Mark Pederson through the Material Genome Initiative and Computational Theoretical Chemistry
• The work on low temperature oxidation was performed under the auspices of the Argonne Sandia Consortium on High Pressure Combustion Chemistry
• The Combustion EFRC provided motivation for a variety of the theoretical developments and applications
Work on expanding these calculations to take advantage of exascale computational environments is just beginning through support from DOE-ASCR
Lecture 5: Ab Initio Transition State Theory

Stephen J. Klippenstein
Outline

Motivation
EStokTP – From Electronic Structure to Temperature and Pressure Dependent Rate Constants Carlo Cavallotti, Matteo Pelucchi, Yuri Georgievskii, SJK

1. Approach
2. Illustrations – Reactions and Methods
   - Abstraction
   - Addition
   - Isomerization
   - Variational Effects
   - Tunneling
   - Multidimensional Torsions
   - Accuracy
Radical-Molecule Additions

Transition State Determination is Trivial
Start with low-level determination; e.g., B3LYP/6-31G* in Gaussian
(B3LYP underestimates barriers and so barriers may be incorrectly absent – use other functionals for low barrier processes)

(i) Setup z-matrix with internal coordinates
(ii) Set atom-atom separation for forming bond to 2.2 Å
(iii) opt=(ts,calcfc,noeigentest,internal)

If this fails

(i) do set of constrained optimizations at R=1.8 to 3.0 Å on 0.2 Å grid
(ii) Find maximum in Eopt (R)
(iii) Use geometry from maximum in Eopt (R) as starting geometry for
(iv) opt=(ts,calcfc,noeigentest,internal)

Proceed to higher level method (composite method)
E.g., CCSD(T)/CBS or ANL0
Radical-Molecule Abstractions

Transition State Determination is Again Straightforward
Consider from Higher Energy Side

(i) do constrained optimization at R=2.6 Å with DFT (e.g., B3LYP/6-31g*)
(ii) repeat with gradually decreasing separation (e.g., by 0.2 Å) until maximum in Eopt is reached
(iii) Use geometry from maximum in Eopt (R) as starting geometry for
(iv) opt=(ts,calcfc,noeigentest,internal) (Gaussian)
(v) Repeat (iv) with better DFT method (e.g., B2PLYPD3/cc-pVTZ

Proceed to higher level method (composite method)
E.g., CCSD(T)/CBS or ANL0
Ab Initio Abstraction Kinetics  \( \text{OH} + \text{CH}_3\text{OCH}_3 \)

**Methods**
- ANL0
- Variational
- Multidimensional Hindered Rotors
- Eckart

PCI, 36, 77 (2017)
EStokTP Aims and Philosophy

Issues with rate constant calculations and PES studies

- The steps necessary for accurate rate constant calculations get more and more complicated as you strive for higher and higher accuracy (hindered rotors, high level energies, variational effects, tunneling, anharmonicities, etc.)
- Data retrieval is time consuming
- Scans of all possible pathways can be complicated
- Transforming electronic structure output to master equation input takes time and is error prone

EStokTP GOALS

• **AIM1**: to provide a tool that **automatically** performs all the steps necessary to determine a rate constant **for a specific reaction**, starting with electronic structure calculations and ending with parameterization of master equation results.
• **AIM2**: to provide procedures that yield **kinetically accurate** rate constants; i.e., within a factor of 2 (at combustion temperatures).
Current EStokTP Implementation

Approach

• not optimized for computational efficiency, but for stability
• not a black box; the user must know about electronic structure calculations and kinetic theories

Classes of reactions implemented:

• Abstraction
• Addition
• Beta-decomposition
• Isomerization
• Frozen coordinate optimizations
• Pressure dependence!
Current EStokTP Features

- Modular (types of calculations; types of species)
- Programming Languages: fortran, c, unix scripts
- Uses: G09 or Molpro independently
- Geometries in z-matrix format for reactants/products – open babel
- Automatic determination of guess for TS structure (1D grid scan)
- Automatic generation of guess for search of van der Waals wells
- Projection of hindered rotors from Hessian (Green approach)
- Multidimensional torsions
- Multidimensional tunneling
- Automatic determination of symmetry
- Composite Energies
- Calls MESS Master Equation System Solver and produces $k(T,P)$
EStoKTP program structure

**THEORY**

**Level 0**
- Geometry Optimization of reactants/products
- Generation of TS guess
- Determination of TS

**Level 1**
- Structures and Freqs of Reactants, Products, TS, van der Waals wells
- 1D/2D/3D Hindered rotor Scans

**High Level**
- High Level Energies

**Level 1**
- Reaction Path Scan (IRC)
- Evaluation of Symmetry numbers
- Master Equation and Rate constants

Stochastic search of conformational minima
With projection of rotors
In general 3-7 Files must be given:

- List of modules to call (1 file)
- Theoretical Level (1-3 files)
- Reacs/Prods/TS inputs (2-4 files)

Primary case specific input is Z-Matrix with proper identification of hindered rotors
Grid search of TS and TS random sampling of torsional configurations

Maximum along grid scan used as input for TS search (1 point sufficient)
Dummy atom added for abstraction
\[
\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2
\]

Stoichiometry  C1H5
Debug  2
ReactionType Abstraction 1TS
Prods

Opt_Reac1
Opt_Reac2
Opt_Prod1
Opt_Prod2

Grid_Opt_TS
Opt_TS_0

Opt_Reac1_1
Opt_Reac2_1
Opt_Prod1_1
Opt_Prod2_1
Opt_TS_1

EStokTP.dat

HL_Reac1
HL_Reac2
HL_Prod1
HL_Prod2
HL_TS

Symm_Reac1
Symm_Reac2
Symm_Prod1
Symm_Prod2
Symm_TS

kTP

End

20,8
numprocll,numprochl
2048MW  2048MW
gmemll,gmemhl
\[ \text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2 \]
\[ \text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2 \]

**react1.dat**

```
nosmp dthresh ethresh
1  1.0  0.00001

ntau number of sampled coordinates
0
-->taumn,taumx sampling interval

nhind
0
-->namehind,hindmn,hindmx,nhindsteps,symm

natom natomt ilin
5 5 0

charge spin atomlabel
0  1
c1
h1 c1 rch1
h2 c1 rch2 h1 ahch1
h3 c1 rch3 h1 ahch2 h2 b1
h4 c1 rch4 h1 ahch3 h2 b2

intcoor
rch1 1.08
rch2 1.08
rch3 1.08
rch4 1.08
ahch1 110.
ahch2 110.
ahch3 110.
b1   120.
b2   -120.

SymmetryFactor
12.

nelec
1
0.  1.

end
```
\[ \text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2 \]

\text{nosmp dthresh,ethresh}
1 1.0 0.00001

\text{ntau}
0
-->scanned dihedral coordinates, minimum and maximum values

\text{isite ji ki}
3 1 2

\text{rmin rmax nr}
1.3 0.8 6
-->aabs1,babs1,aabs2,babs2,babs3 90., 180., 90., 175., 90.

\text{ts.dat}

\text{nhind}
0
-->namehind,hindmn,hindmx,hindstep

\text{charge spin}
0 2

\text{SymmetryFactor}
3.

\text{nelec}
1
0. 2

End
\[ \text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2 \]

---

nosym
End1

!closed shell input
basis=cc-pvDZ-f12
hf
mp2-f12
en_mp2_dz=energy(1)
csd(t)-f12
en_cc_dz=energy(2)

basis=cc-pVTZ-f12
hf
mp2-f12
en_mp2_tz=energy

put,molden,molpro.molden
CBSen = en_cc_dz + (en_mp2_tz - en_mp2_dz) * 1.46286
---

End2

---

!open shell input
basis=cc-pvDZ-f12
rhf
mp2-f12
en_mp2_dz = energy
uccsd(t)-f12
en_cc_dz = energy(2)

basis=cc-pVTZ-f12
rhf
mp2-f12
en_mp2_tz = energy

encorr = en_cc_qz

put,molden,molpro.molden
CBSen = en_cc_dz + (en_mp2_tz - en_mp2_dz) * 1.46286

---

End3
\[ \text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2 \]  

CCSD(T)-F12/DZ - F12+MP2-F12/TZ-F12 - MP2-F12/DZ-F12

Variational Effect  
Less Than 5 %

SCT vs. Eckart  
Increases Tunneling by 1.5 at 500 K

Barriers  
13.4, 13.7 kcal/mol
\[ \text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O} \]

