SAND2013-5707C

Theoretical approaches to compute accurate kinetics of the 1-butyl + O_2 reaction

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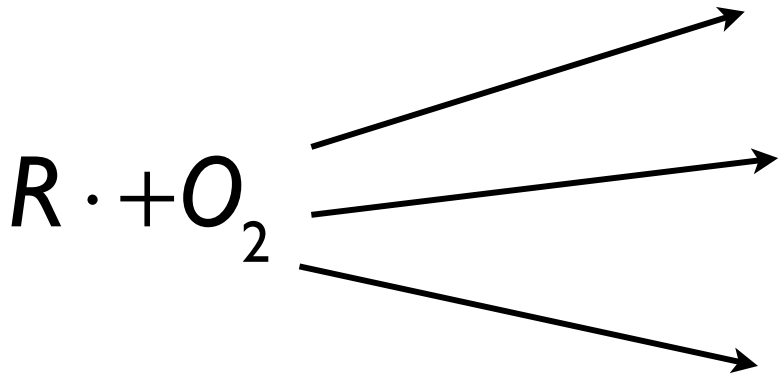
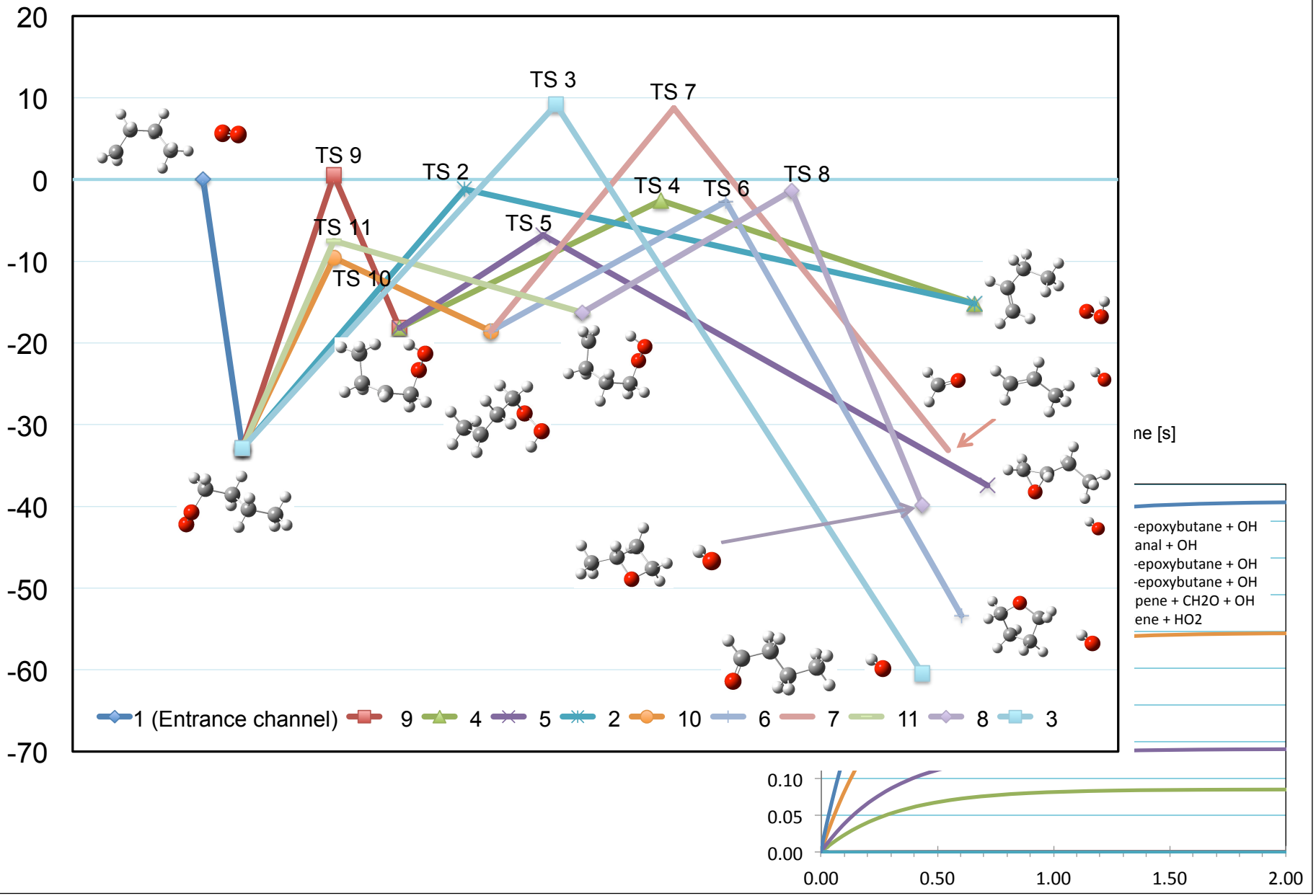
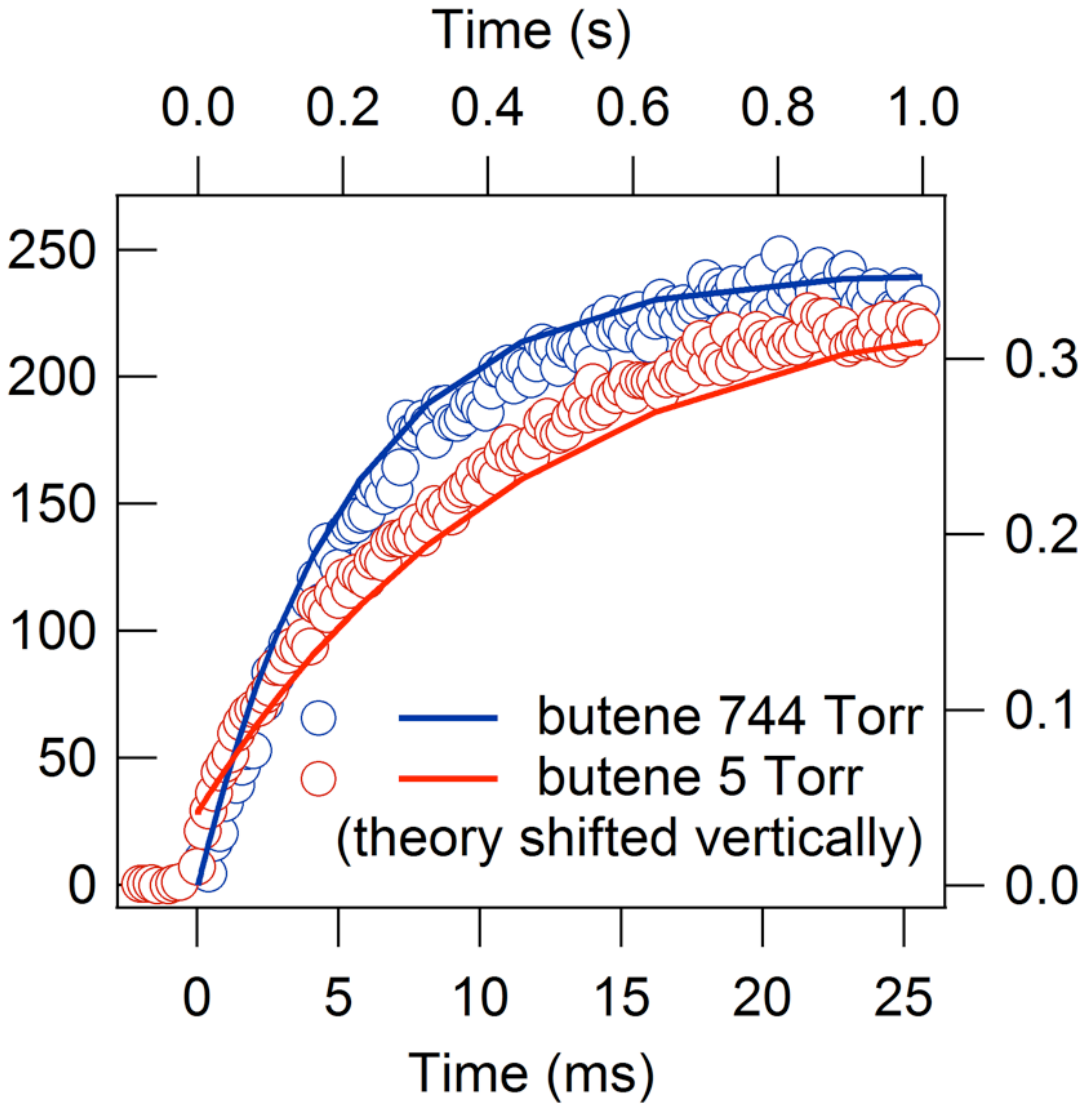
Livermore, CA 94550

