High Level Ab Initio Kinetics as a Tool for Astrochemistry

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Phosphorus Chemistry

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Giant Planets (Saturn, Jupiter): 100 - 400 K; 0.1 to 2 bar

Bulk is in PH_3

Bath = H_2, CH_4; Substantial H, NH_3, NH_2, PH_3, PH_2, C_2H_6

PH_3 Destroyed in NH_3 Photolysis Regions by Radical Reactions

$PH_3 + H = PH_2 + H_2$

$PH_3 + NH_2 = PH_2 + NH_3$

What happens to PH_2?

$PH_2 + PH_2 + M = P_2H_4 + M$

$PH_2 + H + M = PH_3 + M$

$PH_2 + P_2H_4 = P_2H_3 + PH_3$

$PH_2 + P_2H_2 = PH_3 + P_2H$

$PH_2 + NH_2 + M = NH_2PH_2 + M$

Phosphine Photochemistry:
Kaye and Strobel
Icarus, 59, 314-335 (1984)

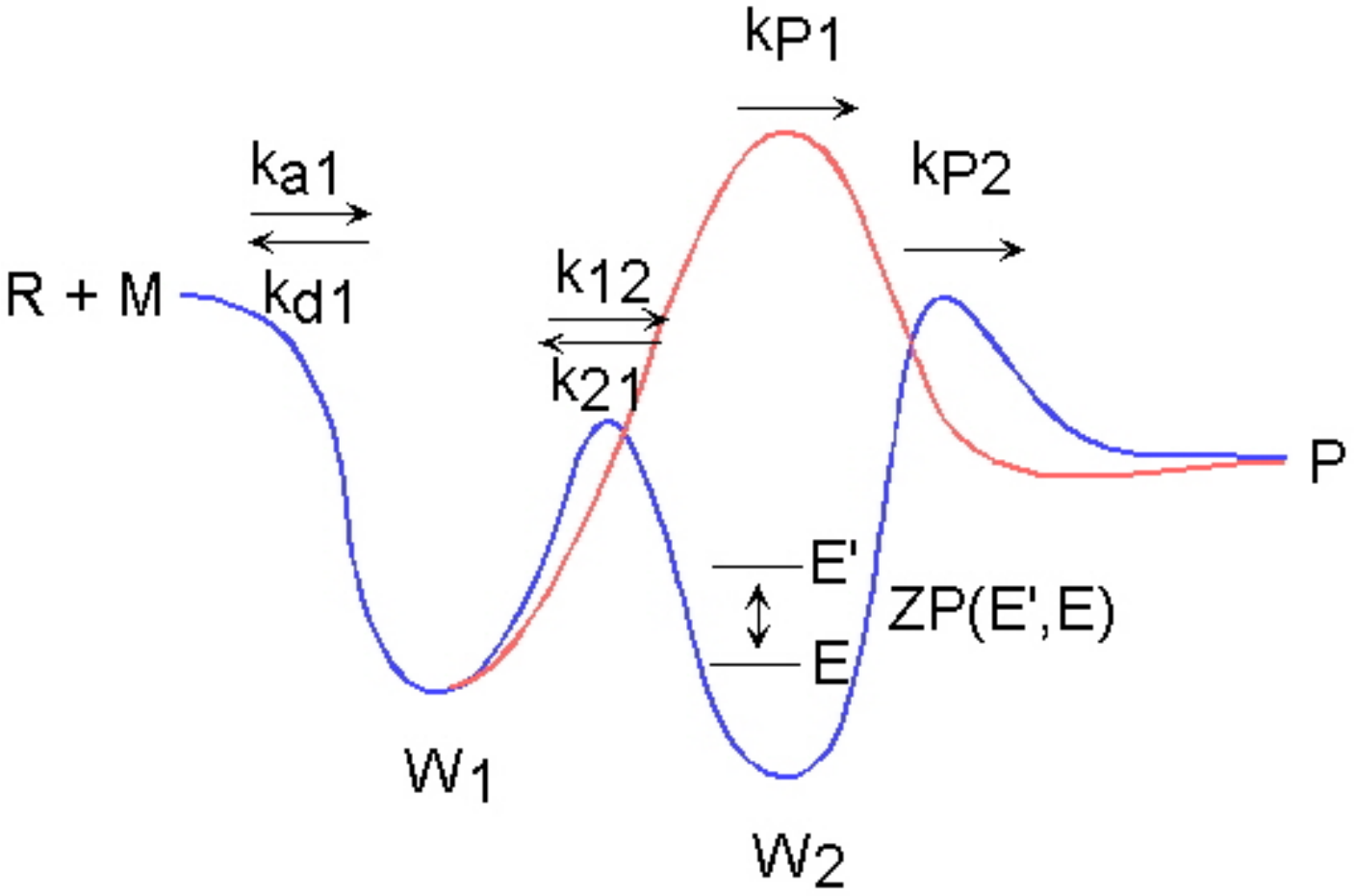
Also, what happens to P_2H_3?

Reactions with PH_3, PH_2, NH_2, H, and P_2H_3

Extrasolar Planets: 300 – 2000 K; 1e-4 to 5 bar

Conditions more varied $P_xO_yH_z$, $P_xC_yH_z$, HCP, PN

The Kinetic Model



Phenomenology

$k_{R+M \rightleftarrows P}$

$k_{R+M \rightleftarrows W1}$

$k_{R+M \rightleftarrows W2}$

$k_{W1 \rightleftarrows W2}$

$k_{W1 \rightleftarrows P}$

$k_{W2 \rightleftarrows P}$

RRKM Theory

k_{d1}

k_{a1}

k_{12}

k_{21}

k_{p1}

k_{p2}

Energy Transfer

Bath Gas B; [B] >> [M] >> [R]

Z; Lennard Jones

P(E',E); Exponential Down

R is Boltzmann

Electronic Structure Methodology

2 or Fewer Heavy Atoms

CCSD(T)/cc-pV(Q+d)Z optimizations and frequency analyses
CCSD(T)/CBS(5+d,6+d)
CCSD(T)/cc-pcVnZ; CBS(T,Q)
CCSDT(Q)/cc-pV(D+d)Z

3 or More Heavy Atoms

Replace QZ with TZ in rovibrational analysis
Sometimes CBS(QZ,5Z) instead of CBS(5Z,6Z)
Somteimes no CCSDT(Q)/cc-pV(D+d)Z

Multireference as needed

CASPT2
CAS+1+2 + Davidson Correction

Phosphorus Heats of Formation

^4P, NH_3 = Ref.

Species	Delta H_0^f(0 K) kcal/mol
^4P	75.42
^3PH	56.70
PH_2	32.30
PH_3	2.68
P_2	34.32
P_2H	52.63
P_2H_2	28.98
PPH_2	53.41
$^3PPH_2$	56.95
$^3P_2H_2$	61.95
P_2H_3	33.46
P_2H_4	7.55
$PHPH_3$	30.54

Species	Delta H_0^f(0 K) kcal/mol	ATcT
^4N	112.42	112.47 (0.01)
NH	85.58	85.74 (0.04)
NH_2	44.98	45.16 (0.03)
N_2	-0.26	0.00 (0.00)
N_2H	59.89	60.33 (0.13)
N_2H_2	49.10	49.56 (0.13)
N_2H_3	55.86	56.29 (0.22)
N_2H_4	26.55	26.22 (0.04)
PN	42.80	
$PHNH$	34.11	
$PHNH_2$	25.23	
NH_2PH_2	-4.44	
PNH	50.84	
PNH_2	48.67	
PH_2NH	44.47	

Related Work: Matus, Nguyen, Dixon, J. Phys. Chem. A, 111, 1726, 2007

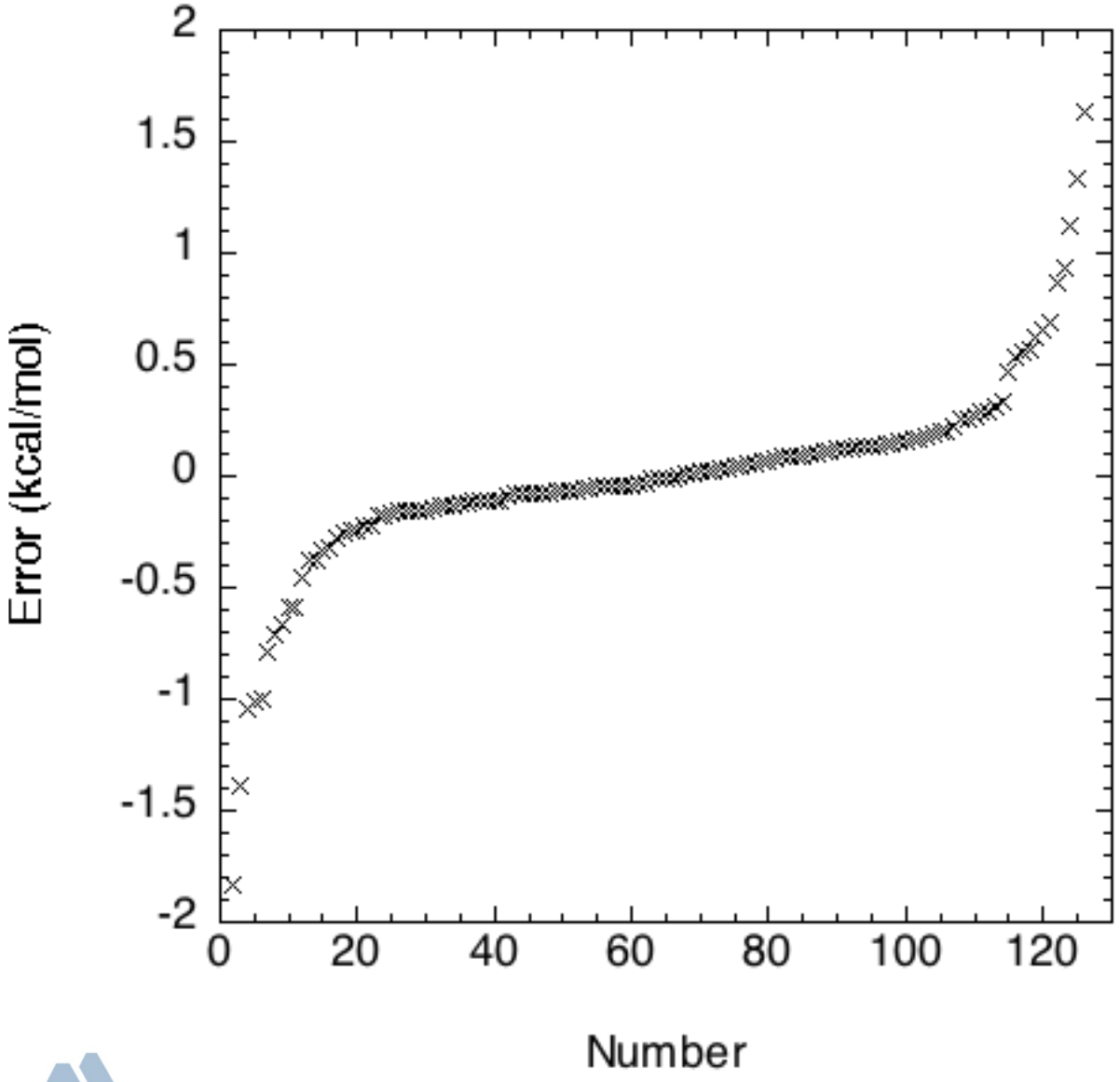
Phosphorus Heats of Formation ^4P, NH_3, CH_4 Ref.