CCSD(T)-F12/DZ -
F12+MP2-F12/TZ-F12 - MP2-F12/DZ-F12

300 K Variational Effect = 0.67

Large ZPE change along reaction coordinate

Barriers
5.1, 19.4 kcal/mol
\[ \text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_5 \]

CCSD(T)-F12/DZ - F12+MP2-F12/TZ-F12 - MP2-F12/DZ-F12

Barriers
3.1, 37.9 kcal/mol

Variational Effect = 0.57 at 2000 K
Multidimensional Hinder Rotors with Adiabatic Orthogonal Frequencies

- 2D hindered rotor scan accounting explicitly for change of frequencies along rotational coordinate in evaluation of density of states
- projection of hindered rotors from Hessian (avoids manual choice among 12x12x33 frequencies and disentangles low vibrational frequencies)
- Two 1D hindered rotor scans
- Eckart tunneling (also tested SCT; not relevant for this system)

We believe it is the **best method** to treat reactions **with multiple conformers**
$\text{CH}_3\text{COOCH}_3 + \text{OH}$
$\text{C}_2\text{H}_5\text{COOCH}_3 + \text{OH}$
MultiWell PES: CH$_3$COOH Decomposition
Uncertainties

Tunneling Factor Close to 1

Barrier Height – Saddle Point

\[ k^{TST}(T) = \kappa \frac{k_B T}{h} \frac{Q^\#(T)}{Q_{\text{react}}(T)} \exp \left( - \frac{V^\#}{k_B T} \right) \]

Partition Functions – Depend on Rovibrational Properties


\[ \frac{\sigma_k^2}{k^2} = \frac{\sigma_\kappa^2}{\kappa^2} + \frac{\sigma_{Q^\#/Q_R}^2}{(Q^\# / Q_R)^2} + \frac{\sigma_{V^\#}^2}{(k_B T)^2} \]
\[
\frac{\sigma_k^2}{k^2} = \frac{\sigma_k^2}{\kappa^2} + \frac{\sigma_{Q^\pm/Q_R}^2}{(Q^\pm/Q_R)^2} + \frac{\sigma_{V^\pm}^2}{(k_BT)^2}
\]

- **CCSD(T)/CBS**
  \[\sigma_V = 1 \text{ kcal/mol}\]

- **SCT vs Eckart**
  \[\frac{\sigma_\kappa}{\kappa} = 20\%\]

- **CASPT2 vs M06-2X**
  Relative \[\sigma_{Q/Q_R} \sim 50\%\]

Correlations:
- \[V^\pm, \kappa\]
- \[Q^\pm, Q_R\]
Isomerizations

Transition State Determination More Complicated

Provide starting and ending structures
Make sure atoms match from start to finish
Opt=qst2 in Gaussian

Often can just guess at structure through geometry
E.g., H atom transfers - make a ring with transferring
H equidistant from beginning and ending atoms

Many other approaches - but I’m not knowledgeable
about them – Carlo has programmed one of them
POLYRATE Program

- Source code: ~ 83,000 lines (Fortran)
- Installation: Perl script
- Manual: 590 pages
- Test runs: 106
- Parallelization: MPI
- Version 2010 available as of June 1, 2010 at http://comp.chem.umn.edu/truhlar/

Simple barrier reactions: RP-VTST
  - Reaction-path variational transition state theory
    - Cartesian dividing surfaces from Garrett & Truhlar 1979
    - Curvilinear dividing surfaces from Jackels, Gu & Truhlar 1995

Barrierless association reactions: VRC-VTST
  - Variable-reaction-coordinate variational transition state theory
    - Multi-faceted dividing surfaces from Georgievskii & Klippenstein 2003

Potential Energy Surface (PES)
  - Defined by energies, gradients, and Hessians calculated by an electronic structure program "on the fly" - direct dynamics
Available without license fee from Truhlar group web site:
http://comp.chem.umn.edu/truhlar
Acknowledgements
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Work on expanding these calculations to take advantage of exascale computational environments is just beginning through support from DOE-ASCR
Lecture 6: Barrierless Reactions
Multiple Transition States
Dynamics

Stephen J. Klippenstein
TST for Barrierless Reactions

1. Variable Reaction Coordinate Approach
2. Potential Energy for Larger Molecules
3. 1-Dimensional Corrections
4. Direct Coupling to Electronic Structure Theory
5. Dynamical Correction
6. Geometric Mean Rule
Where is the Transition State?

Calculate $Q(T,R)$ or $N(E,R)$ as function of $R$.

Transition State is at position of minimum in $Q$ or $N$.

Radical - Molecule
Saddle Point
$\exp(-\beta E)$ dominates

Radical - Radical
No Saddle Point
With Decreasing $R$
Entropy Decreases
$\exp(-\beta V_{\text{min}})$ Increases

$\text{CH}_3 + \text{H}$
Variable Reaction Coordinate
Transition State Theory

• Approximate Separation of Modes
  – Conserved Modes – Vibrations of Fragments
  – Transitional Modes – Fragment Rotations, Orbital Motion, and Reaction Coordinate

• Conserved Modes
  – Quantum Harmonic Vibrators
  – Independent of Reaction Coordinate
  – Direct Sums

• Transitional Modes
  – Classical Phase Space Integrals
  – Fully Coupled and Full Anharmonicity
  – Monte Carlo Integration
Variable Reaction Coordinate
\[ \text{CH}_3 + \text{H} \]

Fixed Distance Between Pivot Points
Multiple Pivot Points on Each Fragment
Multi-Faceted Dividing Surface

Optimize Both \( d \) and \( R \)
Basis Set Dependence

![Graph showing basis set dependence with various labels for different basis sets: cc-pvdz, aug-cc-pvdz, cc-pvtz, aug-cc-pvtz, cc-pvqz, aug-cc-pvqz. The graph plots relative energy (kcal/mole) against CH bond length (atomic units) on the left, and rate constant (k \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) against temperature (K) on the right. Different basis sets are represented by distinct line styles and colors.](image-url)
$\text{CH}_3 + \text{H} : \text{High Pressure}$

$k \left(10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\right)$

$\text{VRC-TST}$

$\text{Su and Michael}$

$\text{Brouard et al}$

$\text{Seakins et al}$

Temperature (K)
$\text{CH}_3 + \text{H} : \text{High Pressure}$

SJK, Georgievskii, Harding, PCI, 29, 1229 (2002)

$k \left(10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}\right)$

Temperature (K)
1D Correction Potentials

\[ V(R,\Omega) = V_{ll}(R,\Omega) + V_{corr}(R) \]

\( V_{ll} = \text{PT2 with small basis} \)

1D Correction Potential
- For Geometry Relaxation
- For Higher Level Method
- For Larger Basis Set
Test of MEP Correction

\[ H + C_2H_3 = C_2H_4 \]

\[ H + C_2H_5 = C_2H_6 \]

\[ k(10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}) \]

Temperature (K)
H + Alkyl Radical

Potential Energy Surface

Blue = attractive contours
Red = repulsive contours

Harding, Georgievskii, SJK, JPCA, 109, 4646 (2005)
H• + R•  Unsaturated Radicals

![Graph showing reaction kinetics](image-url)

- **CCH+H**
- **C2H3+H**
- **C6H5+H**
- **1-C_{10}H_7+H**
- **2-C_{10}H_7+H**

Temperature (K) vs. Reaction Rate Constant ($k$ in $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
Direct Variable Reaction Coordinate TST

- Evaluate configurational integrals $\int \exp(-\beta V) \, dq$
- Arbitrary separation and orientations (6 dimensional)
- Direct Potential Evaluations -- low level - CASPT2/dz
- One dimensional corrections based on high level evaluations along the minimum energy path
- Alkyl + H; Alkyl + Alkyl’;
- Saturated and Unsaturated
- Oxygen and Nitrogen Centered Radicals – Need Diffuse Functions
- Resonantly Stabilized Radicals – Be Careful with Symmetry Breaking; Multiple Pivot Points
- $R + O_2$ – Spin Splitting Approach is the Key
- $^1\text{CH}_2$ + Unsaturated Molecules – Single Reference Good
Procedures for Direct VRC-TST

Program - VaReCoF (Variable Reaction Coordinate Flux)
tcg.cse.anl.gov/papr

- Choose reference method for orientational sampling -
  e.g., CASPT2(2e,2o)/dz
- Evaluate $E(\infty)$ for reference method
- Evaluate 1-D correction along MEP and write subroutine for evaluating it
- Choose sets of dividing surfaces to sample
  - Center-of-mass at long-range (9 to 20 Å)
  - Orbital centered at short range (4 to 8 Å)
- Choose desired accuracy and maximum sampling points
- Run, checking to make sure orbitals don’t switch and energies are consistent with expectations