Seville, July 11, 2013


$R\cdot + O_2$

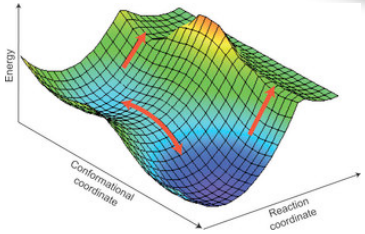

20
10
0
-10
-20
-30
-40
-50
-60
-70
TS 3
TS 7
TS 9
TS 2
TS 4
TS 6
TS 8
TS 11
TS 5
TS 10
1 (Entrance channel)
9
4
5
2
10
6
7
11
8
3
ne [s]
-epoxybutane + OH
anal + OH
-epoxybutane + OH
-epoxybutane + OH
pene + CH2O + OH
ene + HO2
0.10
0.05
0.00
0.00
0.50
1.00
1.50
2.00

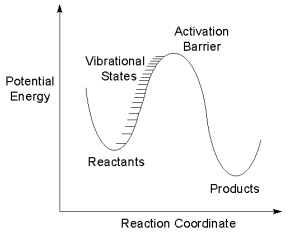


A. Eskola
C. Taatjes

$$E\Psi(\mathbf{r}) = \frac{-\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}) + V(\mathbf{r})\Psi(\mathbf{r})$$

Electronic Structure Theory

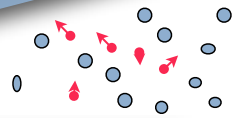




Basis sets
Estimation of the complete basis set limit
Benchmark values for barrier heights
Born-Oppenheimer approximation
Various potential energy surface fitting schemes

Statistical Mechanics

Partition function $Q = \sum_s e^{-\beta E_s}$



Partition function calculation of multiple structures
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Anharmonicity in effects

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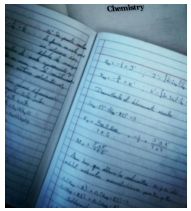

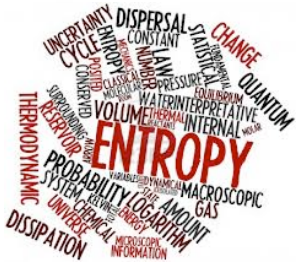

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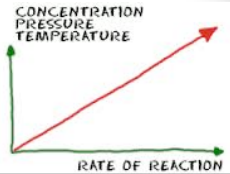

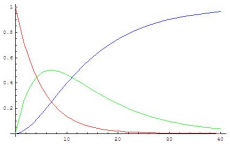

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Rate constants from the relaxation modes
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$$E\Psi(\mathbf{r}) = \frac{-\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}) + V(\mathbf{r})\Psi(\mathbf{r})$$

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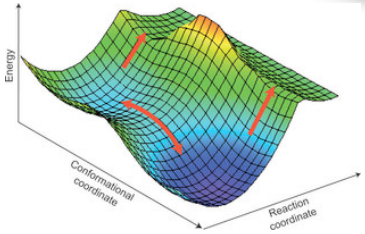

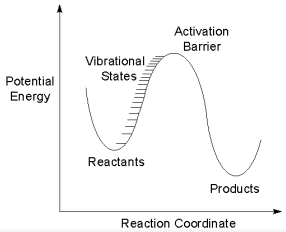

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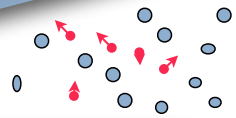

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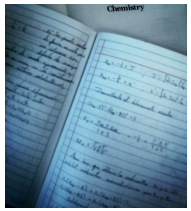

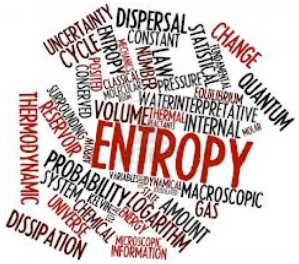

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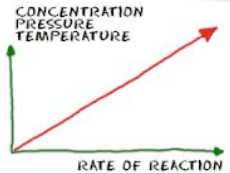