Species	Delta H_0^f(0 K) kcal/mol
CP	119.98
HCP	52.48
H_2CP	53.81
HCPH	4.71
CH_2PH	31.27
$^3CH_3P$	50.99
CH_3P	72.92
CH_3PH	28.12
CH_2PH_2	44.64
CH_3PH_2	-0.30

Combustion Thermochemistry Database

- CCSD(T)/TZ optimizations and Frequencies
- CCSD(T)/CBS from CCSD(T)/AQZ',A5Z'
- CCSDT(Q)/DZ
- Core-Valence CCSD(T)/CBS; TZ and QZ
- Relativistic from DKH with CI/TZ
- DBOC from HF/cc-pVTZ
- Anharmonic corrections from B3LYP/6-311++G**
- Heats of formation relative to H_2, CH_4, H_2O, NH_3
- 5 Heavy Atoms
- All 34 e^- or less CNOH Combustion Species

Heat of Formation Error Distribution



- Relative to ATcT values (Ruscic)
- Distribution is not Gaussian
- Tail – ATcT problems or theory problems
- Gaussian part 2σ = 0.2 kcal/mol

Ab Initio Transition State Theory (High P)

Tunneling Factor

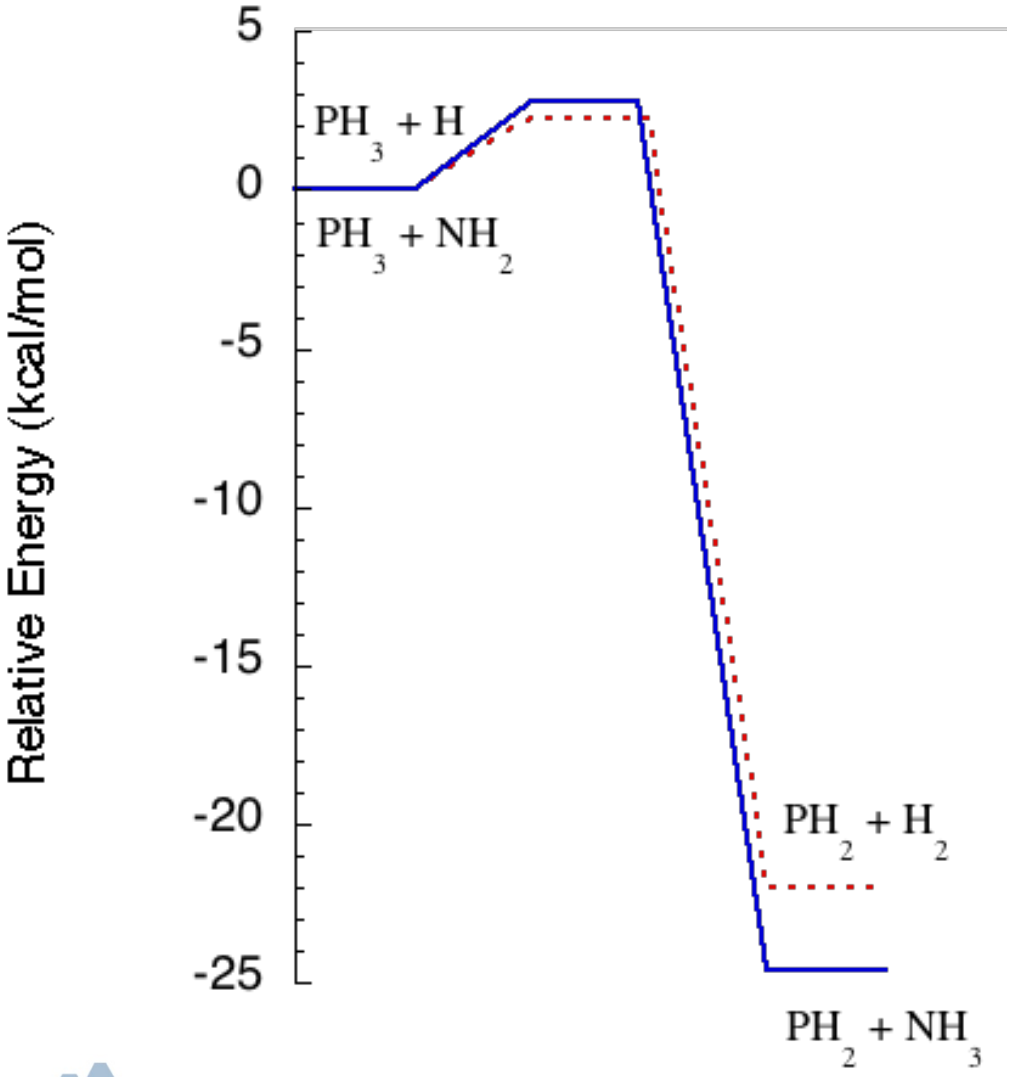
Barrier Height – Saddle Point

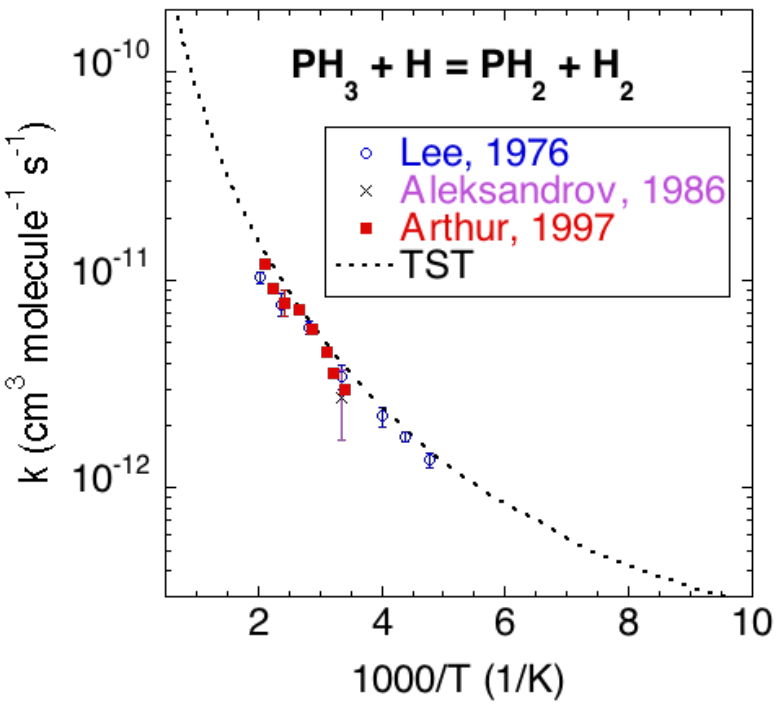
$$k^{TST}(T) = \kappa \frac{k_B T}{h} \frac{Q^{\#}(T)}{Q_{reac}(T)} \exp\left(-\frac{E^{\#}}{k_B T}\right)$$