POLYRATE also has Direct VRC-TST module
\[
\text{CH}_3 + \text{CH}_3 \\
\text{CH}_3 + \text{C}_2\text{H}_5
\]

Trajectory Simulations Suggest VTST Overestimates the Rate Constants by 10-15%

SJK, Georgievskii, Harding, PCCP, 8, 1133 (2006)
Kinetics of Alkyl Radical + Alkyl Radical Addition

Potential Energy Surface
$\text{CH}_3 + R$

Red = Repulsive
Blue = Attractive

High Pressure Addition Rate Coefficient
**Geometric Mean Rule**

\[ k_{AB} = 2.0 \sqrt{k_{AA} \times k_{BB}} \]

![Graph showing the geometric mean rule for various reactions.](image-url)
\[ R + O_2 \]

\[ C_2H_5 + O_2 \]

\[ C_2H_3 + O_2 \]

Goldsmith, Harding, Georgievskii, Miller, SJK, JPCA, 119, 7766 (2015)

SJK, PCI, 36, 77 (2017)
$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$  High Pressure Recombination

Georgievskii, Miller, SJK, PCCP, 9, 4259 (2007)
Comparison with Experiment

$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$
$^1\text{CH}_2 + \text{Alkenes}$

D. Polino, SJK, L. B. Harding, Y. Georgievskii
JPCA 117, 12677 (2013)

CH + Alkanes
Ribeiro, Mebel, SJK
Two or More Transition States, Roaming Radicals and Direct Dynamics

1. Two Transition States for Radical-Molecule Reactions
2. Roaming Radical Reactions
3. Direct Dynamics as a Complement to TST
Elementary Reactions

Every radical-molecule reaction has some form of long-range attraction and concomitant long-range TS. The addition process then requires passage over two transition states. Even most radical-radical recombinations have two transition states.

**IUPAC Definition:** A reaction for which no reaction intermediates have been detected or need to be postulated in order to describe the chemical reaction on a molecular scale. An elementary reaction is assumed to occur in a single step and to pass through a single transition state.

With this definition there are essentially no reactions that are elementary.
Two Transition States

Schematic Potential Energy Surface for Radical Molecule Addition
Two Transition States

- Inner TS
  - Entropic Barrier
  - Covalent Bond Formation
  - Rigid Rotor Harmonic Oscillator

- Outer TS
  - Long Range TST  
  
  Georgievskii, SJK, JCP, 122, 194103 (2005)

- Effective TS
  \[
  \frac{1}{N_{\text{eff}}} = \frac{1}{N_{\text{inner}}} + \frac{1}{N_{\text{outer}}}
  \]
\[ \text{C}_2\text{H}_6 + \text{CN} = \text{C}_2\text{H}_5 + \text{HCN} \]

**CASPT2(7e,6o)/ADZ Potential Energy Surface**
Radical Molecule Kinetics

$\text{C}_2\text{H}_6 + \text{CN}$

Georgievskii, SJK, JPCA, 111, 3802 (2007)
O($^3P$)
• three degenerate orbitals
• split by spin-orbit interaction

O($^3P$) + alkene
• 2 attractive
• 1 repulsive
O(\(^3\)P) + alkene

Dynamics in the van der Waals Region
AKA Roaming
Minimum Energy Path for Roaming Mechanism
Reduced Dimensional Dynamics

• Important Dynamics occurs at large separations -- van der Waals region
• Separation into Conserved Modes (Vibrations of Fragments) and Transitional Modes (Rotations and Translations of Fragments)
• Internal degrees of freedom of the radical fragments are kept fixed
• Analogous to our Variable Reaction Coordinate TST

1) Simplifies surface fitting
   • Atom + Linear: \( 2D \) (\( O+OCN \))
   • Atom + Nonlinear Polyatomic: \( 3D \) (\( H+HCO \))
   • Linear + Linear: \( 4D \) (\( OH+OH \))
   • Linear + Nolinear Polyatomic: \( 5D \) (\( OH+CH_3O \))
   • 2 Nonlinear Polyatomics: \( 6D \) (\( CH_3+HCO \))

2) Simplifies electronic structure calculations
   • Allows very small active spaces (2E,2O)

3) Simplifies Dynamics
   • Eliminates problems with zero point conservation for conserved vibrational modes
Exothermic Reactions: What are the Products?


Use Direct Dynamics As a Complement to TST
HCO Internal Energy Distribution

Much of the HCO will dissociate without further collisions.
HCCO + O_2

Potential Energy Surface
# HCCO + O₂ Product Branching from Dynamics

<table>
<thead>
<tr>
<th>E (kcal)</th>
<th>J</th>
<th>Total #</th>
<th>HCO+CO₂</th>
<th>HCO₂+CO</th>
<th>OCHCO+O</th>
<th>CO+HOOCO</th>
<th>Non Reactive</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>0</td>
<td>9</td>
<td>4(1.0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>37</td>
<td>17(0.77)</td>
<td>1(0.05)</td>
<td>2(0.09)</td>
<td>2(0.09)</td>
<td>5</td>
</tr>
<tr>
<td>25</td>
<td>20</td>
<td>53</td>
<td>18(0.67)</td>
<td>2(0.07)</td>
<td>4(0.15)</td>
<td>3(0.11)</td>
<td>15</td>
</tr>
<tr>
<td>25</td>
<td>50</td>
<td>53</td>
<td>14(0.82)</td>
<td></td>
<td>1(0.06)</td>
<td>2(0.12)</td>
<td>15</td>
</tr>
<tr>
<td>31</td>
<td>0</td>
<td>57</td>
<td>13(0.65)</td>
<td>2(0.10)</td>
<td>4(0.20)</td>
<td>1(0.05)</td>
<td>37</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>209</strong></td>
<td><strong>66(0.73)</strong></td>
<td><strong>5(0.06)</strong></td>
<td><strong>11(0.12)</strong></td>
<td><strong>8(0.09)</strong></td>
<td><strong>119</strong></td>
</tr>
</tbody>
</table>

SJK, Miller, Harding, PCI, 29, 1209 (2002)
Acknowledgements
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Pressure Dependent Kinetics and the Master Equation

Stephen J. Klippenstein
Outline

Pressure Dependent Kinetics & the Master Equation

a) Single Well; Single Channel
b) 2DME
c) Multiple Wells; Multiple Channels
d) Non-Thermal Effects
Lecture 7:
Pressure Dependence for Single Well Single Channel Reactions

Stephen J. Klippenstein
Pressure Dependent Kinetics: Single Well Reactions

Simple Models
• Lindemann-Hinshelwood
• RRKM Theory
• Modified Strong Collider

The Master Equation
• 1-Dimensional (E)
• 2D Master Equation (E,J)
• Energy Transfer
• Troe Fitting

Collision Induced Dissociation
The Physical Picture

Collisions induce changes in E and J - Trying to establish Boltzmann population dist’n

Chemistry induces dissociation – depleting high E tail of Boltzmann dist’n

Low P limit – All that matters is rate of energy transfer from just below to just above dissociation threshold

High P limit – All that matters is rate of dissociation for thermal distribution

Intermediate P – Competition between energy transfer and dissociation
Recombination Kinetics

Recombination is a Multistep Process - not single elementary step

\[ A + B \rightarrow AB(E) \quad k_f(E) \quad [k(T) = \int k(E) P(E)] \]

But, \( E \) is above dissociation threshold so \( AB \) just redissociates

\[ AB(E) \rightarrow A + B \quad k_d(E) \]

Need some process to take away energy and stabilize \( AB \)

Collisions with bath gas \( M \) (or photon emission)

\[ AB(E) + M \rightarrow AB(E') + M' \quad k_c \times P(E \rightarrow E') \]

Effective rate constant is some mix of \( k_f(E), k_d(E), k_c, \) and \( P(E \rightarrow E') \)

Dissociation is related to recombination through equilibrium constant
Assume every collision leads to stabilization
Treat association and dissociation on canonical level

\[ A + B \rightarrow AB^* \quad k_f(T) \]

\[ AB^* \rightarrow A + B \quad k_d(T) \]

\[ AB^* + M \rightarrow AB + M' \quad k_c \]

Steady state for \([AB^*]\) =>

\[ \frac{d[AB]}{dt} = k_{eff} [A] [B] \]

\[ k_{eff} = k_f k_c [M] / (k_d + k_c [M]) = k_f P_{stabilization} \]