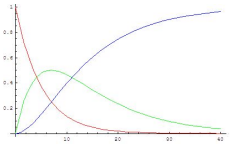

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Functional:
M06-2X

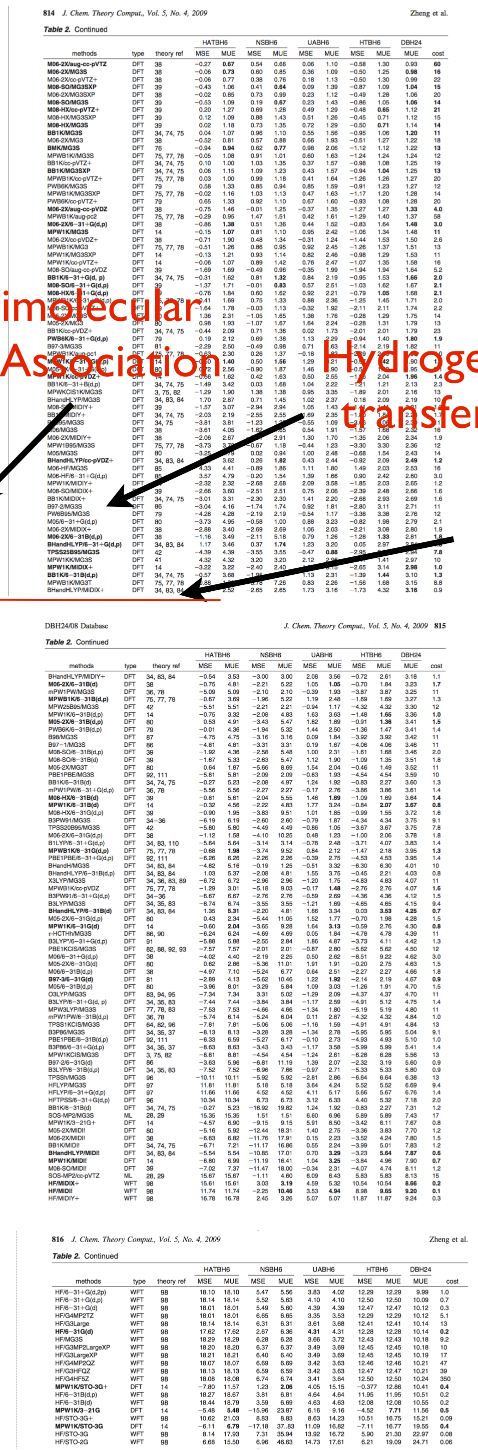
Heavy atom transfer

Nucleofilic substitution

Unimolecular and Association

Hydrogen transfer

Overall:
24 barriers

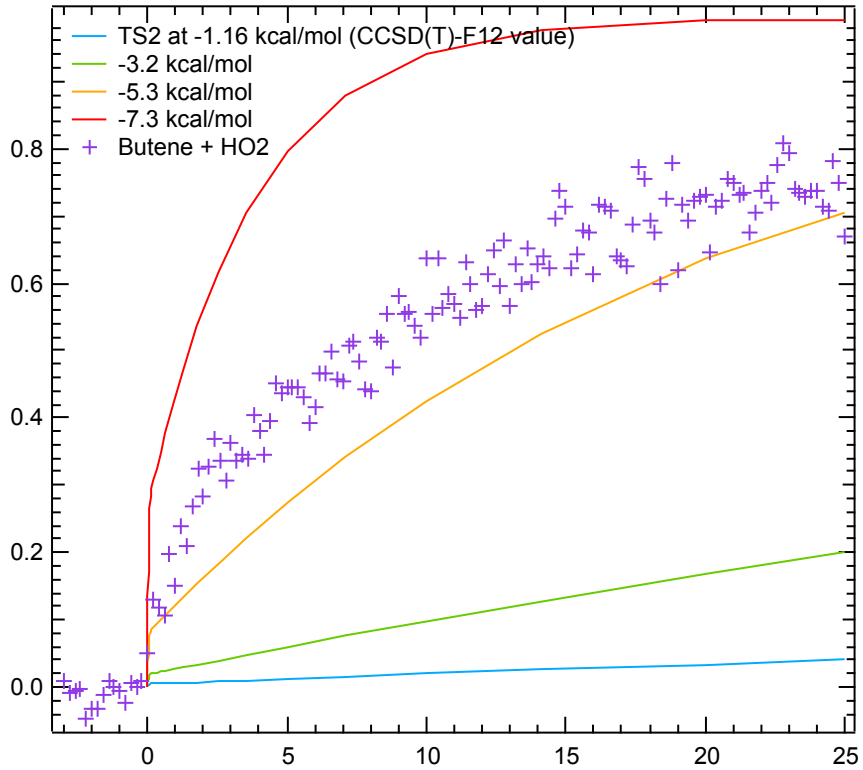


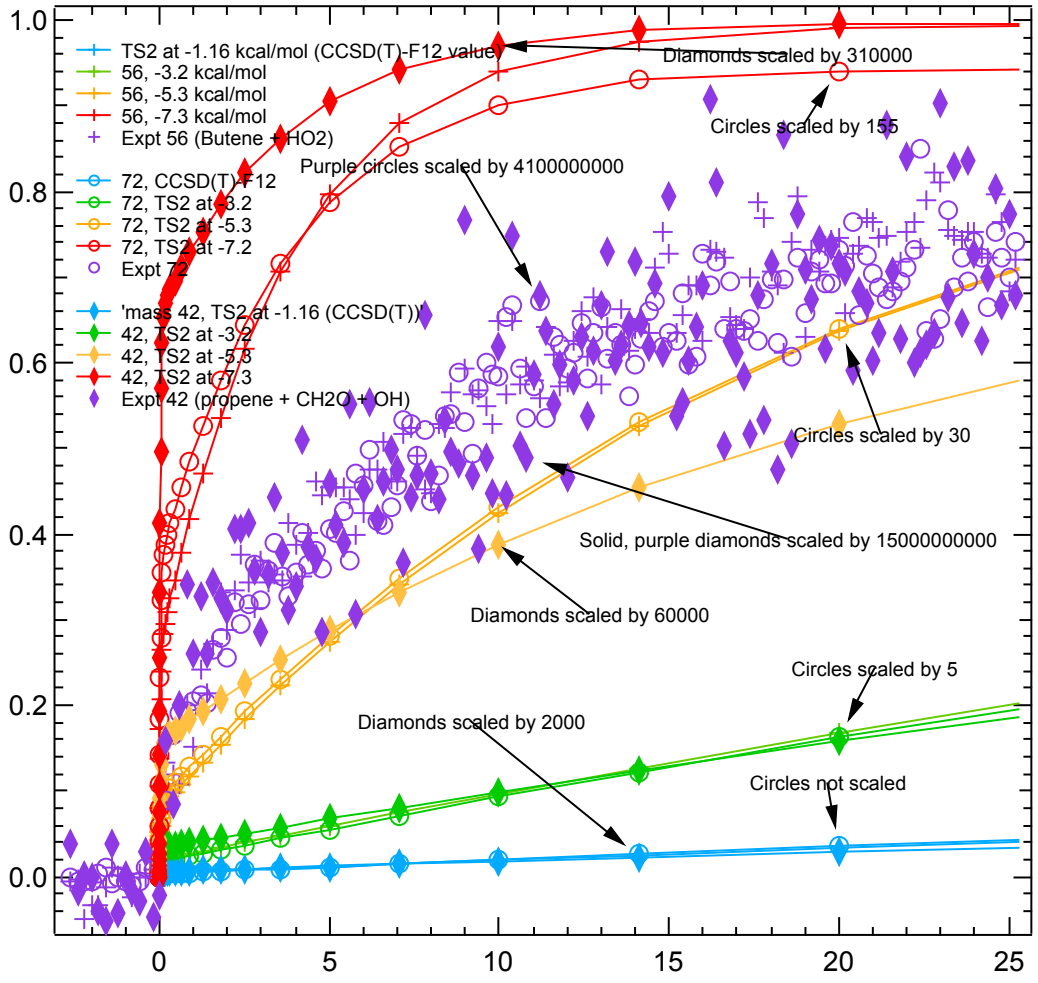
Accuracy of the energy values

	Electronic energy + harmonic zero-point vibrational energy		
	M06-2X[a]	CCSD(T)[b]	QCISD(T)[c]
1-butyl + O_2	–	–	–
peroxy radical	-33.50	-32.89	-33.2
TS 9	1.75	0.52	0.2
QOOH-2	-19.49	-18.16	-19.5
TS 4	-0.83	-2.57	-1.9
butene + HO_2	-13.57	-15.22	–
TS 5	-1.72	-6.81	-5.2
1,2-epoxybutane	-38.24	-37.45	–
TS 2	0.65	-1.16	-3.2
TS 10	-9.96	-9.57	-10.9
QOOH-3	-20.30	-18.55	-19.4
TS 6	4.05	-2.72	(10.9)
1,4-epoxybutane	-52.30	-53.38	–
TS 7	8.15	8.72	–
Propene + formaldehyde + OH	-29.28	-33.13	–
TS 11	-8.76	-7.51	-9.3
QOOH-4	-17.8	-16.27	-16.3
TS 8	2.18	-1.35	-2.3
1,3-epoxybutane + OH	-38.38	-39.82	–
TS 3	11.19	9.19	–
butanal + OH	-57.93	-60.45	–

a M06-2X/MG3S electronic energy + zero-point vibrational energy
b UCCSD(T)-F12a/cc-pVDZ-F12//M06-2X/MG3S electronic energy + M06-2X/MG3S zero-point vibrational energy
a E(MP2/6-311++G(2df,2pd) + E(QCISD(T)/6-31G(d)) – E(MP2/6-31G(d)) including B3LYP/6-31G* ZPE (Faraday Discuss., **199**, 101-120 (2001))

Just the TS2 barrier




TS2 at -1.16 kcal/mol (CCSD(T)-F12 value)
56, -3.2 kcal/mol
56, -5.3 kcal/mol
56, -7.3 kcal/mol
Expt 56 (Butene + HO2)
72, CCSD(T)-F12
72, TS2 at -3.2
72, TS2 at -5.3
72, TS2 at -7.2
Expt 72
'mass 42, TS2 at -1.16 (CCSD(T))'
42, TS2 at -3.2
42, TS2 at -5.3
42, TS2 at -7.3
Expt 42 (propene + CH2O + OH)
Diamonds scaled by 310000
Circles scaled by 155
Purple circles scaled by 4100000000
Circles scaled by 30
Solid, purple diamonds scaled by 15000000000
Diamonds scaled by 60000
Circles scaled by 5
Diamonds scaled by 2000
Circles not scaled
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25

Conformational surfaces

DFT surface ⟶ Hind. rotor part. fxn. MS-T part. fxn.

CCSD(T) surface ⟶ Hind. rotor part. fxn. MS-T part. fxn.

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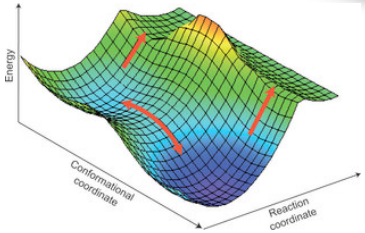

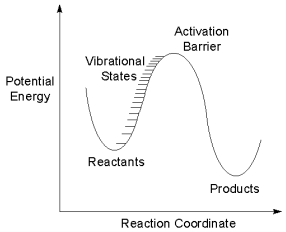

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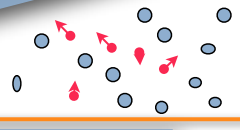

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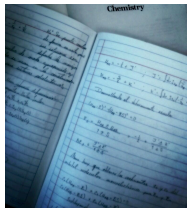

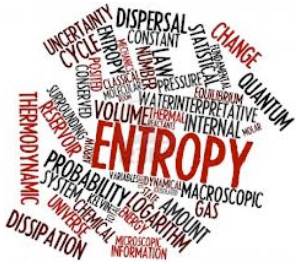

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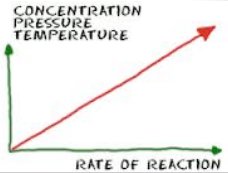