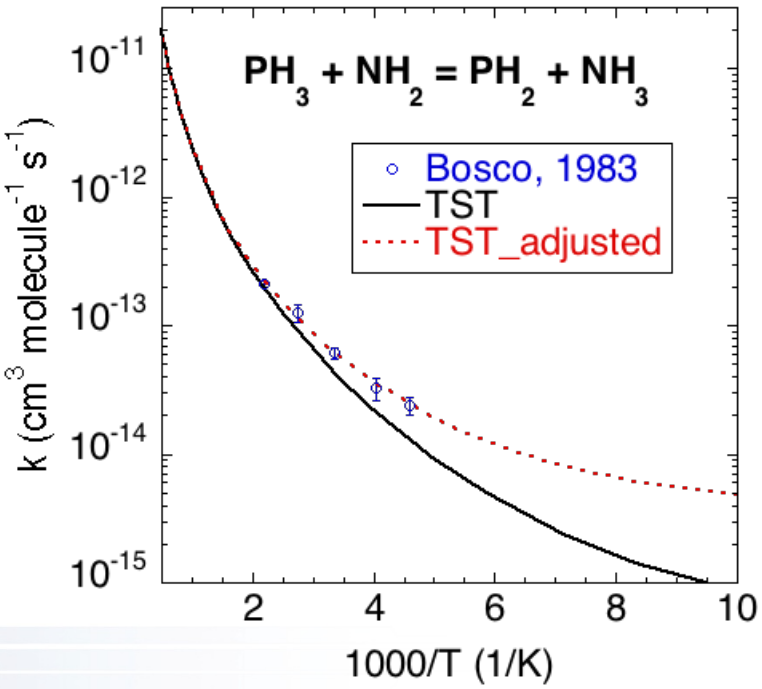
Rate Coefficient

Partition Functions – Depend on Rovibrational Properties

PH_2 Formation Reactions
$PH_3 + H$; $PH_3 + NH_2$

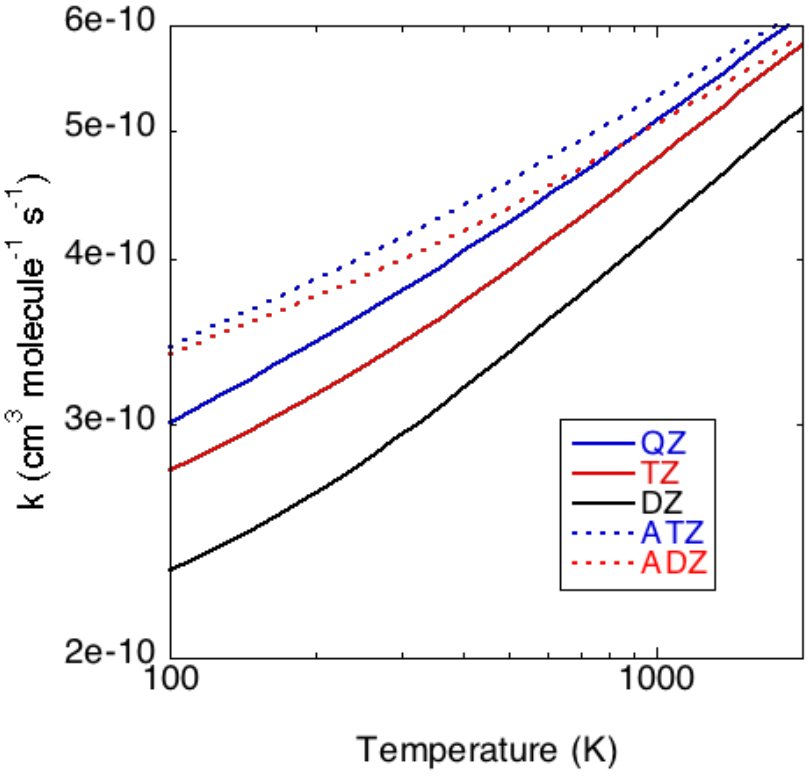


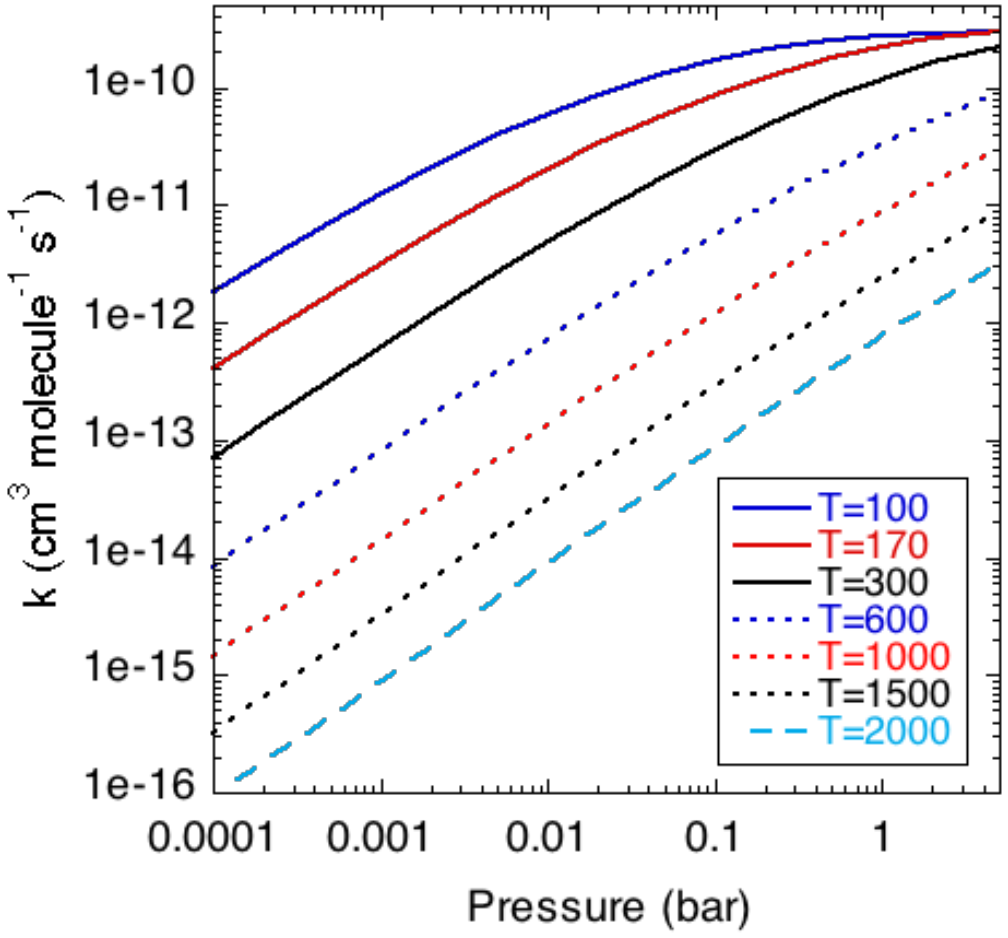




$PH_2 + H$

High Pressure Recombination





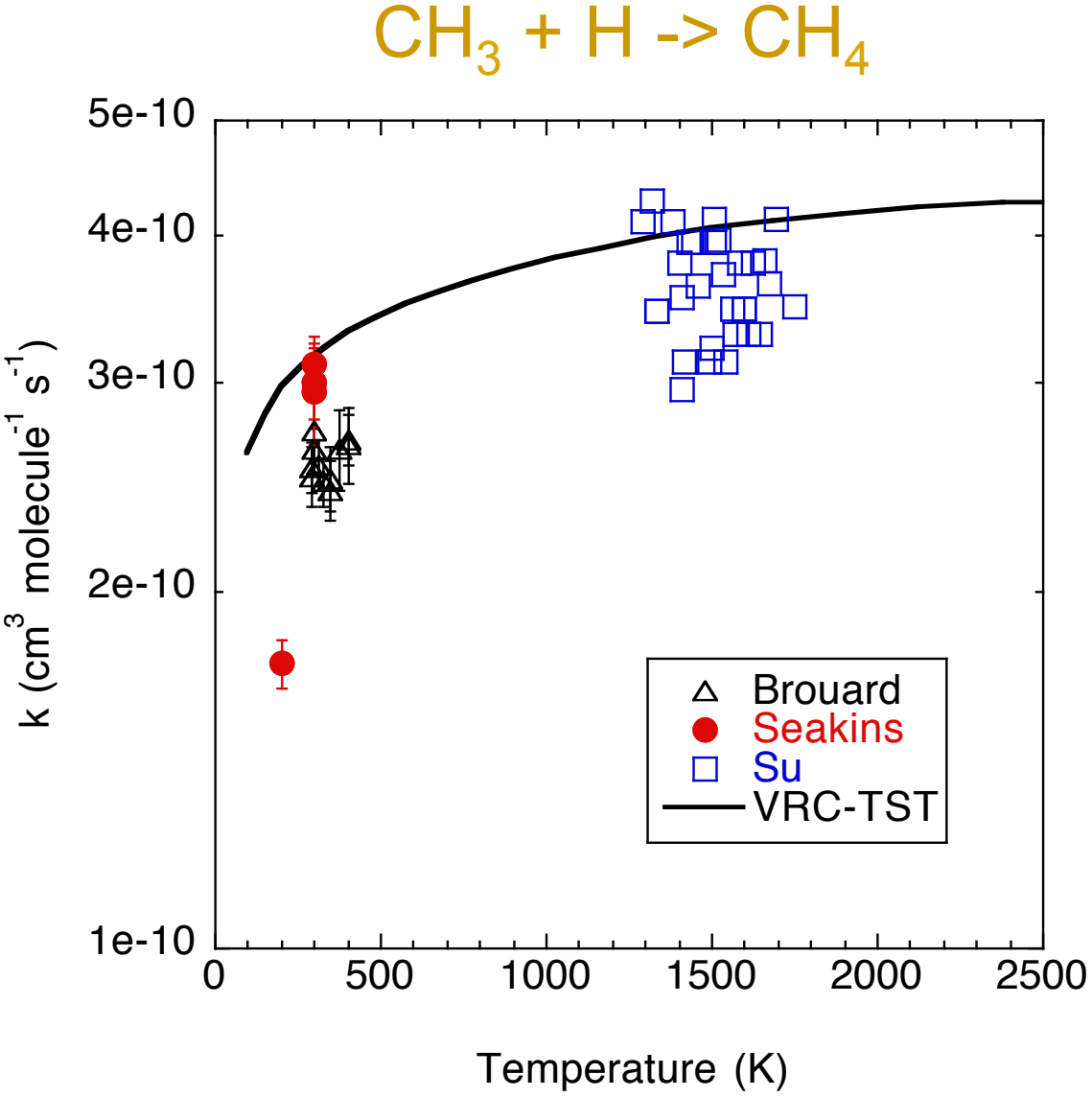
High Pressure Recombination Rate Coefficients

Ab Initio Transition State Theory for Barrierless Reactions

Harding, Georgievskii, SJK

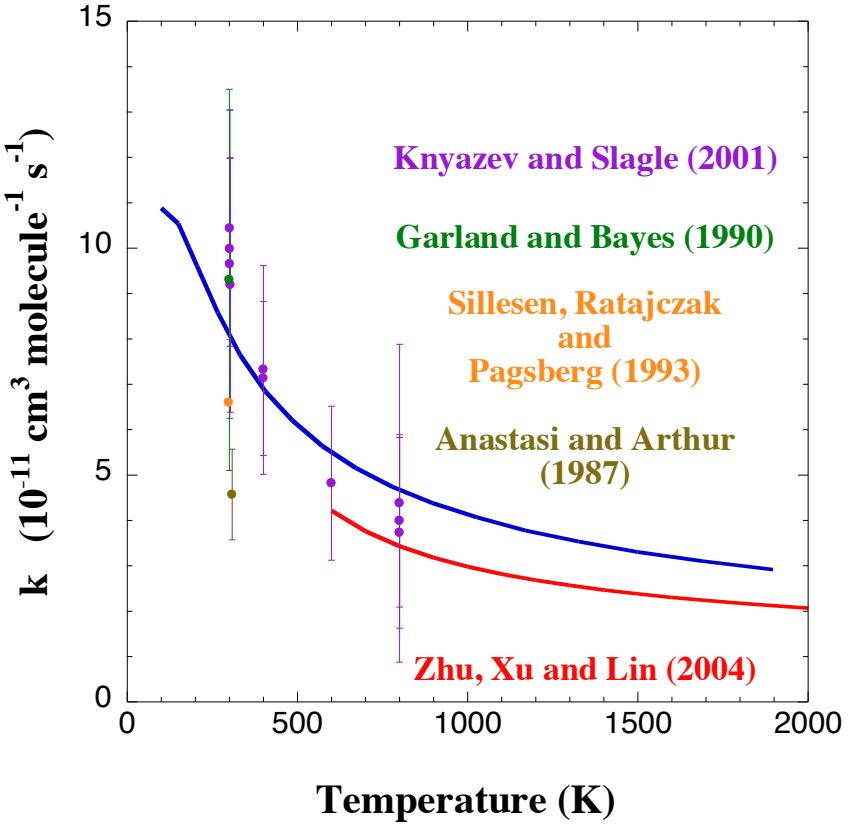
Direct Variable Reaction Coordinate TST

- Fully Coupled Anharmonic Treatment
- CASPT2 MultiReference Electronic Structure
- Dynamical Corrections
- Predictions Accurate to About 20%