High Pressure limit \(([M] \rightarrow \infty)\)

\[ k_{eff} = k_f \]

Low Pressure limit \(([M] \rightarrow 0)\)

\[ k_{eff} = k_f k_c / k_d \]

Not accurate but good for qualitative thought
Simple Models RRKM Theory

Treat energy dependence of association and dissociation rate constants \( k_f(E) \) and \( k_d(E) \)

\[
k_{\text{eff}}(T,p) = \int dE \ k_{\text{eff}}(E) \ P(E) = \int dE \ k_f(E) \ P(E) \ P_{\text{stabilization}}(E,p)
\]

Use transition state theory with quantum state counting to evaluate \( k_f, k_d \)

\[
k_{\text{eff}} = \int dE \ \frac{N^\pm(E)}{h \rho_{\text{reactant}}(E)} \ \frac{\rho_{\text{reactant}}(E) \exp(-\beta E)}{Q_A Q_B} \ \frac{k_c[M]}{k_d(E) + k_c[M]}
\]

\[
k_{\text{eff}} = \frac{1}{hQ_A Q_B} \int dE N^\pm(E) \exp(-\beta E) \ \frac{k_c[M]}{k_d(E) + k_c[M]}
\]

Consider High Pressure Limit; \([M] \rightarrow \infty\)

\[
k_{\text{eff}}^\infty = \frac{1}{hQ_A Q_B} \int dE N^\pm(E) \exp(-\beta E) = \frac{k_B T}{hQ_A Q_B} \int dE \rho^\pm(E) \exp(-\beta E)
\]

\[
k_{\text{eff}}^\infty = \frac{k_B T}{h} \ \frac{Q^\pm}{Q_A Q_B}
\]
Simple Models

Modified Strong Collider

Assume only a fraction $\beta_c$ of collisions lead to stabilization

$$k_{\text{eff}} = \frac{1}{hQ_A Q_B} \int dE N^\pm (E) \exp(-\beta E) \frac{\beta_c k_c [M]}{k_d(E) + \beta_c k_c [M]}$$

Consider low pressure limit; $[M] \to 0$

$$k_{\text{eff}}^0 = \frac{1}{hQ_A Q_B} \int dE N^\pm (E) \exp(-\beta E) \frac{\beta_c k_c [M]}{k_d(E)}$$

$$k_{\text{eff}}^0 = \frac{\beta_c k_c [M]}{Q_A Q_B} \int_0^\infty dE \rho_{AB}(E) \exp(-\beta E)$$

$k_{\text{eff}}^0$ does not depend on transition state! Only the threshold $E$ matters

$\beta_c$ is a fitting parameter - typical value $\sim 0.1$
Master Equation

Consider $n(E,t)$ = time-dependent population of AB molecule at energy $E$

**Irreversible Formulation**

$$\frac{dn(E)}{dt} = k_c[M] \int dE' [P(E,E')n(E',t) - P(E',E)n(E,t)] - k_d(E)n(E,t)$$

Replace $n(E,t)$ with normalized population $x(E,t) = n(E,t)/\int dE n(E,t)$

Steady state for $x$ =>

$$-k(T,p)x(E) = k_c[M] \int dE' P(E,E')x(E') - k_c[M]x(E) - k_d(E)x(E)$$

**Reversible Formulation**

$$\frac{dn(E)}{dt} = k_c[M] \int dE' [P(E,E')n(E',t) - P(E',E)n(E,t)] - k_d(E)n(E,t) + k_f(E) \frac{\rho_{\text{react}}(E)\exp(-\beta E)}{Q_A Q_B} n_A n_B$$
Master Equation  Symmetrized Form

\[ f^2(E) = \rho(E) \exp(-\beta E) = F(E)Q(T) \]

\[ y(E) = x(E)/f(E) \]

Discretize master equation

\[
\frac{dy}{dt} = G' y
\]

\[
G'_{ij} = k_c[M]P(E_i,E_j) \frac{f(E_j)}{f(E_i)} \delta E - \left[ 1 + \frac{k_d(E)}{k_c[M]} \right] \delta_{ij}
\]

Diagonalize

\[
|y(t)\rangle = \sum_{j=1}^{N} \exp(\xi_j t) |g_j\rangle \langle g_j | y(0)\rangle
\]

Eigenvalues are all negative

One with smallest magnitude defines the rate coefficient

\[ k(T,p) = -\xi_1 \]

Others are related to rate of energy transfer - form continuum
Collision Rates

Hard Sphere

\[ k_c^{HS} = \sqrt{\frac{8kBT}{\pi \mu}} \pi d^2 \]

Lennard-Jones

\[ k_c^{LJ} = k_c^{HS} \Omega_{2,2}^* \]

\[ \Omega_{2,2}^* = \frac{1.16145}{(T^*)^{0.14874}} + \frac{0.52487}{\exp(0.7732T^*)} + \frac{2.16178}{\exp(2.437887T^*)} \]

\[ T^* = \frac{k_B T}{\varepsilon} \]

Underestimates collision rate
Correct with larger average energy transferred
Dipole Corrections
Energy Transfer Forms

Exponential Down

\[ P(E,E') = \frac{1}{C_N(E')} \exp(-\Delta E / \alpha) \]

\[ \alpha = \alpha_0 (T/298)^n \]

\[ \alpha_0 \sim 50-400 \text{ cm}^{-1} \]

\[ \alpha_0 \text{ - grows with size of molecule} \]

\[ n \sim 0.85 \]

Gaussian Down

\[ P(E,E') = \frac{1}{C_N(E')} \exp\left[-(\Delta E / \alpha)^2\right] \]

Double Exponential Down

\[ P(E,E') = \frac{1}{C_N(E')} \left[(1-f)\exp(-\Delta E / \alpha_1) + f \exp(-\Delta E / \alpha_2)\right] \]

\[ \alpha \sim 0.85 \text{ cm}^{-1} \]

\[ \alpha_0 \text{ - grows with size of molecule} \]

\[ n \sim 0.85 \]

Fit to experiment
Energy Transfer Moments

Average Energy Transferred

$$\langle \Delta E \rangle = \int dE (E' - E) P(E, E')$$

Average Downwards Energy Transferred

$$\langle \Delta E_d \rangle = \int_0^{E'} dE' (E' - E) P(E, E') / \int_0^{E'} dE' P(E, E')$$

$$\langle \Delta E_d \rangle \approx \alpha \quad \text{for exponential down}$$

Average squared energy transfer

$$\langle \Delta E^2 \rangle = \int dE (E - E')^2 P(E, E')$$
Pressure Dependence  

\[ \text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{Products} \]

\[ T = 300 \text{ K} \]

\[ \Delta E_{\text{Down}} \text{ Parameter} \]

Low \( T \) – Fit to data

Higher \( T \) – no data to fit

Empirical

Size Dependent

T Dependent

Collider Dependent

~Factor of 2 Uncertainty
Fig. 8 Values of $\langle \Delta E_d \rangle$ as a function of temperature for several molecules and collision partners.
Troe Fitting

Need to represent $k(T,p)$ for Global Models
Standard is Troe Fitting [Troe, JPC, 83, 114 (1979)]

\[
k(T,p) = \frac{k_0[M]k^\infty}{k^\infty + k_0[M]} F
\]

\[
\log_{10} F = \frac{\log_{10} F_{cent}}{1 + \left[ \frac{\log_{10}(p^*) + c}{N - d(\log_{10}(p^*) + c)} \right]^2}
\]

\[
p^* = \frac{k_0[M]}{k^\infty}
\]

\[
d = 0.14
\]

\[
c = -0.4 - 0.67 \log_{10} F_{cent}
\]

\[
N = 0.75 - 1.27 \log_{10} F_{cent}
\]

Fit $k_0$ & $k^\infty$ to modified Arrhenius

\[
k_0 = A_0 T^{n_0} \exp(-E_0 / T)
\]

Fit $F_{cent}$ to:

\[
F_{cent} = (1 - a) \exp(-T/T^{**}) + a \exp(-T/T^*) + \exp(-T^*/T)
\]
Troe Fitting Problems

Limited Accuracy
Typical Errors ~ 10 to 20%

Improved Fitting Formulas

Still problems for tunneling
Multiple channels - actual P dependence is dramatically different from Troe Form

Use Log Interpolation

\[ \log k = \log k_i + (\log k_{i+1} - \log k_i) \frac{(\log p - \log p_i)}{(\log p_{i+1} - \log p_i)} \]