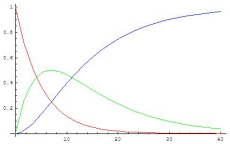

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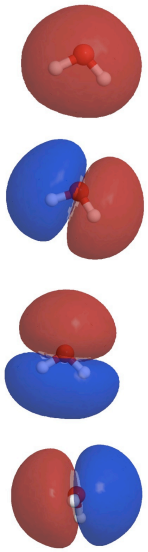
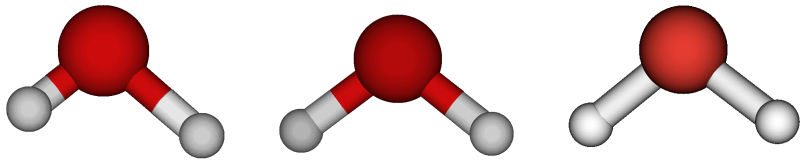
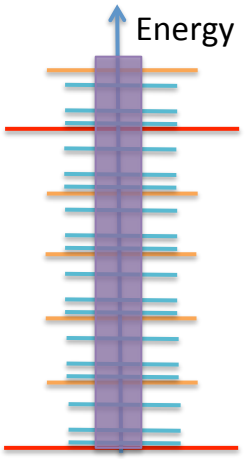


Partition function $Q = \sum_s e^{-\beta E_s}$

$H\Psi = \mathcal{E}\Psi$





$$(H_{electronic} + H_{translation} + H_{rotation} + H_{vibration})\Psi = \mathcal{E}\Psi$$

$(H_{translation})\Psi = \mathcal{E}_t\Psi$ ← Particle in a box

$(H_{rotation})\Psi = \mathcal{E}_r\Psi$ ← Rigid rotor

$(H_{vibration})\Psi = \mathcal{E}_v\Psi$ ← Harmonic oscillator

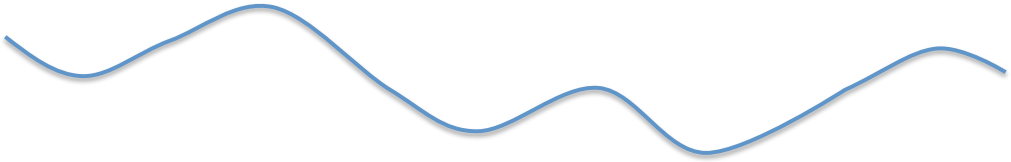
$(H_{electronic})\Psi = \mathcal{E}_e\Psi$ ← Electronic structure methods

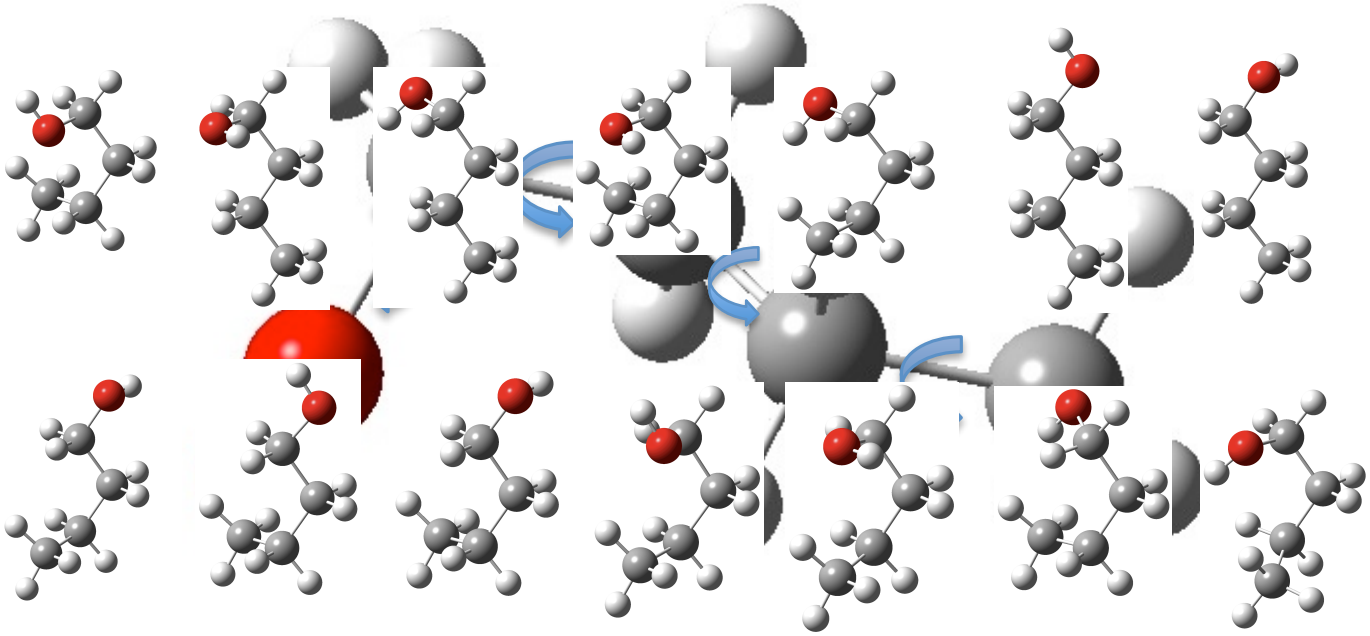
$$Q = q_{electronic} q_{translation} q_{rotation} q_{vibration}$$

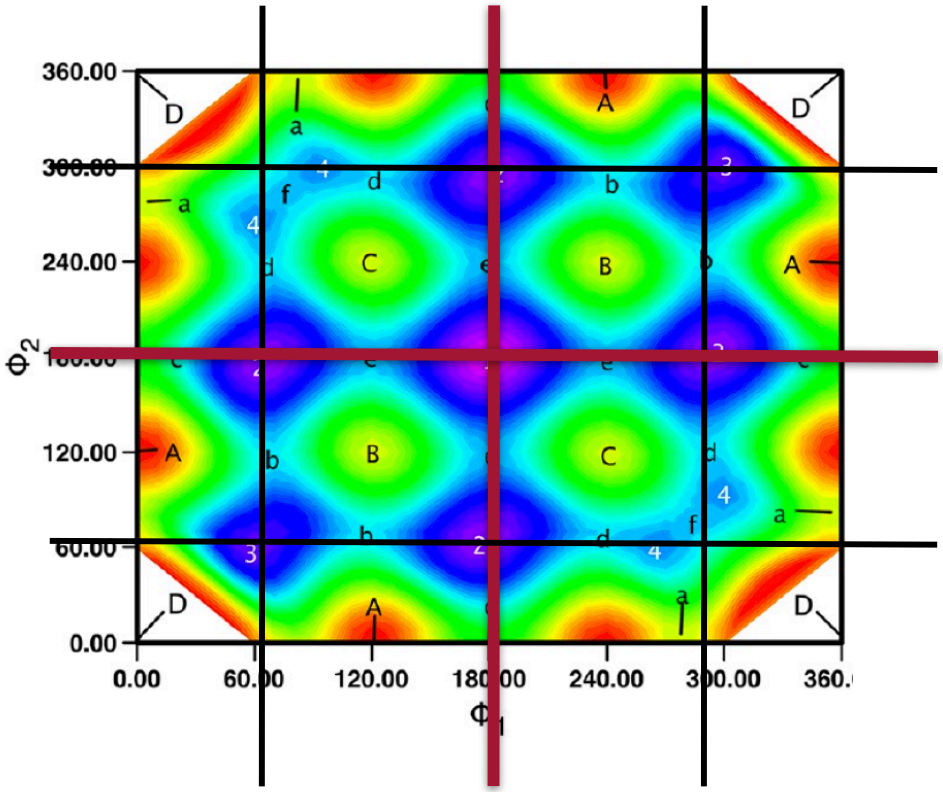
$$\left[\frac{2\pi mkT}{h^2}\right]^{3/2} V \left[\frac{8\pi^2 IkT}{\sigma h^2}\right] \left[\frac{e^{-\frac{h\nu}{2kT}}}{1 - e^{-\frac{h\nu}{kT}}}\right]$$