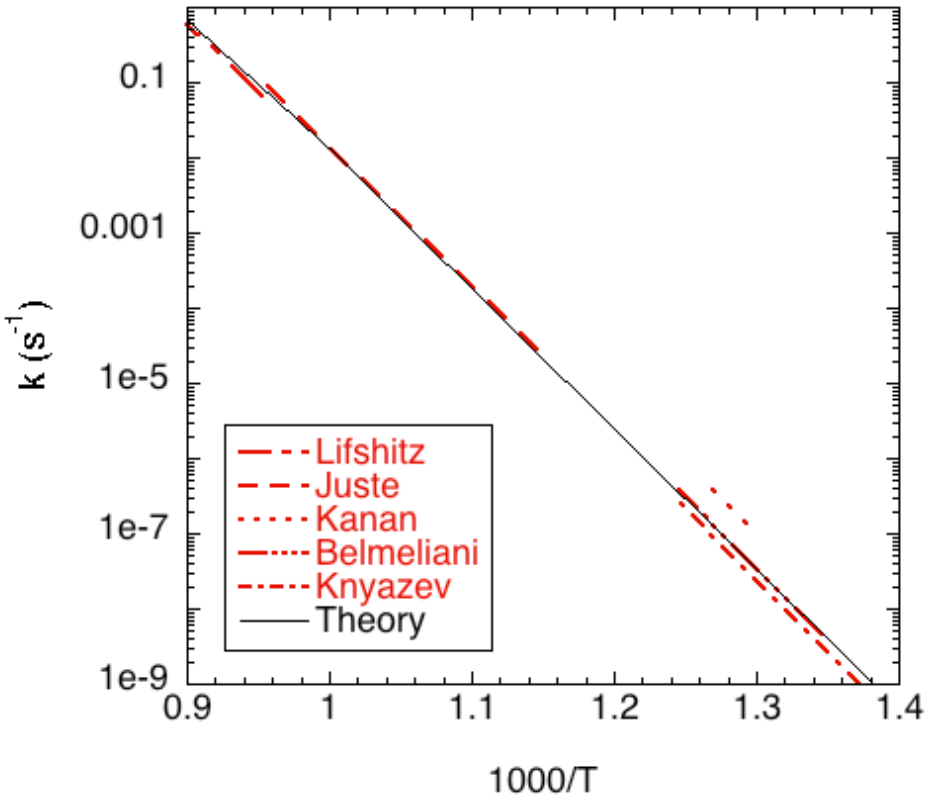


Radical-Radical Reactions

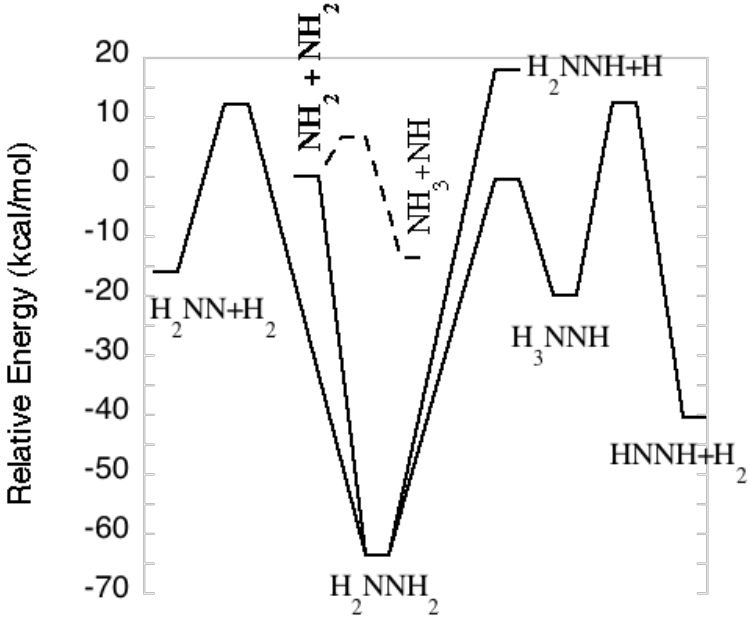
$CH_3 + C_2H_5 \rightarrow C_3H_8$

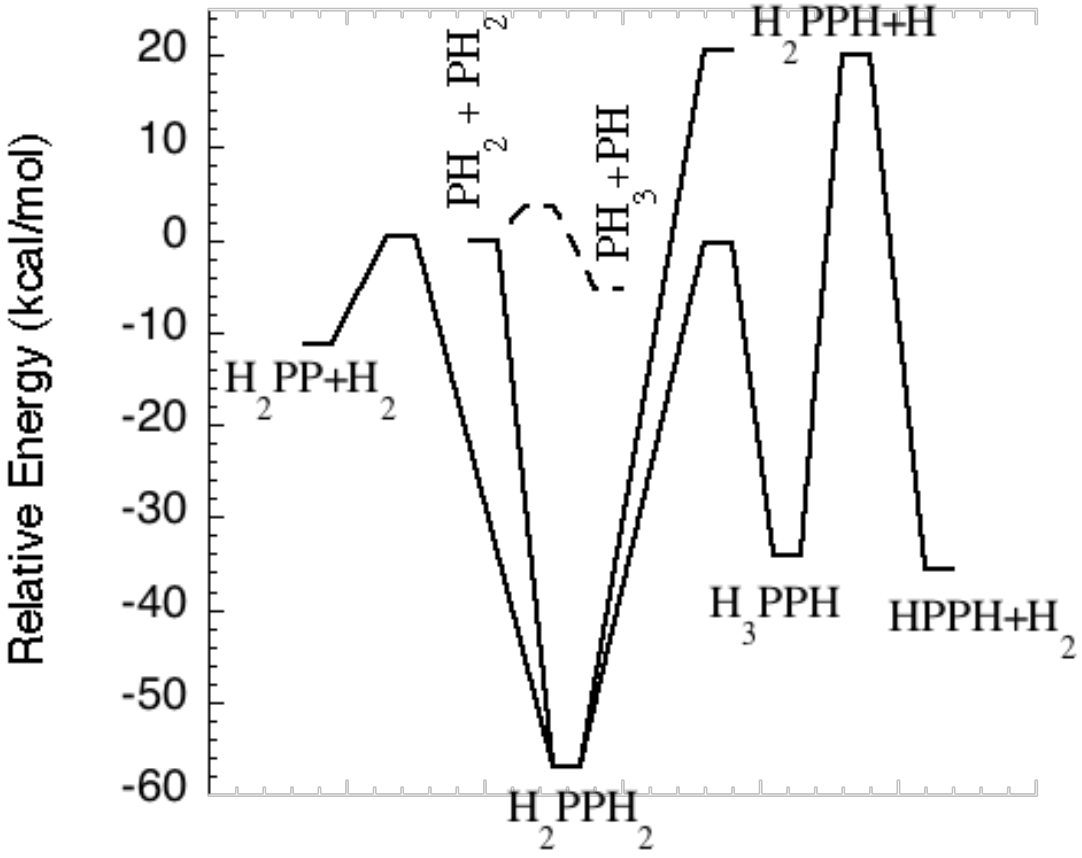


$C_3H_8 \rightarrow CH_3 + C_2H_5$



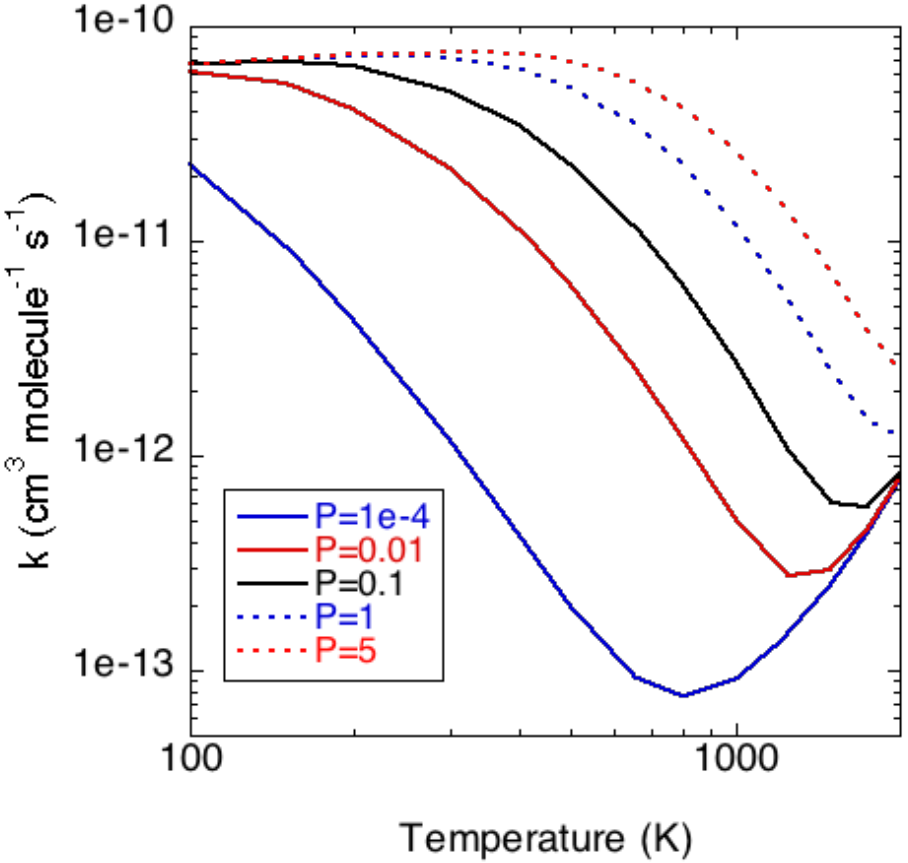
$PH_2 + PH_2$


Relative Energy (kcal/mol)
20
10
0
-10
-20
-30
-40
-50
-60
-70
H2NN+H2
NH2 + NH2
NH3+NH
H2NNH2
H2NNH+H
H3NNH
HNNH+H2

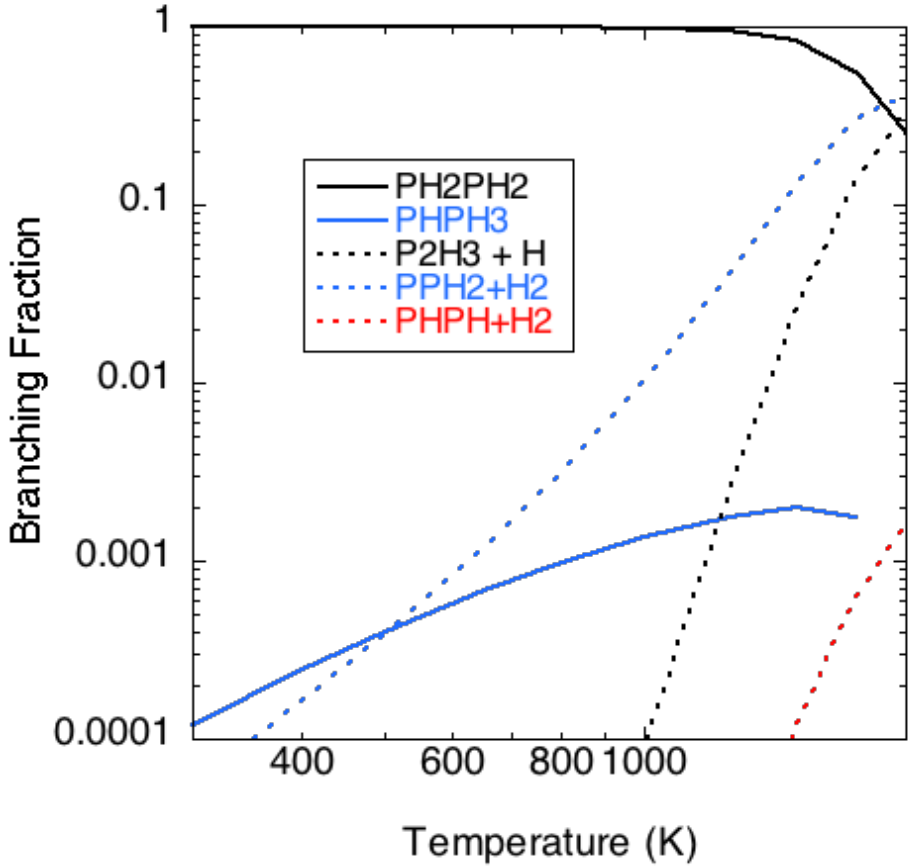

Relative Energy (kcal/mol)
20
10
0
-10
-20
-30
-40
-50
-60
H2PP+H2
PH2 + PH2
PH3+PH
H2PPH2
H2PPH+H
H3PPH
HPPH+H2