Part of Current ChemKin
Master Equation

Problems at Low T

numerical difficulties with diagonalization due to large dynamic range

Various Solutions

1. Integrate in time
2. Quadruple Precision
3. Reformulate with sink for complex => Matrix inversion
Master Equation Problems at high T

Boltzmann population extends beyond dissociation threshold

Dissociation occurs on same time scale as energy relaxation

Nonequilibrium factor \( f_{ne} \)

\[
f_{ne} = \frac{\left( \int dEc(E) \right)^2}{\left( \int dE \frac{c^2(E)}{F(E)} \right)^2}
\]

\( c(E) = \text{steady state distribution} \)

Deviation of \( f_{ne} \) from unity indicates how much dissociation happens before relaxation

Detailed balance is still satisfied for fraction that happens after relaxation
Figure 8. Relative values of $f(E;T)$. The functions are normalized so that the peak is always unity.
Boltzmann Distributions

$C_2H_5O_2$
Non-equilibrium factors

$\text{Temperature (K)}$

$\text{f_{ne} (dimensionless)}$

Miller, SJK, JPCA, 110, 10528 (2006)
Master Equation 2-Dimensional

Total Angular Momentum J - conserved between collisions

Master equation in E and J

\[ n(E,J,t) \quad \text{or} \quad x(E,J,t) \]

\[ P(E,J,E',J') \quad k(E,J) \]

Numerical solution timeconsuming

Need more information on energy transfer than we have
Approximate Reduction from 2D to 1D

E model

\[ P(E,J,E',J') = P(E,E') \, \varphi(E,J) \]

Rotational energy transfer like vibrational
J distribution given by phase space volume
\[ \varphi(E,J) = (2J+1) \frac{\rho(E,J)}{\rho(E)} \]
\[ \rho(E) = \sum_J (2J+1) \rho(E,J) \]
\[ k(E) = \sum_J (2J+1) \frac{N^+(E,J)}{h\rho(E)} \]

Use \( k(E) \) and \( P(E,E') \) in 1D Master Eqn

Does not resolve J dependent thresholds
All rotational degrees of freedom are active
Incorrect low pressure limit
2D Master Equation    E,J Model

E,J model

like E model, but treat averaging of $k(E,J)$ properly

$$k(E) = \sum_J k(E,J) \frac{y(E,J)}{\sum_J y(E,J)}$$

$$y(E,J) = \frac{\varphi(E,J)}{k_c[M] + k(E,J)}$$

$$x(E) = \sum_J x(E,J)$$

$$x(E,J) = \frac{k_c[M] \varphi(E,J)}{Z + k(E,J)} \int dE' P(E,E') x(E')$$

Proper treatment of J dependent thresholds
Proper zero-pressure limit
Proper high-pressure limit
Consistent with detailed balance
Still microcanonical strong collider in J
Steady State Distribution

$\text{CH}_4$

E model

E, J model
Low Pressure Limit

\[
\text{H} + \text{C}_2\text{H}_2 + \text{He} \rightarrow \text{C}_2\text{H}_3 + \text{He}
\]

Miller, SJK, PCCP, 6, 1192 (2004)
2D Master Equation \( \varepsilon, J \) Model

\( \varepsilon, J \) model

Active energy - does not include overall rotation

\[ \varepsilon = E - E_J \]

\[ E_J = BJ(J+1) \]

\[ P(\varepsilon, J, \varepsilon', J') = P(\varepsilon, \varepsilon') \Phi(\varepsilon, J) \]

\[ \Phi(\varepsilon, J) = (2J+1)\rho(\varepsilon, J)\exp(-\beta E_J)/\Sigma_J(2J+1)\rho(\varepsilon, J)\exp(-\beta E_J) \]

\[ \rho(\varepsilon, J) = \text{density of states for active degrees of freedom} \]

Thermally equilibrated J distribution

Satisfies Detailed balance
A Priori Pressure Dependence

Model as \( P(E,E') \sim \exp(-\Delta E/\alpha) \)

Past: \( \alpha \) treated as empirical parameter; fit to experiment

Can we Calculate \( \alpha = \langle \Delta E_{\text{down}} \rangle \)?

Jasper – use classical trajectory simulations


Focus on moment of distribution – allows for small ensembles of trajectories

Direct Dynamics – use to validate PES methods
Energy Transfer from Trajectories

Collisional energy transfer in unimolecular reactions: Direct classical trajectories for CH$_4$=CH$_3$+H in Helium


$\alpha_0=110 \text{ cm}^{-1}$ $n=0.81$

Problem:
This ignores effect of anharmonicities $\rho_{\text{anh}} \sim 2*\rho_{\text{har}}$

A Priori rate prediction is 2 times too high
Trajectory Simulations and the Two Dimensional Master Equation


Jasper – calculate $<\Delta E_{\text{down}}>$, $<\Delta J_{\text{down}}>$, $<\Delta E_{\text{down}}^2>$, $<\Delta J_{\text{down}}^2>$ $<\Delta E_{\text{down}} \Delta J_{\text{down}}>$; all as a function of $J$

Take simple model for $P(E,J;E',J')$

$P \sim \exp[-(\Delta E_d/\alpha(J'))^{\varepsilon_E}] * \exp[-(\Delta J_d/\gamma(J'))^{\varepsilon_J}]$

Adjust parameters $[\alpha(J'), \gamma(J'), \varepsilon_E, \varepsilon_J, Z_{LJ}]$ to reproduce the moments from trajectories

Employ model form in 2-Dimensional Master Equation


CH$_3$ + H $\rightarrow$ CH$_4$
C$_2$H$_3$ System

Trajectories
1000 K, $J = \sim 22$, $\Delta E = \sim 100$ cm$^{-1}$

$\Delta J = 8$  $\Delta J = -16$

C$_2$H$_2$ + H $\rightarrow$ C$_2$H$_3$

T = 300 K

H + O₂ (+Ar) -> HO₂ (+Ar) \[ \text{How Accurate?} \]

Verdicchio, Jasper, Pelzer, Georgievskii, Klippenstein, work in progress

Most Important Pressure Dependent Reaction in Combustion
Competes with H + O₂ -> OH + O

Sensitivities in H₂/O₂

$\text{H} + \text{O}_2 \, (+\text{Ar}) \rightarrow \text{HO}_2 \, (+\text{Ar})$  \hspace{1cm} \text{Higher Temperature}
\[ \text{H} + \text{O}_2 (+M) \rightarrow \text{HO}_2 (+M) \]

**Different Colliders**

(i) Exhaust Gas Recirculation  
(ii) MILD Combustion  
(iii) Oxy Fuel Combustion  
(iv) Chemical Looping Combustion

**Collider Efficiencies are Temperature Dependent**

Cannot use this Data Effectively in ChemKin
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Work on expanding these calculations to take advantage of exascale computational environments is just beginning through support from DOE-ASCR
Lecture 8:  
Multiple-Well  
Multiple-Channel  
Master Equation  

Stephen J. Klippenstein
Multiple-Well Multiple-Channel
Time Dependent Master Equation

1. The Kinetic Model
2. Collisionless Limit
3. Time Dependent Populations
4. Kinetic Phenomenology
5. Species Merging
6. Uncertainties
The Kinetic Model

Energy Transfer
Bath Gas B; [B] >> [M] >> [R]
Z; Lennard Jones
P(E',E); Exponential Down

Phenomenology
- $k_R + M \leftrightarrow P$
- $k_R + M \leftrightarrow W_1$
- $k_R + M \leftrightarrow W_2$
- $k_W \leftrightarrow W_1$
- $k_W \leftrightarrow W_2$
- $k_W \leftrightarrow P$

RRKM Theory
- $k_{d1}$
- $k_{a1}$
- $k_{12}$
- $k_{21}$
- $k_{p1}$
- $k_{p2}$
MultiWell MultiChannel Reactions

Master Equation Generalization
Straightforward; just more connections
P_i(E,t) for each well i

Two approaches to obtaining P(t)

Stochastic Model for time dependence
Barker – MultiWell – 2001 … 2017
Vereecken, Peeters
Cavallotti