Partition function $Q = \sum_s e^{-\beta E_s}$

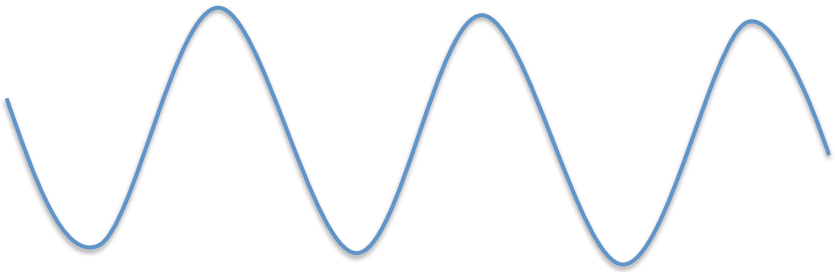
✓ many low-energy states that should be accounted for in Q

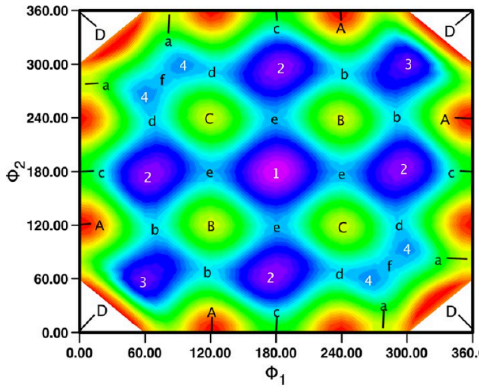






Hindered rotor approximation





$$Q = q_{electronic} q_{translation} q_{con-rovib}$$

Multi-structural all-structure approximation

Anharmonicity

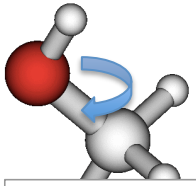
Non-separability – avoid assigning torsions to specific normal modes

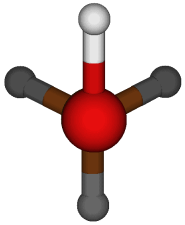
$$f_{j,\tau} = \sigma_\tau \left[\frac{q_{j,\tau}^{\mathrm{RC}}}{q_{j,\tau}^{\mathrm{CHO}}} \right]$$

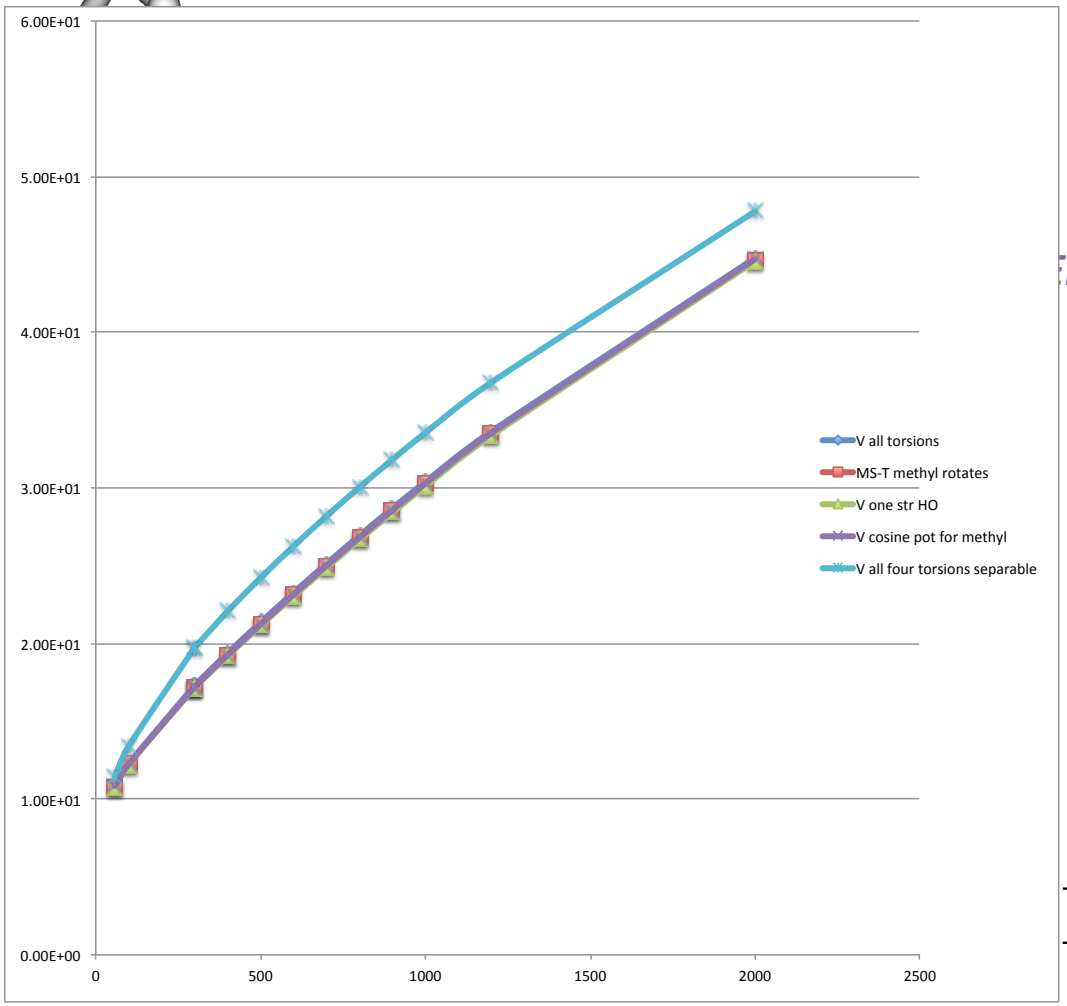
$$Q_{\text{con-rovib}}^{\text{MS-T}} = \sum_{j=1}^{J} Q_{\text{rot},j} \exp\left(-\beta U_j\right) Q_j^{\text{HO}} Z_j \prod_{\tau=1}^{t} f_{j,\tau}$$

is used to reach a correct high-T limit

Zheng, J.; Yu, T.; Papajak, E.; Alecu, I. M.; Mielke, S.; Truhlar, D. G. *Phys. Chem. Chem. Phys. 13*, 10885–10907 (2011)







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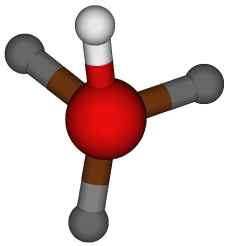

$$\prod_{\tau=1}^{t} f_{j,\tau}$$

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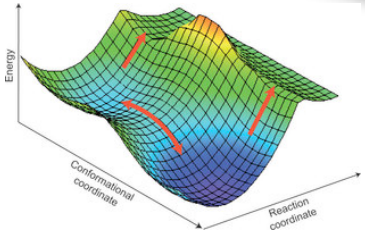

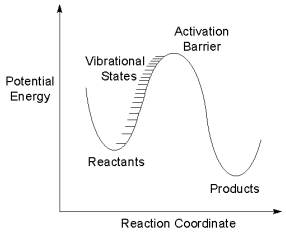

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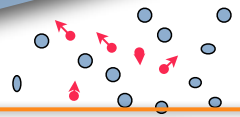

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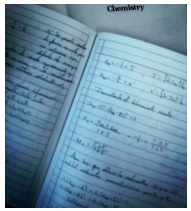
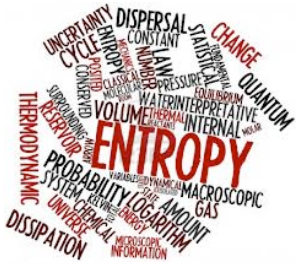
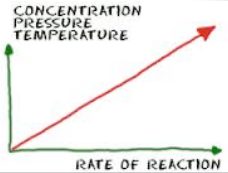
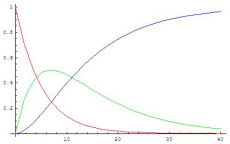




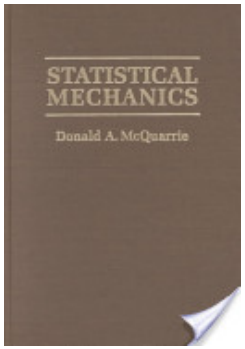
Thermodynamic functions for species in this reaction
Estimation of the relative stability of the intermediate species (radicals, TS's)

Kinetics





Master equation
Rate constants from the relaxation modes
Time evolution of the system - compare with the experiment
Product branching ratios - compare with experiment



Thermodynamics

Enthalpy $$H_T^\circ = -\frac{\partial \ln \tilde{Q}}{\partial\left(1/k_{\mathrm{B}}T\right)} + k_{\mathrm{B}}T$$