$PH_2 + PH_2$

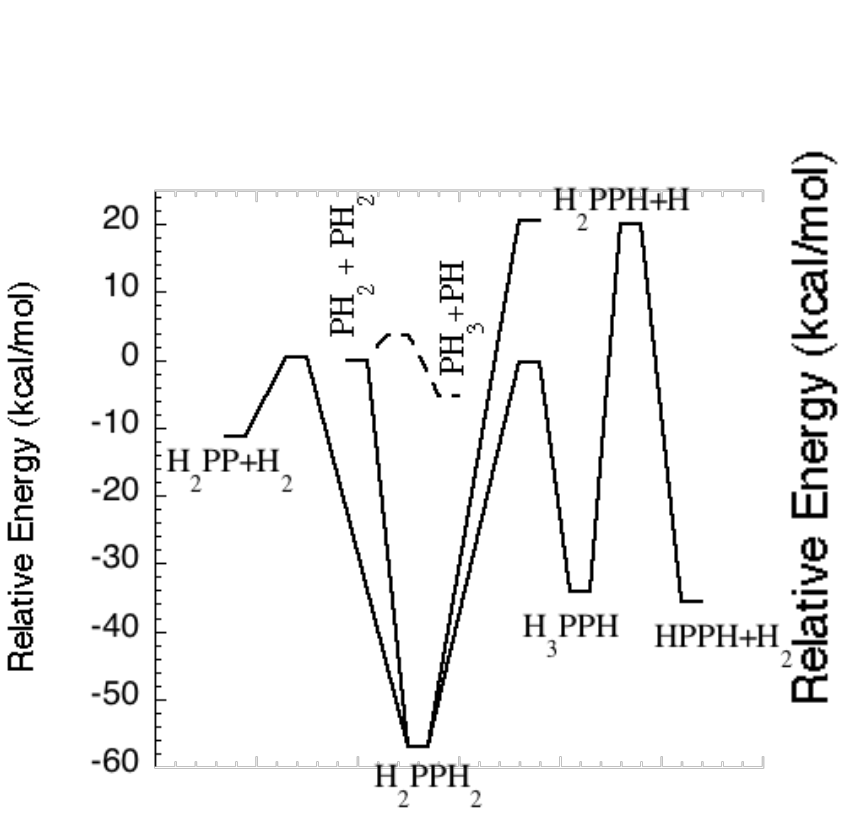
Total Reaction Rate

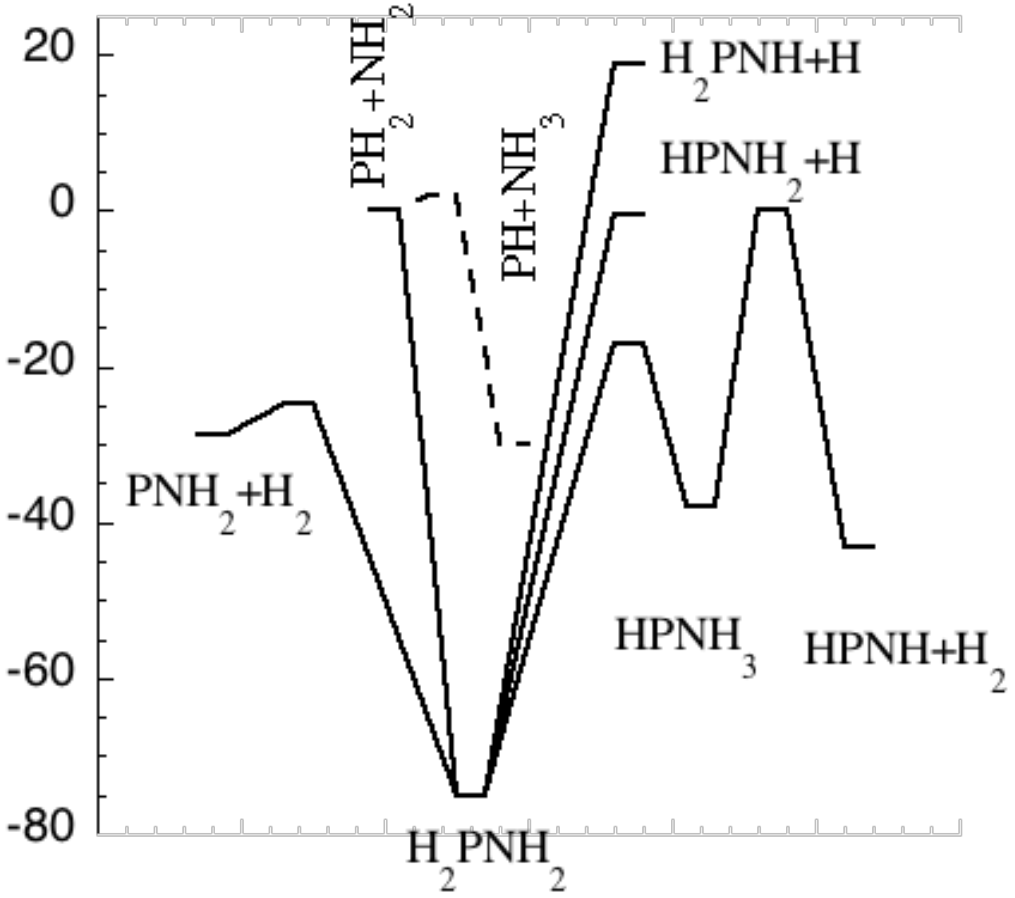


Branching Fraction
P=0.5 bar



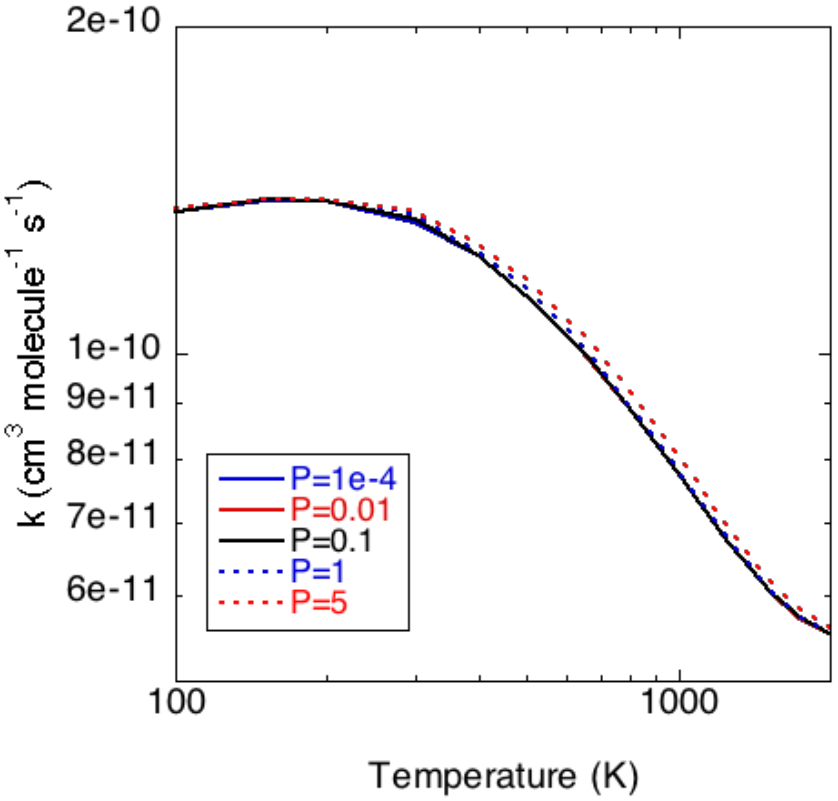
$PH_2 + NH_2$


Relative Energy (kcal/mol)
20
10
0
-10
-20
-30
-40
-50
-60
H2PP+H2
PH2 + PH2
PH3+PH
H2PPH+H
H3PPH
HPPH+H2
H2PPH2

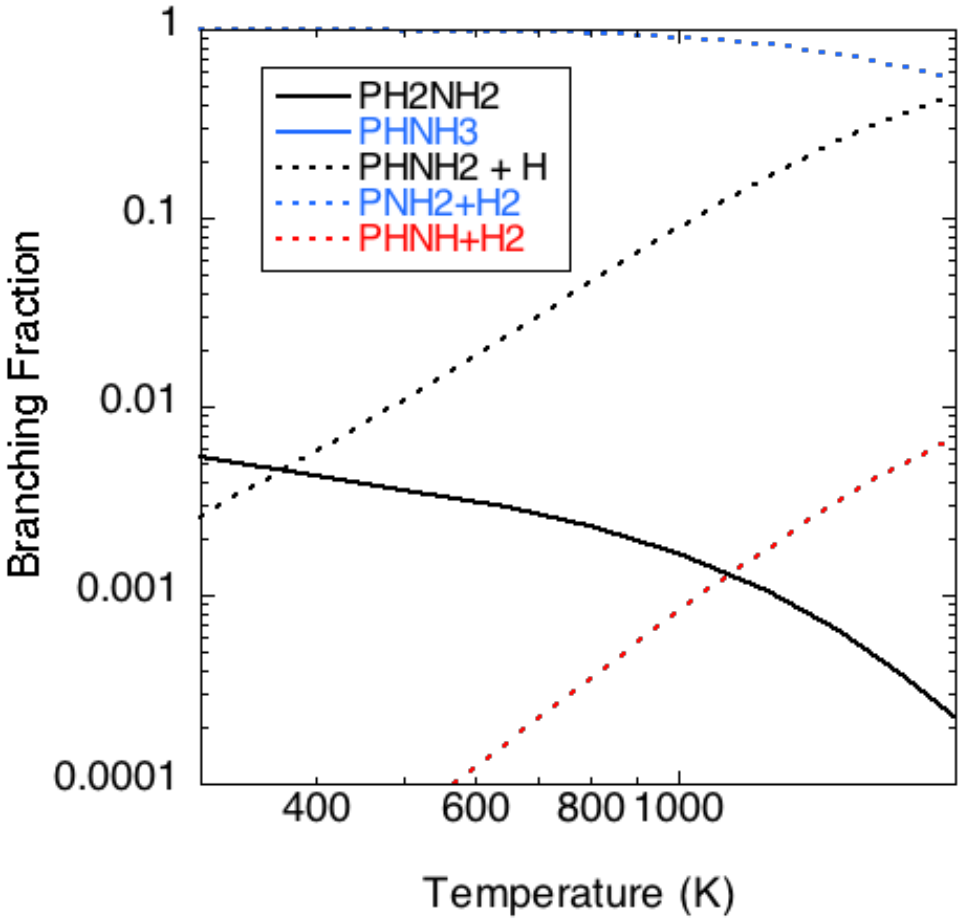

Relative Energy (kcal/mol)
20
0
-20
-40
-60
-80
PH2+NH2
PH+NH3
H2PNH+H
HPNH2+H
PNH2+H2
HPNH3
HPNH+H2
H2PNH2