Use eigensolutions to express time propagation analytically
Robertson/Pilling
Klippenstein/Miller
SJK – Extend VariFlex (2000)
Multiple-Well Multiple-Channel Master Equation

\[
\frac{dn_i(E)}{dt} = k_c n_B \int dE' P_i(E, E') n_i(E') - k_c n_B n_i(E) - k_{d_i}(E)n_i(E) - \sum_{p=1}^{N_p} k_{p_i}(E)n_i(E) - \\
\sum_{j \neq i}^M k_{j \text{isom}}(E)n_i(E) + \sum_{j \neq i}^M k_{i \text{isom}}(E)n_j(E) + K_{eq_i} k_{d_i}(E)F_i(E)n_R n_m
\]

\[
\frac{dn_R}{dt} = \sum_{i=1}^M \int dE k_{d_i}(E)n_i(E) - n_R n_m \sum_{i=1}^M K_{eq_i} \int dE k_{d_i}(E)F_i(E)
\]

M Wells \quad N_p \text{ Products} \quad M+1 \text{ Chemical Species} \quad n_B >> n_m >> n_R \quad B=\text{Bath}, \ m=\text{Molecule}, \ R=\text{Radical} \quad \text{Linear Master Equation}
Collisionless Limit

Consider \( Z \rightarrow 0 \)

\[
\frac{d}{dt} \left| n(E,J) \right\rangle = -K(E,J) \left| n(E,J) \right\rangle + n_R n_m \left| b(E,J) \right\rangle \rho_{Rm}(E,J) \exp(-\beta E)/Q_{Rm}
\]

\[
\frac{d}{dt} \left| P(E,J) \right\rangle = D(E,J) \left| n(E,J) \right\rangle
\]

Steady State for \( n(E,J) \)

\[
\frac{d}{dt} \left| P(E,J) \right\rangle = D(E,J) \left| b(E,J) \right\rangle n_R n_m \rho_{Rm}(E,J) \exp(-\beta E)/Q_{Rm}(T)
\]

\[
\left| k_0(T) \right\rangle = \frac{1}{Q_{Rm}(T)} \sum_{J} (2J + 1) \int dED(E,J) \left| b(E,J) \right\rangle \rho_{Rm}(E,J) \exp(-\beta E)
\]

Flux coefficients
Time-Dependent Populations

- **Discretize** Energy Levels
- Transition Matrix; **Renormalize** -> real, symmetric; $G$

\[
\frac{d}{dt} |w(t)\rangle = G |w(t)\rangle \quad y_i(E,t) = x_i(E,t)/f_i(E)
\]

\[
|w(t)\rangle = \left[ y_I(E_{0_I}), \ldots, y_I(E_{\text{max}}), \ldots, y_i(E_{0_i}), \ldots, y_i(E_{\text{max}}), \ldots, \left( \frac{n_m}{QR_m \delta E} \right)^{1/2} X_R, \ldots \right]^T
\]

- **Diagonalize**

\[
|w(t)\rangle = \sum_{j=1}^{N_I+\ldots+N_M+1} e^{\lambda_j t} |g_j\rangle \langle g_j| w(0)\rangle
\]
From Time Solutions to Rate Coefficients

Historical
Pretend you are an experimentalist
1. Look for exponential decays
2. Correlate decay rates with rate constants
3. Problems when there are nearly degenerate eigenvalues
   - When is decay close enough to single exponential?
Suppose 2nd eigenvector contributes to only 1% of the initial decay but that $\lambda_2/\lambda_1 = 100$
Rate coefficient will differ by a factor of two from apparent exponential decay
Branching similarly incorrect

$C_3H_3 + C_3H_3$ Disaster
Eigenvalues $C_3H_3 + C_3H_3$
CSE Approach  SJK, Miller, JPCA, 106, 9267 (2002)

System with \( N \) Wells and \( M \) Energy Levels per Well
Master Equation has \( \sim N \times M \) Eigenvalues; e.g. \( 10 \times 100 = 1000 \)

Two Types of Eigenvalues/Eigenvectors
1. Large Eigenvalues
   - Transitions in Energy
   - very many, closely spaced – Quasicontinuum
   - IERE (Internal Energy Relaxation Eigensystem)
2. Small Eigenvalues
   - Chemical Changes
   - \( N - 1 \) Only
   - CSE (Chemically Significant Eigensystem)

All we care about is chemistry
• One to one correspondence between CSE and Rate Coefficients
• Klippenstein/Miller 2002; Widom - 1970s
• IERE\( s \) decay rapidly

VariFlexm  Klippenstein
MESMER  Glowacki, Liang, Morley, Pilling, Robertson, JPCA, 116, 9545 (2012)
MESS  Y. Georgievskii, J. A. Miller, M. P. Burke, SJK, JPCA, 117, 12146 (2013)
A Simple Solution: Separation of Timescales

- M+1 modes corresponding to chemical change have least negative eigenvalues.
- $\lambda'$ s for chemical modes (CSE) well separated from remaining $\lambda'$ s for energy transfer (IERE)
- After energy relaxation can treat populations as

$$ w_{\ell}(t) = \sum_{j=1}^{M+1} e^{\lambda_j t} g_{j\ell} \langle g_j | w_A(0) \rangle $$

$$ \frac{dX_i}{dt} = -\sum_{j=1}^{M+1} \lambda_j e^{\lambda_j t} \Delta X^{(A)}_{ij}; \quad \Delta X^{(A)}_{ij} = -\langle g_j | w_A(0) \rangle \delta E \sum_{l\in i} f_i(E_l) g_{j\ell} $$

- Eigenpairs ($\lambda_i, \Delta X_i$) correspond to Normal modes of chemical relaxation
Method 1 \( t=0 \) Limit and Start in Well A

- **Phenomenology**
  \[ \frac{dX_A}{dt} (0) = -k_{TA} X_A (0) \]

- **Master Equation**
  \[ \frac{dX_A}{dt} (0) = - \sum_{j=1}^{M+1} \lambda_j \Delta X^{(A)}_{Aj} \]

- \( k_{TA} = \sum_{j=1}^{M+1} \lambda_j \Delta X^{(A)}_{Aj} \)

- Similarly, consider \( dX_i/dt \) implies
  \[ k_{Ai} = - \sum_{j=1}^{M+1} \lambda_j \Delta X^{(A)}_{ij} \]

- \( k_{AR} = - \sum_{j=1}^{M+1} \lambda_j \Delta X^{(A)}_{Rj}; \quad \Delta X_{Rj} = -\left( \frac{Q_{Rm} \delta E}{n_m} \right)^{1/2} g_{j\ell} \langle g_j | w_A (0) \rangle \)

- \( k_{Ap} = - \sum_{j=1}^{M+1} \lambda_j \Delta X^{(A)}_{pj}; \quad \left( \Delta X_R + \Delta X_p + \sum_{i=1}^M \Delta X_i \right)_j = 0 \)
Method 2  Long time limit

- \( X_i(t) = \sum_{j=0}^{M+1} a_{ij} e^{\lambda_j t} \equiv \sum_{j=0}^{M+1} a_{ij} v_j \)
  \[ |X\rangle = A |v\rangle \quad |v\rangle = B |X\rangle \]

- \( \frac{dX_i}{dt} = \sum_{j=0}^{M+1} \sum_{\ell=1}^{M+2} \lambda_j a_{ij} b_{j\ell} X_\ell \)
  Long time relative to IERE eigenvalues

- \( \frac{dX_i}{dt} = \sum_{\ell \neq i} k_{\ell i} X_\ell - \sum_{\ell \neq i} k_{i\ell} X_i \)
  Relate time dependent populations to kinetic phenomenology

- \( k_{\ell i} = \sum_{j=0}^{M+1} \lambda_j a_{ij} b_{j\ell} \quad \ell \neq i \)

VariFlex – Implements both these methods
MESMER – Builds from these methods
High Temperature Kinetics

Apparent Problem
• High Temperatures CSE eigenvalues merge with quasicontinuum
• Species are no longer distinct
• Rate description is not possible for original space of N species
• Rate description for reduced space with merged species is still well defined

Example – Two Isomers – cis and trans HOCO
• Low T
  cis HOCO
  trans HOCO
  isomerization slow (relative to collision rate)
  Each with their own chemistry
• High T
  cis and trans isomerize rapidly
  can’t possibly separate cis and trans species in a bottle
  think of HOCO as merging of cis and trans
  Consider kinetics for HOCO
$\text{C}_2\text{H}_5 + \text{O}_2$  \hspace{1cm} PES & Eigenvalue Spectrum
Species Merging
Equilibration of 2 Wells
Merge Wells 1 and 2
Evaluate total density and total microcanonical rates from merged species
Species Merging
Equilibration of 2 Wells

Merge Wells 1 and 3
Evaluate total density and total microcanonical rates from merged species
Miller, SJK, PCCP, 15, 4744 (2013)
Species Merging
Equilibration of 1 Well with Reactants