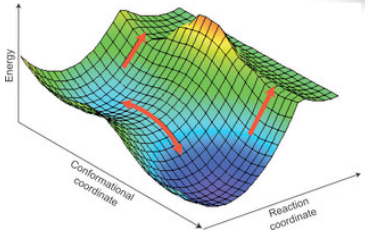
Heat capacity $$C_P^\circ\left(T\right) = -\left(\frac{\partial H^\circ}{\partial T}\right)_p$$

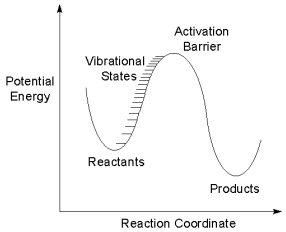
Entropy $$S_T^\circ = k_B + k_B \ln \tilde{Q} - \frac{1}{T}\left(\frac{\partial \ln \tilde{Q}}{\partial\left(1/k_{\mathrm{B}}T\right)}\right)_V$$

Gibbs Free Energy $$G_T^\circ = H_T^\circ - TS_T^\circ$$

$$E\Psi(\mathbf{r}) = \frac{-\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}) + V(\mathbf{r})\Psi(\mathbf{r})$$

Electronic Structure Theory

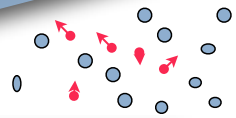




Basis sets
Estimation of the complete basis set limit
Benchmark values for barrier heights
Born-Oppenheimer approximation
Various potential energy surface fitting schemes

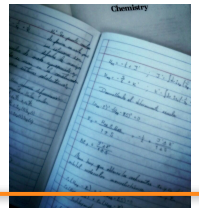
Statistical Mechanics

Partition function $Q = \sum_s e^{-\beta E_s}$



Partition function calculation of multiple structures
Hindered rotor approximation
Anharmonicity in effects

Thermodynamics



Thermodynamic functions for species in this reaction
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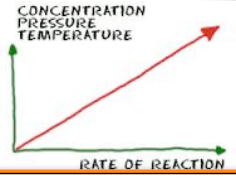