$PH_2 + NH_2$

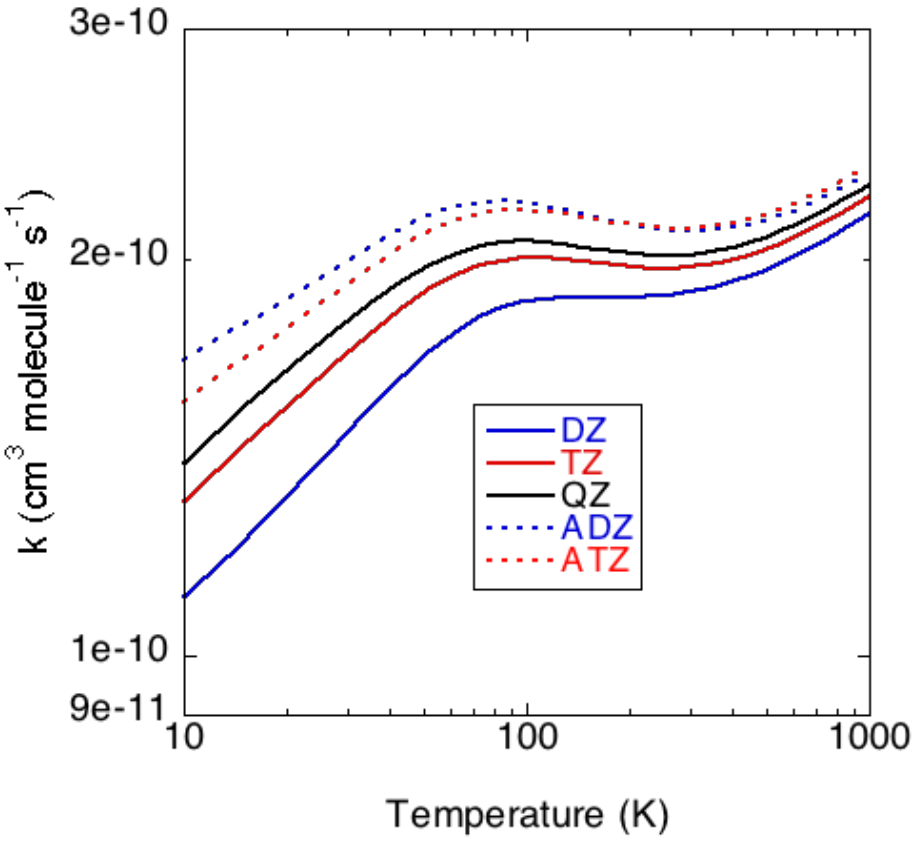
Total Reaction Rate

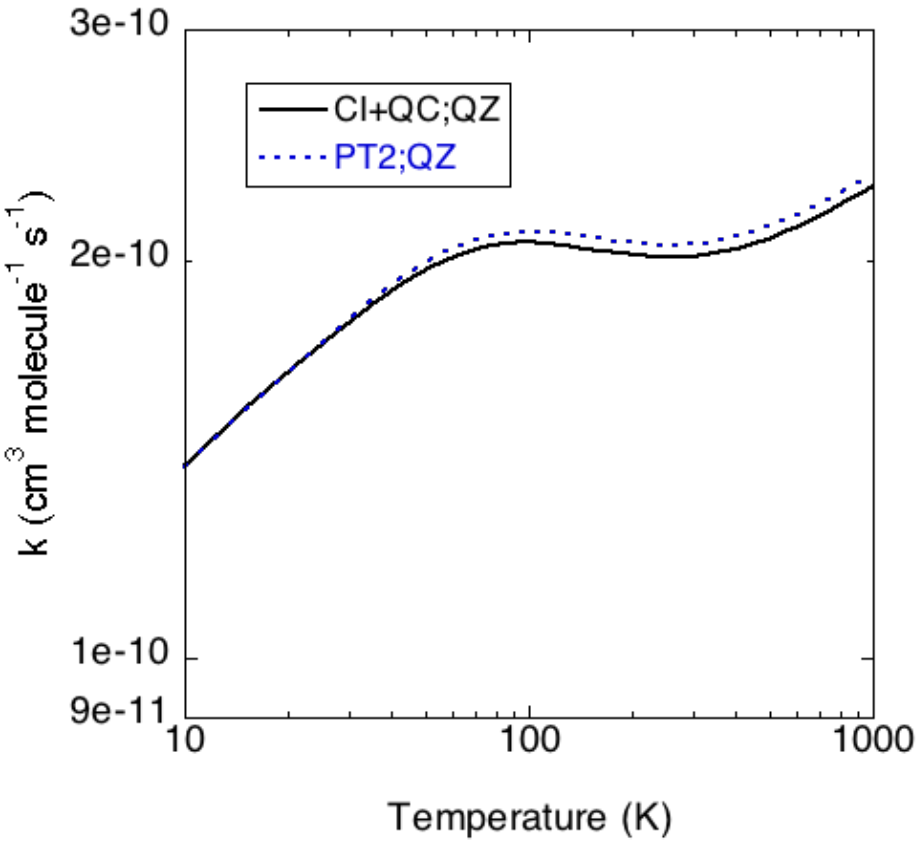


Branching Fraction
P=0.5 bar

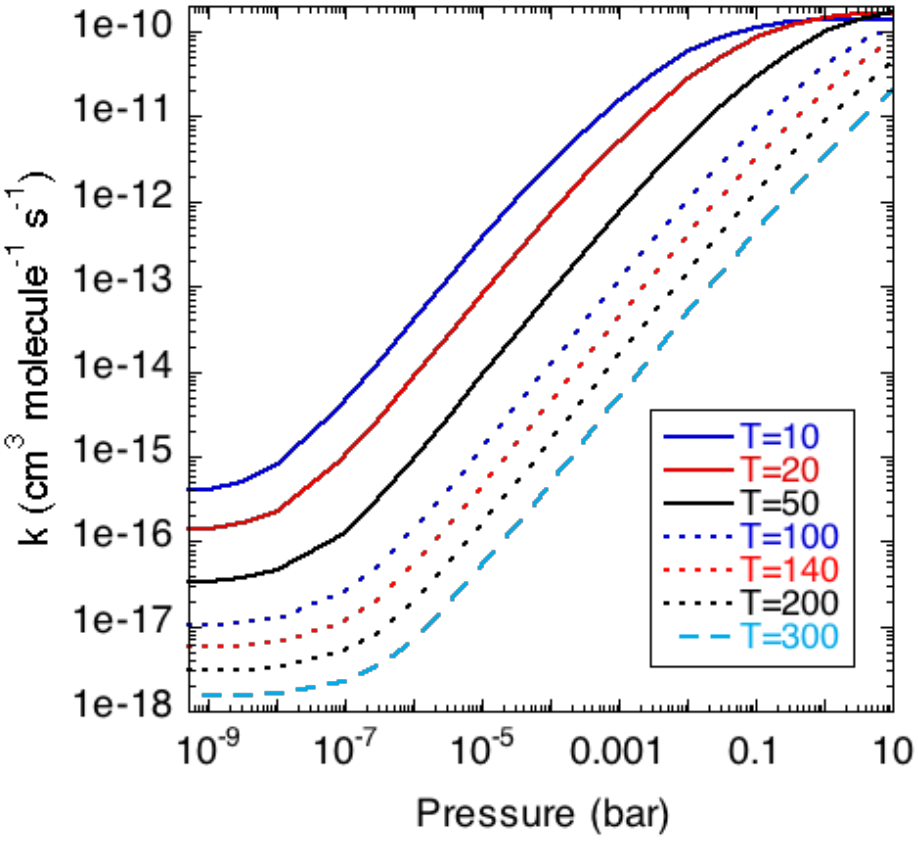


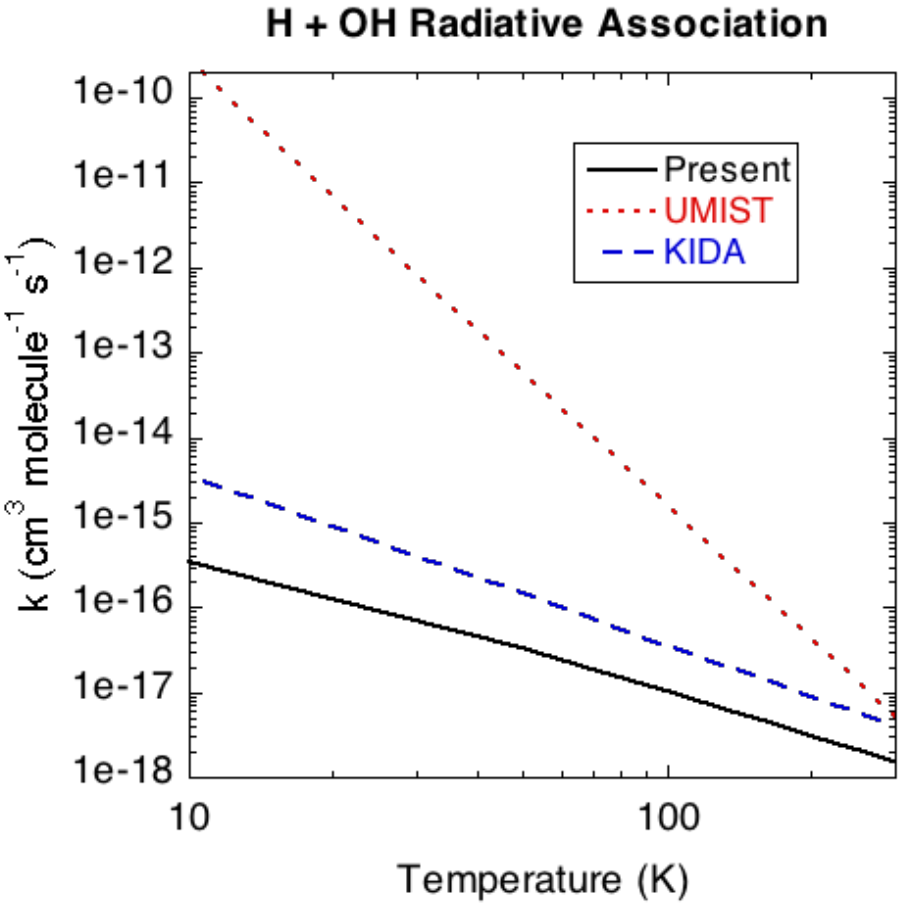
OH + H High Pressure Recombination





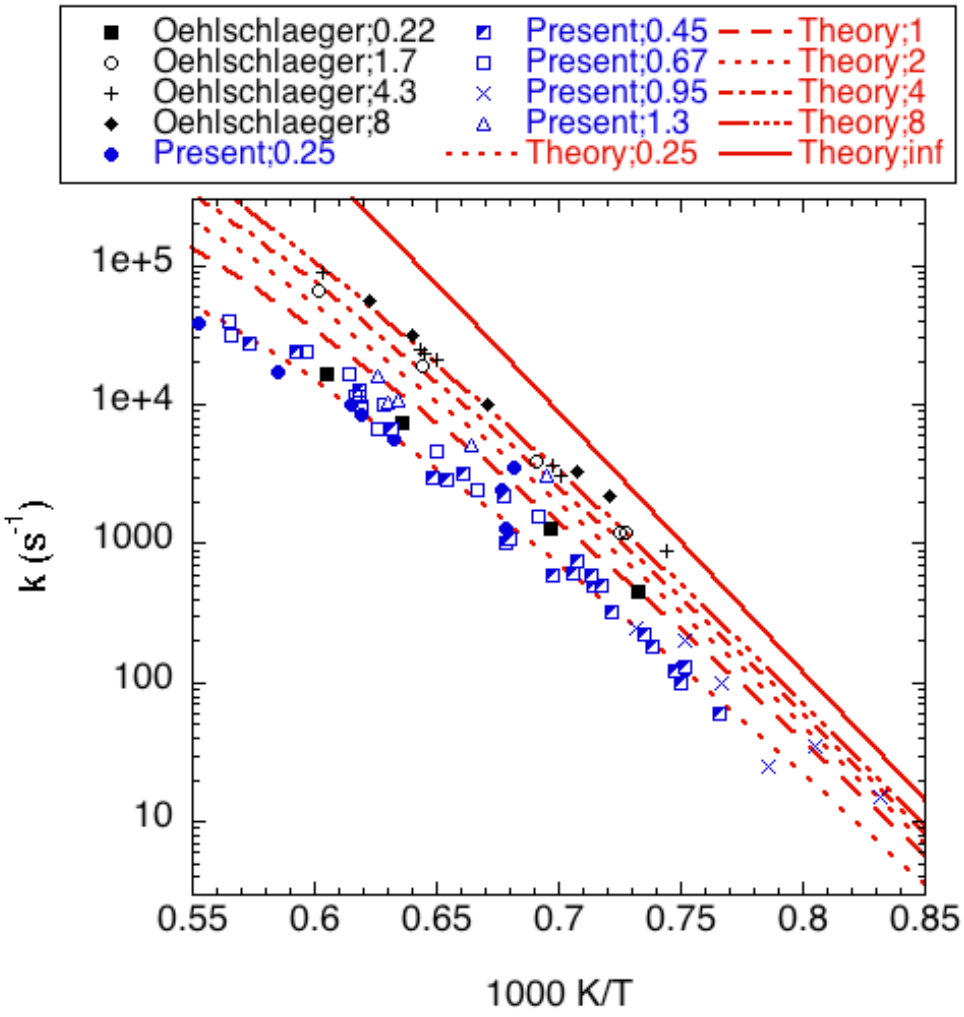
OH + H Pressure Dependence



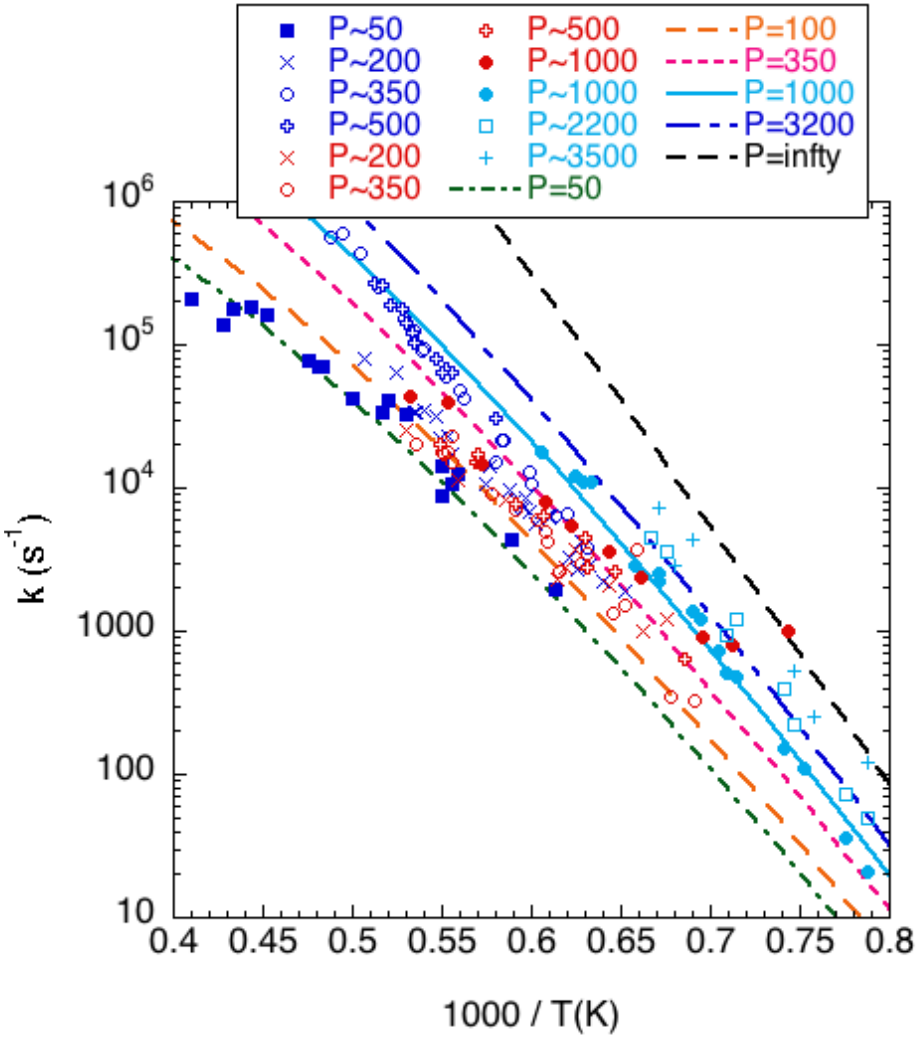


Pressure Dependence: Comparison with Expt

Propane Decomposition



Acetaldehyde Decomposition



$\langle \Delta E_{down} \rangle = 100\ (T/300)^{0.85}\ cm^{-1}$

$\langle \Delta E_{down} \rangle = 150\ (T/300)^{0.85}\ cm^{-1}$