Merge Wells 1 and Reactants
Evaluate total density and total microcanonical rates from merged species
Species Merging
Equilibration of 1 Well with Products

![Graph showing energy levels and reaction rates as functions of temperature.](image)
Xylyl Decomposition
Cavallotti, SJK

Eigenvalue Spectrum for Master Equation

Black = Chemically Significant

Blue = Internal Energy Relaxation
Only First 10 Plotted

Red = Collision Rate
MESS Advance  Automated Species Reduction

• Analysis is Tedious
  – Variflex requires prespecification of the equilibration partners
  – Trial and error of possible reductions

• Automate the reduction process
  – Use threshold for ratio of highest chemically significant eigenvalue to lowest quasi-continuum eigenvalues
  – Consider all possible reductions
  – Evaluate overlap of reduced subspace with remaining chemically significant eigenvectors
  – Reduction with best overlap is maintained
$C_6H_5 + C_2H_2$

$P1$ + $H$

Merge $W1$ with $W2$
\( \text{C}_6\text{H}_5 + \text{C}_2\text{H}_2 \rightarrow \text{Products} \)

W3 Merges with W1 at 1200 K

W1,3 Merges with Reactants (0.52) and Products (0.48) at 1500 K

C\(_8\)H\(_7\) Not Chemically Stable Beyond 1500 K

A. M. Mebel, Y. Georgievskii, A. W. Jasper, SJK, PCI, 36, 919 (2017)
Master Equation Codes

Eigenvalue Eigenvector Methods

- VariFlex
- Klippenstein
  Research Code - Not usable without personal training
- MESMER
  Pilling (Leeds)
  http://sourceforge.net/projects/mesmer/
- MESS
  Georgievskii
  tcg.cse.anl.gov/papr

Stochastic Master Equation Solvers

Experimental Perspective

- Multiwell
  Barker (Michigan)
  http://esse.engin.umich.edu/multiwell/MultiWell/MultiWell%20Home/MultiWell%20Home.html
- Vereecken and Peeters (Leuven)

Steady State Solvers

- ChemRate
  Tsang (NIST)
  http://www.mokrushin.com/ChemRate/chemrate.html
Low Temperature Chemistry

Propane Oxidation \( n\text{-propyl} + O_2 \)

Phenomenological Rate Coefficients from Multiple Well Master Equation

Coupling of Uncertainties: n-propyl + O₂

Uncertainties
+/- 0.5 kcal/mol in \( \Delta H_{rxn} \)
+/- 1.0 kcal/mol in \( \Delta H^{\dagger} \)
+/- 10% in 5 lowest frequencies
\( \Delta E_{down} = (200 +/- 20\%) (T/298)(0.85 +/- 0.15) \)

Entrance rate +/− 60%

2σ uncertainty typically a factor of 5

C. F. Goldsmith, A. S. Tomlin, SJK
C$_2$H$_5$OH

Lili Xing, Shuang Li, Zhaohui Wang, Bin Yang, SJK, Feng Zhang

Competition Between:
C$_2$H$_4$ + H$_2$O \quad \text{(R1)}
CH$_3$ + CH$_2$OH \quad \text{(R2)}

Low Pressure Limit:
$k_{CH3+CH2OH} \sim \exp(-20/\alpha)$
$C_2H_5OH$

$P = 0.01$ atm
Acknowledgements
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Lecture 9:
Non-Thermal Effects

Stephen J. Klippenstein
Non-Thermal Effects

1. Prompt Dissociation
   - HCO
   - KetoHydroPeroxide in Propyl Oxidation

2. Secondary Reaction Effects
   - $\text{C}_2\text{H}_2 + \text{OH} + \text{O}_2$
   - QOOH + O$_2$
   - H + O$_2$ + Radical

3. DME Oxidation
**HCO in Combustion**  
**Prompt Dissociation**

HCO is Key Species for Flame Speeds

Decomposition: \( \text{HCO} + \text{M} \rightarrow \text{H} + \text{CO} + \text{M} \)

Competes with Oxidation: \( \text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO} \)

H \(\rightarrow\) chain branching: \( \text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH} \)

In contrast, \( \text{HO}_2 \) is at best chain propagating.

HCO Formed by Abstraction

\( \text{H}_2\text{CO} + \text{X} \rightarrow \text{HCO} + \text{HX} \)

versus

\( \text{H}_2\text{CO} + \text{X} \rightarrow \text{H} + \text{CO} + \text{HX} \)

OH, H, \( \text{HO}_2 \), \( \text{CH}_3 \) are key radicals  
Abstractions are Exothermic  
Does HCO dissociate prior to thermalization?

Direct Dynamics for $\text{H}_2\text{CO} + \text{X}$

- Propagate trajectories to determine internal energy in HCO products
- Propagate from TS on to products
- M06-2X/6-311++G(d,p) – Calibrated against CCSD(T)
- 280 trajectories for $\text{CH}_2\text{O} + \text{OH}$
- 690 trajectories for $\text{CH}_2\text{O} + \text{H}$
- Three different initial energies; 1, 10, 40 kcal/mol above saddle point
Sample trajectory for CH$_2$O + OH
Sample trajectory for CH$_2$O + H
Direct Dissociation  \( \text{CH}_2\text{O} + X \rightarrow \text{CO} + \text{H} + \text{HX} \)
Thermal Direct Dissociation

Even thermal distribution has nonzero $P_{\text{diss}}$

$$P_{\text{diss}} = 1 - f_{ne}$$

where $f_{ne}$ is the non-equilibrium factor of Gilbert and Smith

$$f_{ne} = \frac{1}{\int_0^{\infty} \frac{c(E)}{F(E)} c(E) dE}$$

equilibrium energy distribution

Steady-state energy distribution
Kinetic Modeling

\[ k(T) \]

\[ \text{CH}_2\text{O} + \text{R} \rightleftharpoons \text{HCO} + \text{RH} \]

\[ [1 - P_{\text{diss}}(T, P)] \times k(T) \]

\[ \text{CH}_2\text{O} + \text{R} \rightleftharpoons \text{HCO} + \text{RH} \]

\[ + \]

\[ P_{\text{diss}}(T, P) \times k(T) \]

\[ \text{CH}_2\text{O} + \text{R} \rightleftharpoons \text{H} + \text{CO} + \text{RH} \]
Trioxane Flame Speeds and Speciation Profiles

**Flame Speed [cm/s]**

- Experimental data: Santner et al. 2015 P = 1 atm
- Model results:
  - Aramco Mech 1.3: blue solid line
  - USC Mech II: red solid line
  - Original: solid lines w/ $P_{HCO}$ dotted lines

**Mole Fraction**

- $\text{HO}_2 \times 4$
- $\text{H}$
- $\text{O}$
- $\text{OH}$

**Distance from Burner [mm]**
Global Effects of Prompt HCO Dissociation

**H$_2$CO Ignition Delay**

**Heptane Flame Speed**

![Graph showing CO production time vs. 1000/T](image1)

- Aramco Mech 1.3
- USC Mech II
- original
- $w/ P_{diss,HCO}$

![Graph showing flame speed vs. equivalence ratio](image2)

- $P = 1$ atm
- $P = 2$ atm
- $P = 5$ atm
- $P = 10$ atm

PRF high T model:
- original
- $w/ P_{diss,HCO}$
KHP Formation and Decay in Propyl Oxidation

OQ’OOH Distribution from O$_2$QOOH Dissociation
O$_2$QOOH Non-Thermal Dissociation
Direct M06-2X Trajectory Simulations
Prompt Reaction Probabilities for KHP from Propane Oxidation

$E_{TS} = 0$

$E_{TS} = 12$ kcal/mol

$E_{TS} = 30$ kcal/mol
C$_2$H$_2$ + OH + O$_2$

“Prompt” Reaction
Glowacki, Lockhart, Blitz, Klippenstein, Pilling, Seakins
Science, 337, 1066 (2012)

Populations
XO$_2$ = 0.

Populations
XO$_2$ = 0.9
$\text{C}_2\text{H}_2 + \text{OH} + \text{O}_2$
Why is Experimental Activation for Ethers Much Less Than Calculated?