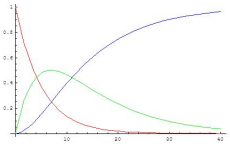

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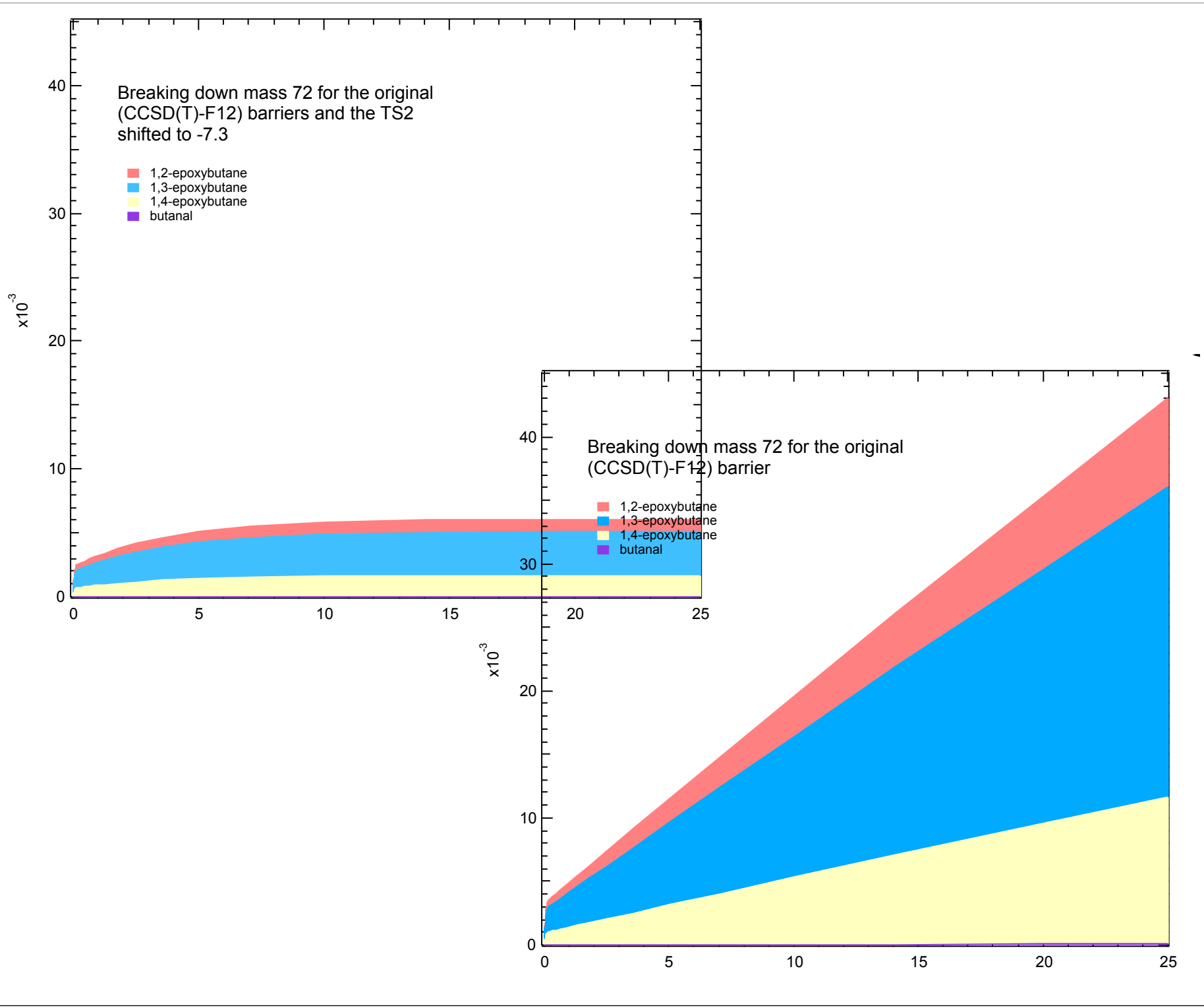
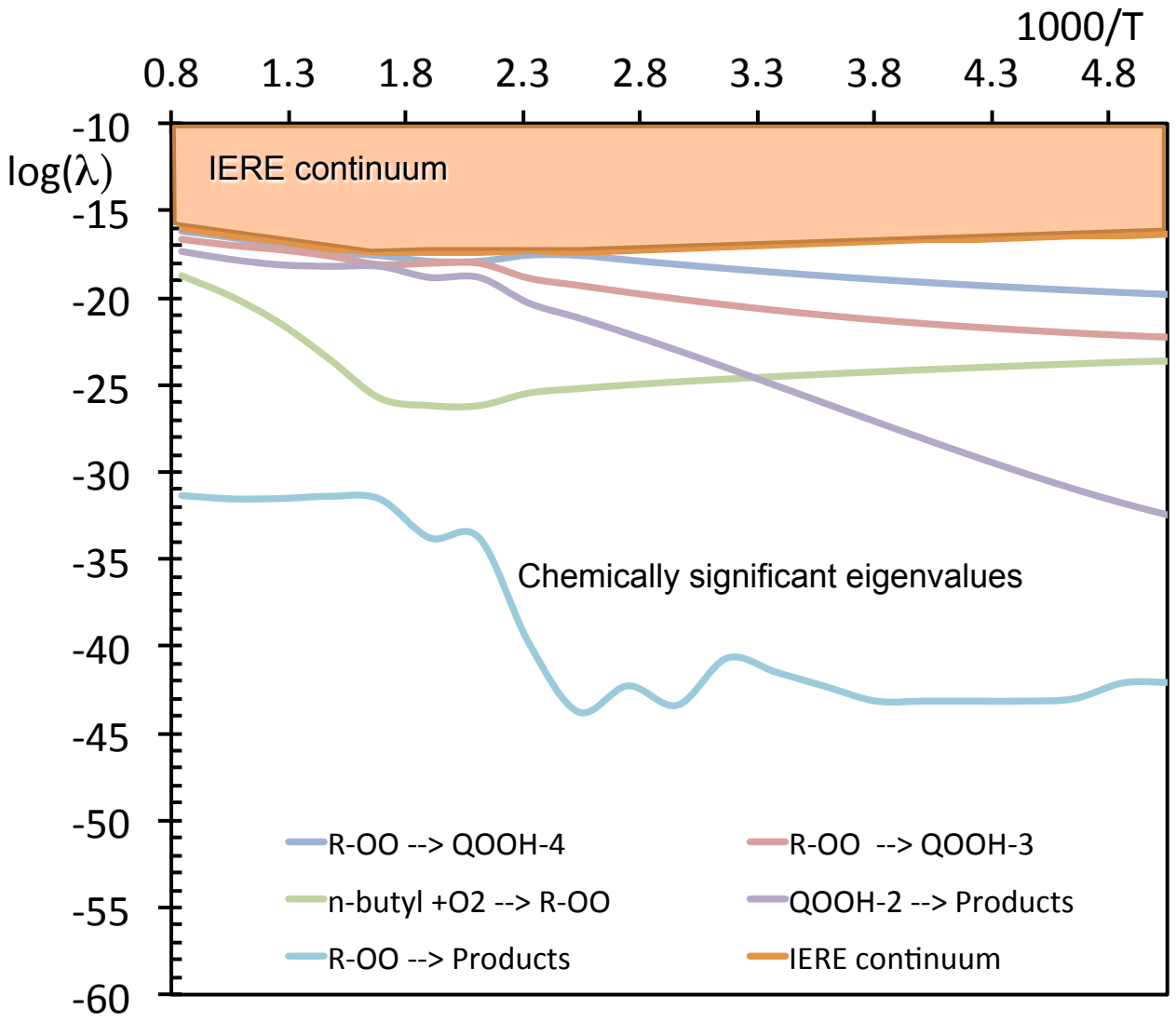
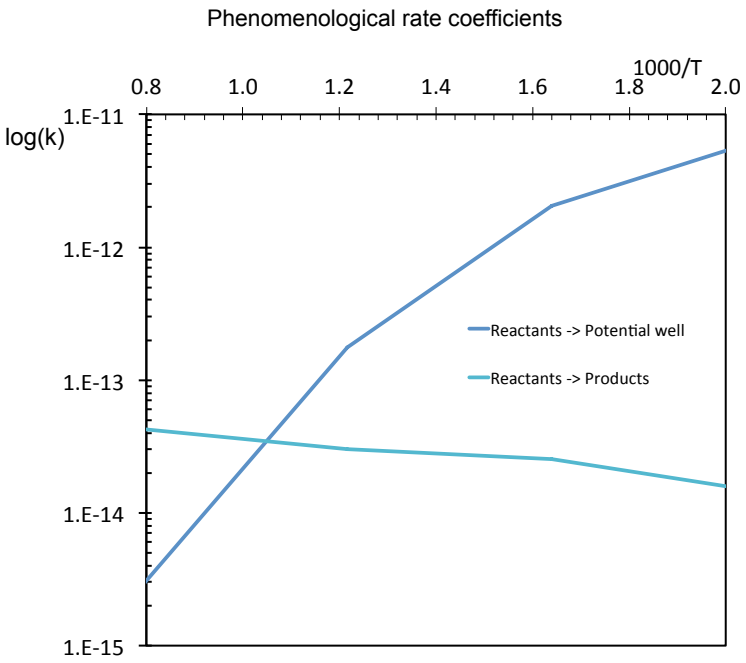
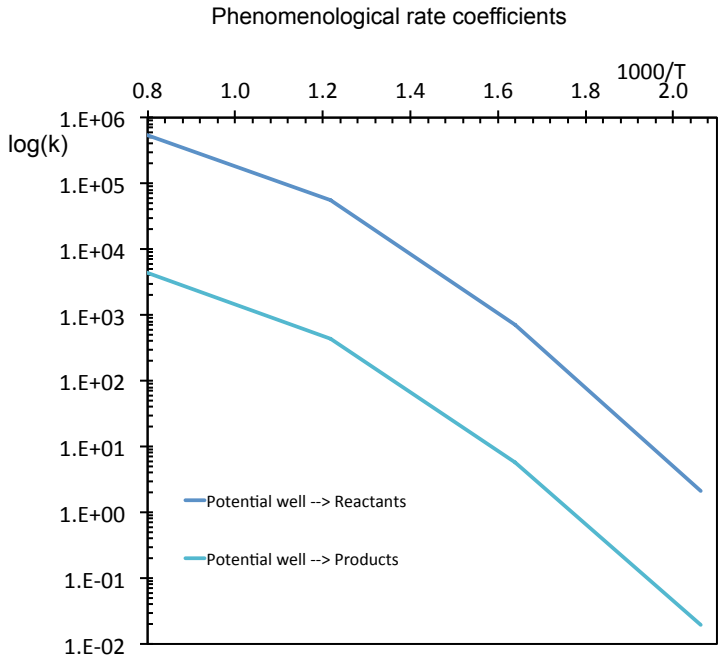
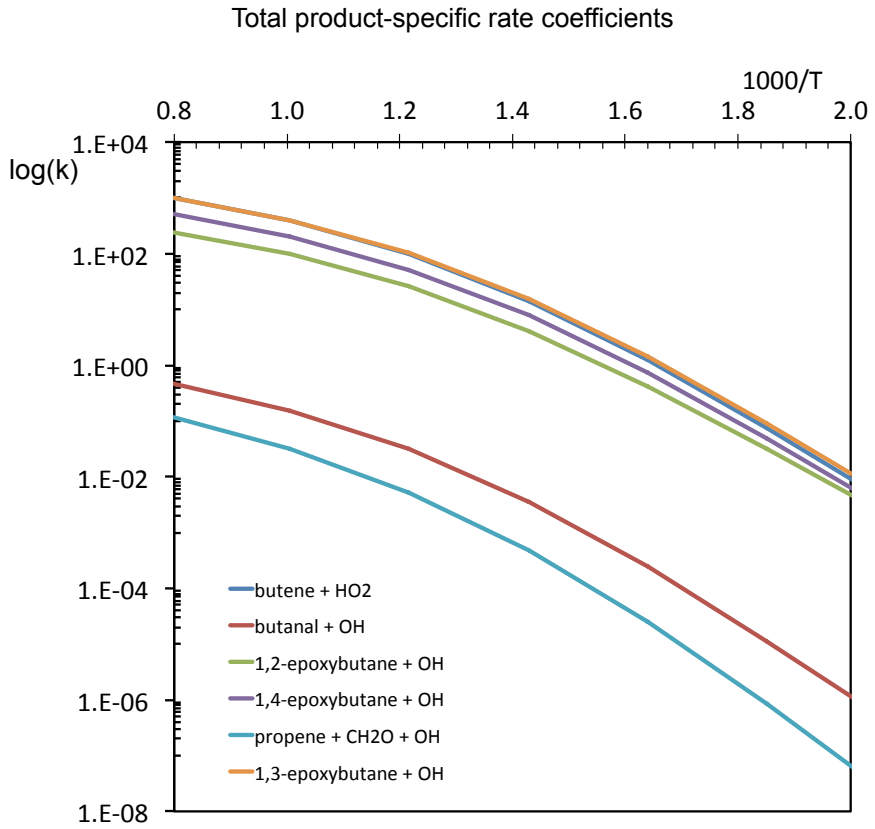
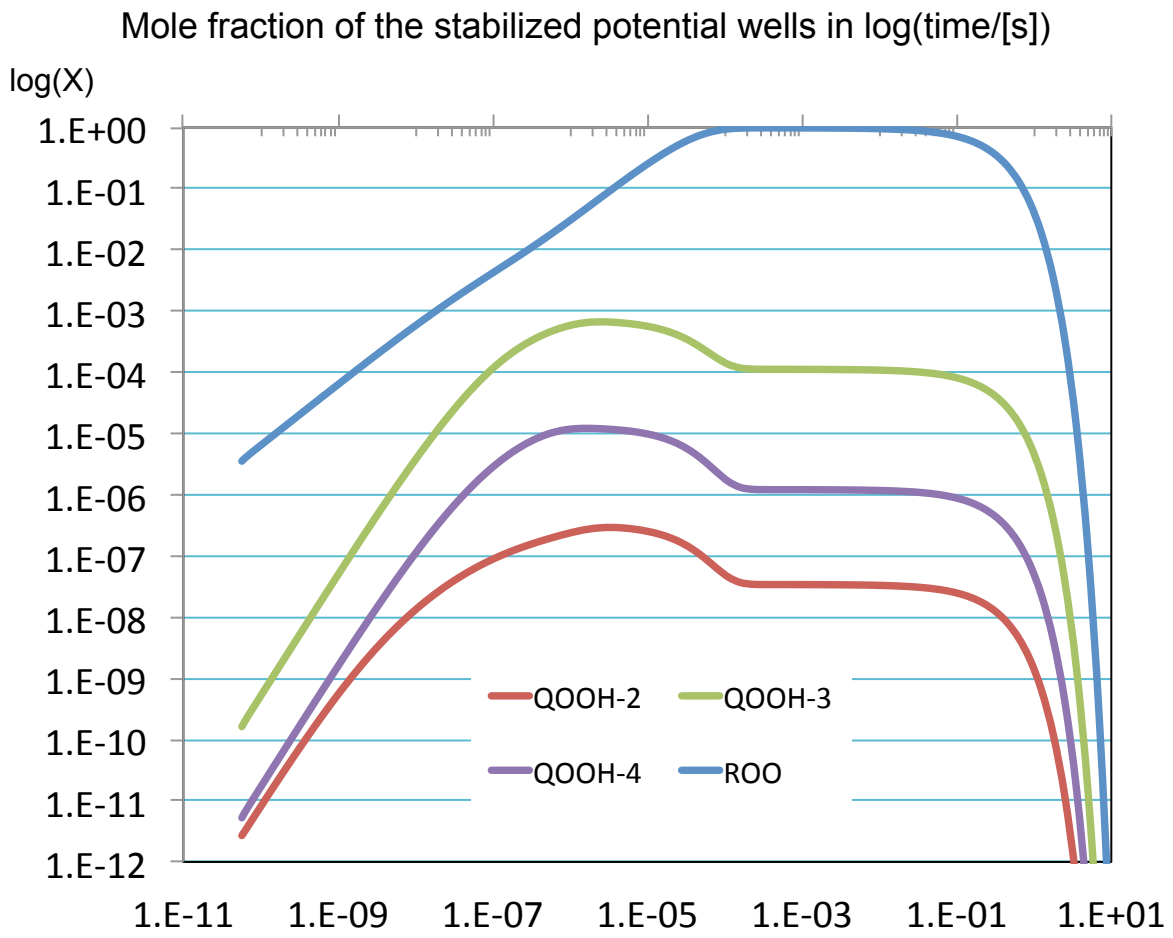