A Priori Pressure Dependence: Coupling Trajectory Simulations with the Two Dimensional Master Equation

Jasper, Pelzer, Miller, Kamarchik, Harding, Klippenstein, Science, 346, 1212 (2014).

Jasper – calculate $\langle \Delta E_{down} \rangle$, $\langle \Delta J_{down} \rangle$, $\langle \Delta E_{down}^2 \rangle$, $\langle \Delta J_{down}^2 \rangle$ $\langle \Delta E_{down} \Delta J_{down} \rangle$; 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 [$\alpha(J')$, $\gamma(J')$, ε_E, ε_J, Z_{LJ}] to reproduce the moments from trajectories

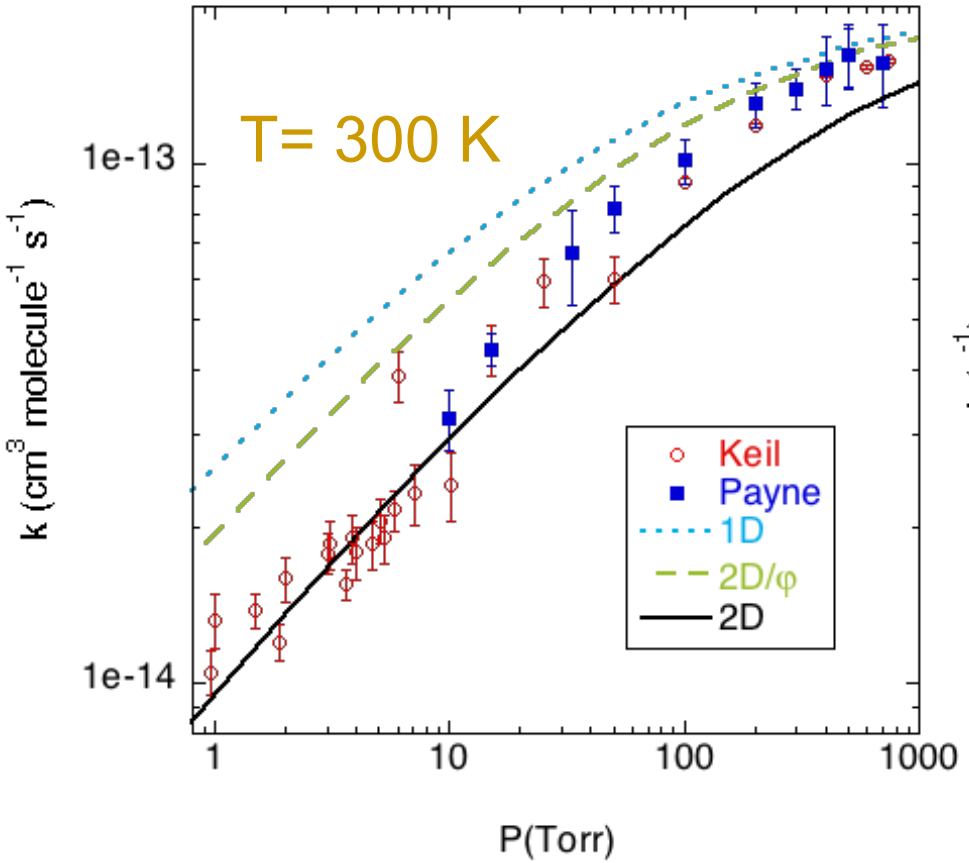
Employ model form in 2-Dimensional Master Equation