Heinz Pitsch
Net Enthalpy Change for DME is 25 kcal/mol greater than for Propane

KetoHydroPeroxide (KHP) Formation Step is Much More Exothermic in DME

M. Dontgen, K. Leonhard, H. Pitsch, SJK, In progress
Dimethyl Ether Oxidation

Simplest Ether; Exhibits NTC Behavior
Chemistry Turbulence Interactions
DNS Modeling; Engine Models
Interest in DME as Additive

Speciation Experiments:
Suzaki  JPCA, 2007, 111, 3776
PLP; OH and HO₂
Guo      PCI, 2013, 34, 573
Flow Reactor; H₂O₂
Eskola    JPCA, 2014, 118, 6773
PLP; OH
Herrmann  Comb. Flame 2014, 161, 384
Flow Reactor; TOF-MS
Kurimot   PCI, 2015, 35, 457
Flow Reactor; HO₂, H₂O₂
Moshammer JPCA 2015, 199, 7361
JPCA, 2016, 120, 7890.
JSR; ALS; Many Species Incl. HPMF Identification
Sheps    Preliminary Results

Theory:
DFT; R+O₂; QOOH+O₂;
HPMF Dissn; Direct Dynamics; Kin.
Suzaki    JPCA, 2007, 111, 3776;
G2M and MRMP2//CAS
Eskola    JPCA, 2014, 118, 6773;
CBS-QB3 + Master Equation
Xing Chin J Chem. Phys. 2015, 28, 563
QCISD(T)/CBS//B3LYP + Master Equation for HPMF Dissn.
Wang      PCCP, 2016, 18, 7707
CBS-QB3 + Master Equation

- Goal is to learn about non-equilibrium effects
- Ultimate plan is to compare with multi-species expts in same way as was done for propyl oxidation
Ketohydroperoxide (HPMF) Formation

CCSD(T)/CBS//B2PLYPD3

Product Energy Distribution

Statistical fraction \(~0.8\) in KHP

\(\Rightarrow\) Peak at 54, 58, 61 kcal/mol for 400, 500, 600 K

2 sigma \(~15\) kcal/mol
Ketohydroperoxide (HPMF) Decomposition

- HCOOH + Criegee
- OQ'O + OH
- HCOOH + HCO + OH
- PFA + CO + H₂
- HPMF
- H₂CO + Carbonic Acid
- FAA + H₂O
- FA + FA
- HOOCH₂OCHO

Korcek
Ketohydroperoxide Incipient Direct Decomposition

JSR + ALS MultiSpecies Measurements at 1 Bar
CH₃OCH₂ + O₂

Suzaki:
Key Transition States
Have Large Degree
of Multireference
Character

Eskola:
QOOH -> Products
Lowered 9.4 kcal/mol
to -8.2 kcal/mol

RO₂⁻→QOOH
Lowered 3.7 kcal/mol
-13.6 kcal/mol

This Work:
QOOH -> Products
-3.5 (+/- 3) kcal/mol
Lower Conformer
RO₂⁻→QOOH
-11.8 (+/- 0.4 kcal/mol); 2 TSs
Zwitterionic vs Radical

Related:
$C_4H_9O + O_2$
Welz, SJK, Harding, Taatjes, Zador, JPCL, 4, 350 (2013)
**CH$_3$OCH$_2$ + O$_2$ Loss Rate**

**Reference Prediction**

- TS2 – 2 kcal/mol
- TS1 – 0.5 kcal/mol
- Nu_imag = 3000 cm$^{-1}$
- $E_{down} = 250(T/298)^{1.1}$
- $k_{add} * 1.1$

**Optimized Prediction**
OH Yield From CH$_3$OCH$_2$ + O$_2$

TS2 – 3 kcal/mol
TS1 – 1 kcal/mol
nu$_{imag}$ = 4000 cm$^{-1}$
$k_{add} \times 1.1$
\[ X = \text{Abstractor} \]
\[ \text{OH, H, HO}_2, \text{O, O}_2, \text{CH}_3 \]

<table>
<thead>
<tr>
<th>High Temperature</th>
<th>Heat</th>
<th>Low Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ R' + \text{Alkene} ]</td>
<td>[ \text{Heat} ]</td>
<td>[ \text{O}_2 \rightarrow \text{RO}_2 \rightarrow \text{Alkene} + \text{HO}_2 ]</td>
</tr>
<tr>
<td>[ \ldots ]</td>
<td>[ \text{C}_6\text{H}_6, \text{PAHs} ]</td>
<td>[ \text{O}_2 \rightarrow \text{QOOH} \rightarrow \text{O}_2\text{QOOH} \rightarrow ]</td>
</tr>
<tr>
<td>[ \text{H, CH}_3 + \text{Unsaturated Hydrocarbons} + \text{Resonantly Stabilized Radicals} ]</td>
<td>[ \text{C}_3\text{H}_3, \text{C}_2\text{H}_2 \rightarrow \text{Hydrocarbon Growth} ]</td>
<td>[ \text{OO'O} + \text{OH} ]</td>
</tr>
<tr>
<td>[ \text{Heat, O}_2 \rightarrow \text{O} + \text{OH} \rightarrow \text{Chain Branching} \rightarrow \text{OO'O} + \text{OH} ]</td>
<td>[ \text{CH}_3 \rightarrow \text{CH}_3\text{O} + \text{O} ]</td>
<td>[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 ]</td>
</tr>
<tr>
<td>[ \text{CH}_2\text{O} + \text{OH} \rightarrow \text{HCO} + \text{XH} ]</td>
<td>[ \text{Heat} ]</td>
<td>[ \text{Heat} \rightarrow 2\text{OH} ]</td>
</tr>
</tbody>
</table>
Ab Initio Abstraction Kinetics $\text{OH} + \text{CH}_3\text{OCH}_3$

\[ k^{TST}(T) = \kappa \frac{k_B T}{h} \frac{Q^#(T)}{Q_{\text{reac}}(T)} \exp\left(-\frac{E^#}{k_B T}\right) \]

Methods
- ANL0
- Variational
- Multidimensional Hindered Rotors
- Eckart
DME Dissociation
Next

DME + $O_2$  DME + $HO_2$

Modelers:
Toluene + $O_2$
Increase by a Factor of 10

SJK:
Rates aren’t wrong by that much

Raghu:
Impurities
Can’t measure Fuel + $O_2$
MET and the Foundations of Kinetic Modeling

- **Model Failure is the Key to New Science**
  - Optimize Rate Coefficients within Uncertainties
  - Missing Channels?

- **Flaws in Foundational Assumptions**
  - What is a Rate Constant?
    - Connection from Multi-Well Master Equation to Phenomenological Rate Coefficients; Miller, SJK, Robertson, Pilling, Shannon, Zador, Jasper, Goldsmith, Burke, JPCA, 120, 306 (2016).
  - Formally Direct Reactions
  - Species Merging
  - High T (e.g., 2000 K) Still a Problem

- **Non-Thermal Effects**
  - Species Do Not Equilibrate Between Successive Reaction Steps
    - QOOH Reacts with O$_2$ Before Cooling $\Rightarrow$ More QOOH Than Expected
  - Prompt Dissociation – Precursor Reaction Produces Kinetically Unstable Species
    - H$_2$CO + OH $\rightarrow$ HCO* + H$_2$O $\rightarrow$ H + CO + H$_2$O
Tight Constraints Illuminate Shortcomings

- **Single Experiment, Low Accuracy Theory**
  - Easy to reproduce data with apparently reasonable rate representations
- **More Experiments**
  - Speciation – many constraints
  - High P Experiments – more relevant constraints
  - SubMechanisms – more details for key chemistry
- **Higher Accuracy Theory**
  - Better TS analysis
  - Dynamics Simulations
  - 2-Dimensional Master Equation
  - Anharmonicity Treatments
  - Better Representations; What is a Rate Constant; When do we need to go beyond a Rate Constant
- **Model Full Set of Data with One Model**
  - Flow tubes, shock tubes, RCM, flames
  - Speciation, ignition delay, flame speeds, submechanism chemistry
Predictive Automated Combustion Chemistry Exascale Next Generation Fuel Simulation CODE

- Integrated Suite of Massively Parallel Computer Codes for Fuel System to Obtain Industry Transforming Improvement in Fidelity of Simulations
- Uncertainty Driven Iterative Theoretical/Computational Refinement of Mechanisms
- Parallelization via Simultaneous Characterizations of the Reactions in the Mechanism
- Couple RMG, EStokTP (MESS, KinBot, Gaussian/MOLPRO/NWChem, ...) Zero-RK, DRGASA, Dakota, NEK5000
- Fuels Team – Bair, Green, Jasper, Klippenstein, Lu, Wagner, Wozniak, Zador
- 0.8 Million/Yr
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Chemical Dynamics: Ahren Jasper
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