Breaking down mass 72 for the original (CCSD(T)-F12) barriers and the TS2 shifted to -7.3
1,2-epoxybutane
1,3-epoxybutane
1,4-epoxybutane
butanal
x10-3
0
10
20
30
40
0
5
10
15
20
25
Breaking down mass 72 for the original (CCSD(T)-F12) barrier
1,2-epoxybutane
1,3-epoxybutane
1,4-epoxybutane
butanal
x10-3
0
10
20
30
40
0
5
10
15
20
25

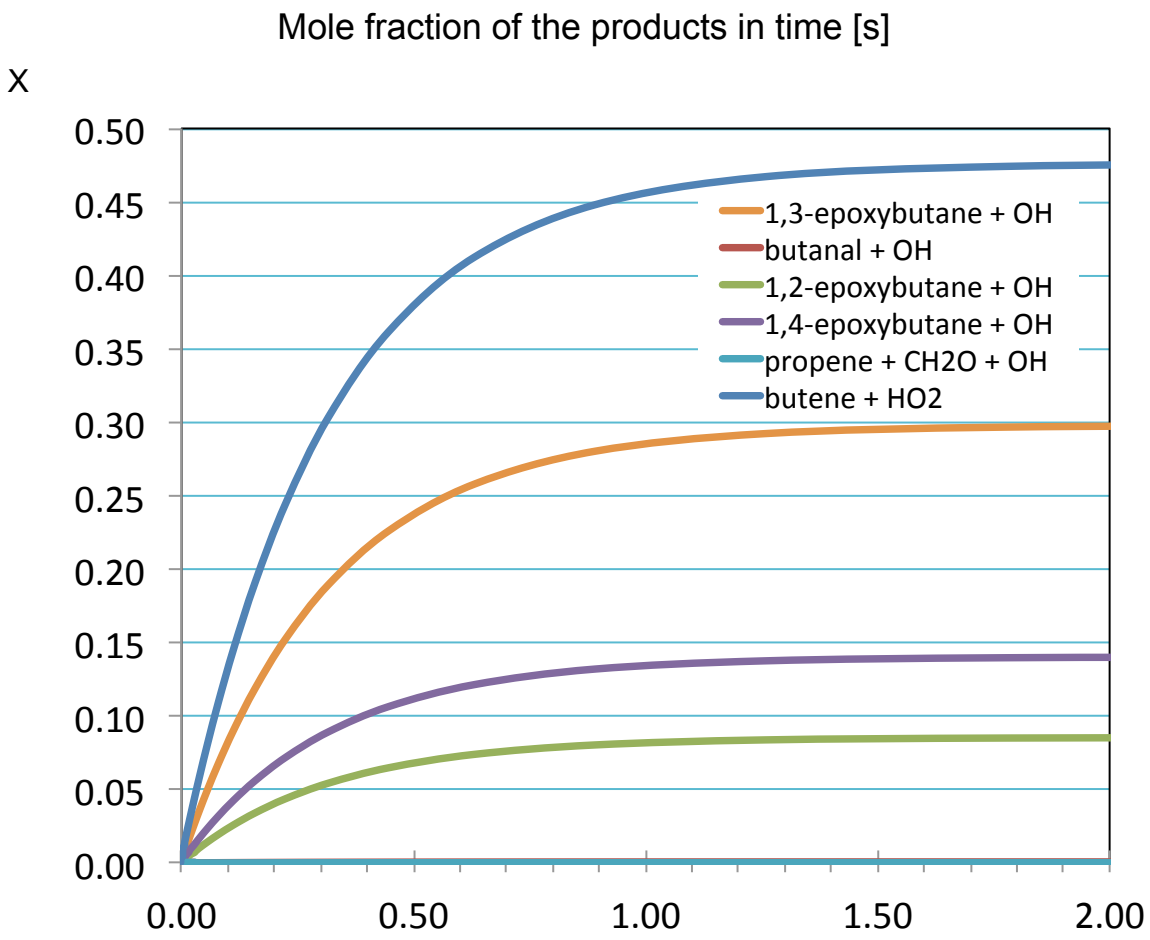

1000/T
0.8
1.3
1.8
2.3
2.8
3.3
3.8
4.3
4.8
log(λ)
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
IERE continuum
Chemically significant eigenvalues
R-OO --> QOOH-4
R-OO --> QOOH-3
n-butyl +O2 --> R-OO
QOOH-2 --> Products
R-OO --> Products
IERE continuum


Phenomenological rate coefficients
1000/T
0.8
1.0
1.2
1.4
1.6
1.8
2.0
log(k)
1.E-11
1.E-12
1.E-13
1.E-14
1.E-15
Reactants -> Potential well
Reactants -> Products


Phenomenological rate coefficients
1000/T
0.8
1.0
1.2
1.4
1.6
1.8
2.0
log(k)
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
1.E-02
Potential well --> Reactants
Potential well --> Products


Total product-specific rate coefficients
1000/T
0.8
1.0
1.2
1.4
1.6
1.8
2.0
log(k)
1.E+04
1.E+02
1.E+00
1.E-02
1.E-04
1.E-06
1.E-08
butene + HO2
butanal + OH
1,2-epoxybutane + OH
1,4-epoxybutane + OH
propene + CH2O + OH
1,3-epoxybutane + OH


Mole fraction of the stabilized potential wells in log(time/[s])
log(X)
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
1.E-09
1.E-10
1.E-11
1.E-12
1.E-11
1.E-09
1.E-07
1.E-05
1.E-03
1.E-01
1.E+01
QOOH-2
QOOH-3
QOOH-4
ROO


Mole fraction of the products in time [s]
X
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.00
0.50
1.00
1.50
2.00
1,3-epoxybutane + OH
butanal + OH
1,2-epoxybutane + OH
1,4-epoxybutane + OH
propene + CH2O + OH
butene + HO2

Summary

Electronic structure

Thermodynamics

Partition function

JZ is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the U. S. Department of Energy. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.

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