S. J. Jeffrey, K. E. Gates, S. C. Smith, J. Phys. Chem. 100, 7090 (1996) – Solution to 2D Master Equation

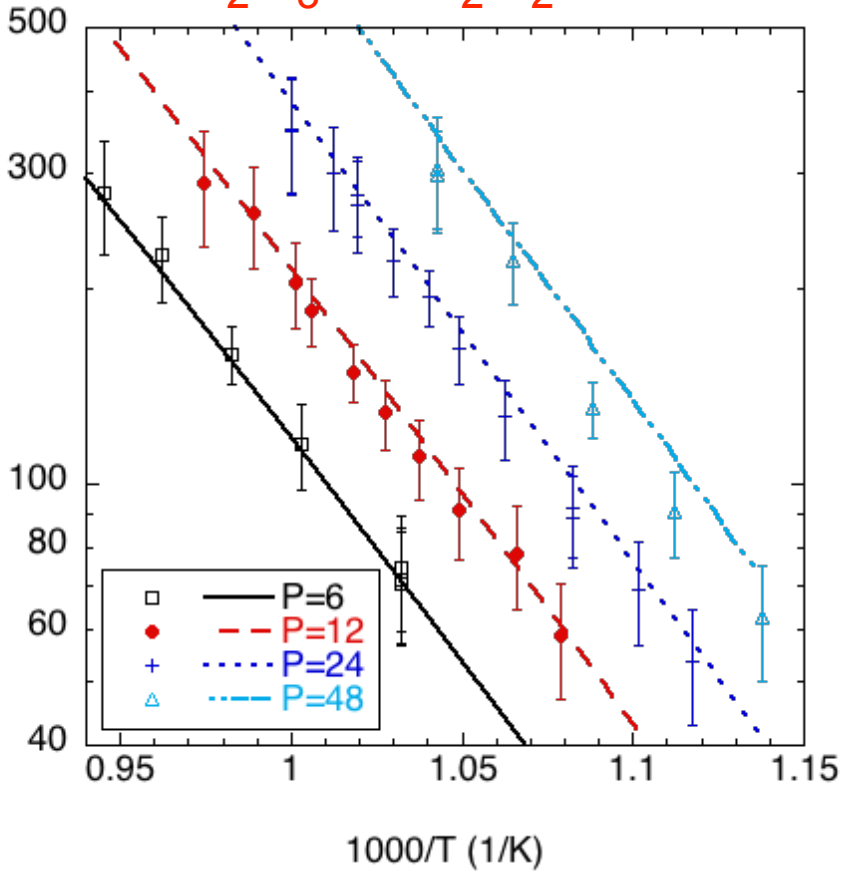
J. R. Barker, R. E. Weston, J. Phys. Chem. A, 114, 10619 (2010) Represent full P(E,J;E',J') as sum of basis functions

C_2H_3 Reaction System

$C_2H_2 + H \rightarrow C_2H_3$



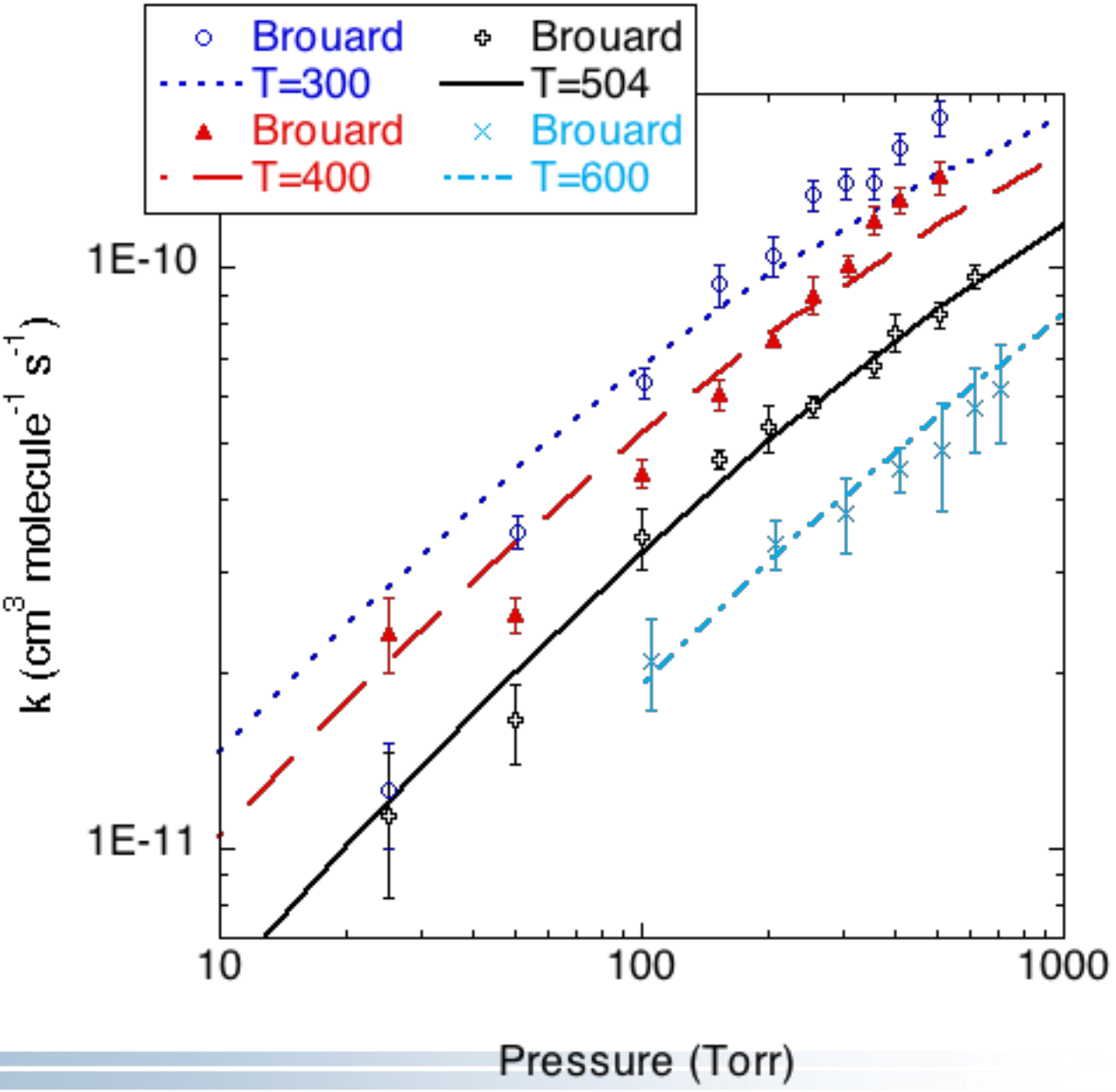
$C_2H_3 \rightarrow C_2H_2 + H$



Discrepancies Range From 10 to 30 %

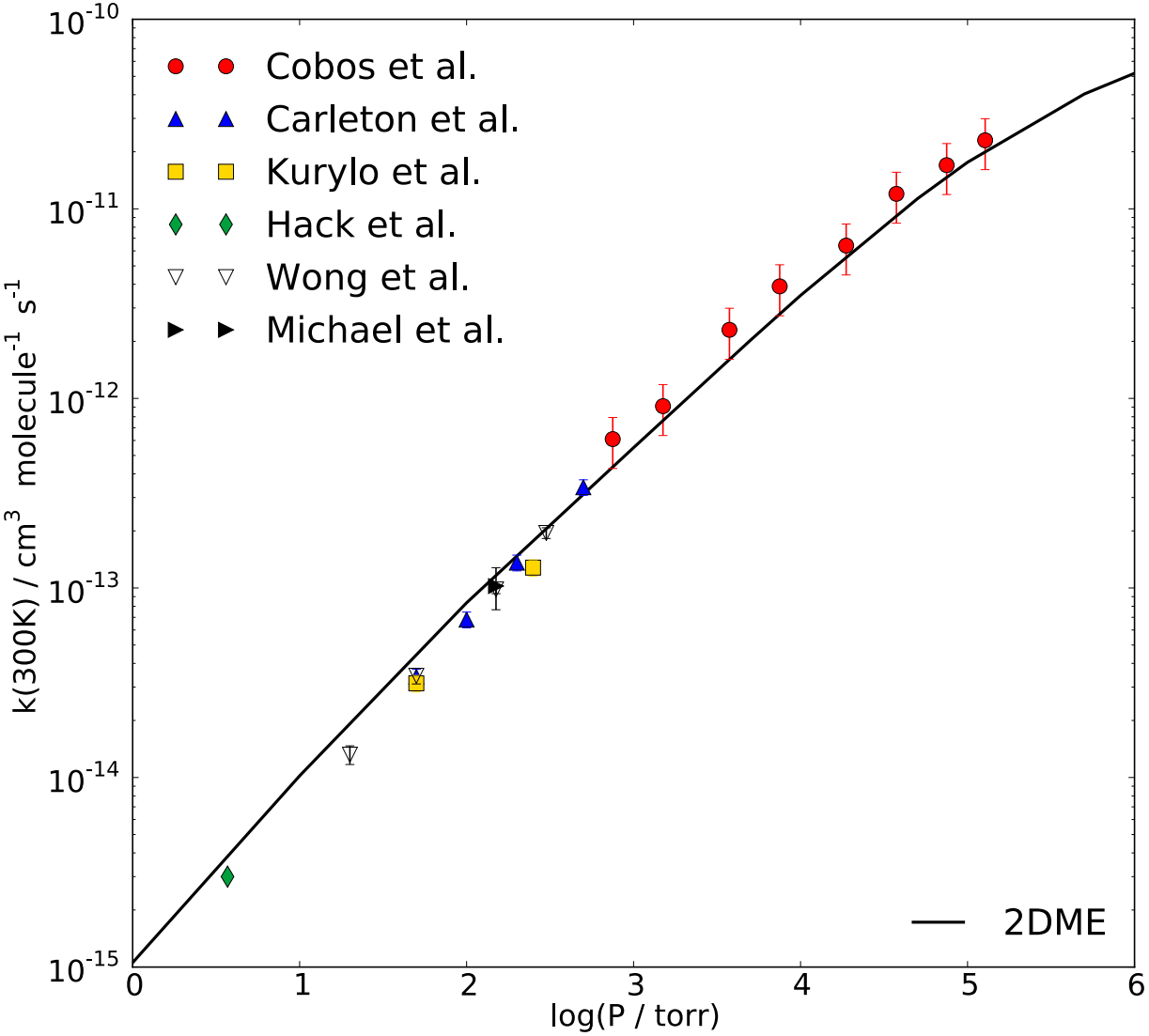
Knyazev, Slagle, J Phys Chem 100, 16899 (1996)

$CH_3 + H \rightarrow CH_4$



$H + O_2 (+M) \rightarrow HO_2 (+M)$

Verdicchio, Jasper, Pelzer, Georgievskii, Klippenstein



Completely A Priori Predictions Agree with Experimental Data to Within about 20% Over ~5 Decades of Pressure!

H_2O is only 7 times more efficient than Ar

Conclusions

- Theoretical kinetics provides a valuable tool for mechanism development
- For small molecules barrier heights accurate to about 0.4 kcal/mol (2σ) are readily obtained
- Kinetic accuracy (factor of two) is readily attainable for many reactions
- Coupling trajectory simulations of E,J collision kernels with 2D master equations provides accurate a priori predictions of pressure dependent kinetics

Funding
NASA
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