A QUANTITATIVE KINETIC ANALYSIS OF CO ELIMINATION FROM PHENOXY RADICALS

Hans-Heinrich Carstensen and Anthony M. Dean

ICCK

July 10 - 14 2011
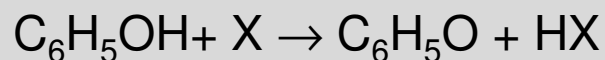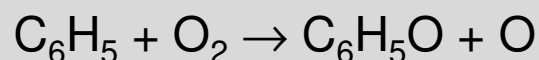
@ MIT Cambridge, MA

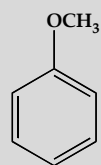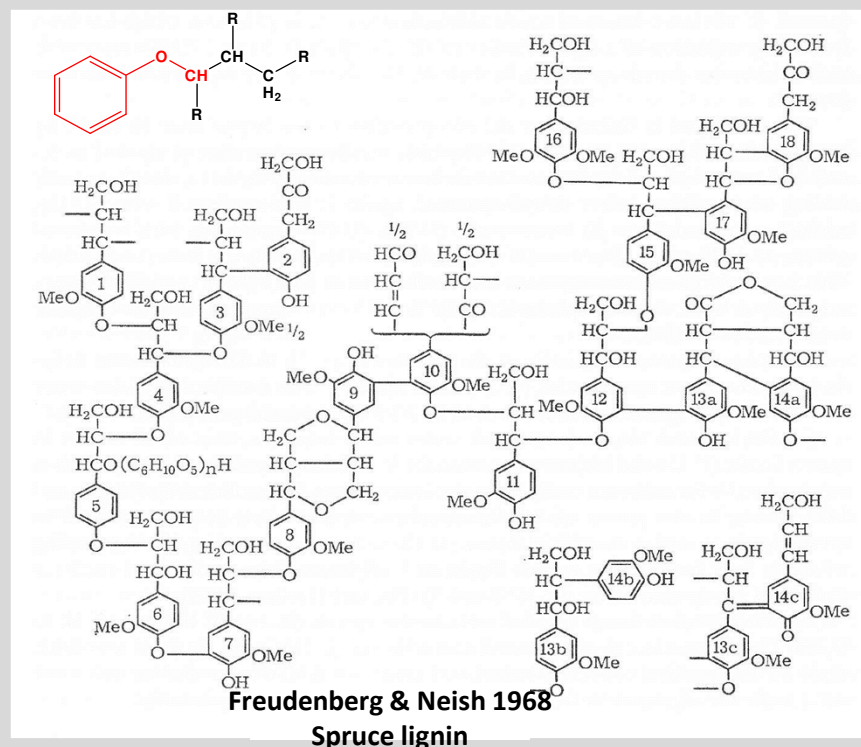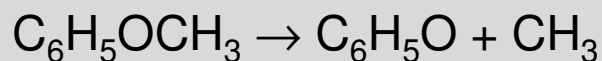**COLORADO**SCHOOLOF**MINES**

EARTH ● ENERGY ● ENVIRONMENT

Motivation: Phenoxy Radicals Are Important Reaction Intermediates

Key intermediates in:

1. Oxidation of aromatics

$$C_6H_5 + O_2 \rightarrow C_6H_5O + O$$

$$C_6H_5OH + X \rightarrow C_6H_5O + HX$$

2. Pyrolysis of lignin model compounds

$$C_6H_5OCH_3 \rightarrow C_6H_5O + CH_3$$

Freudenberg & Neish 1968
Spruce lignin
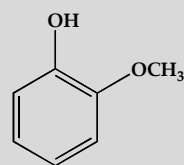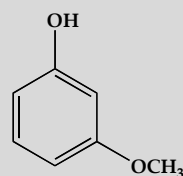
anisole   *o*-guaiacol   *m*-guaiacol   *p*-guaiacol   coniferyl alcohol   sinapyl alcohol
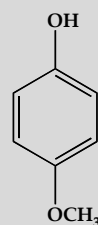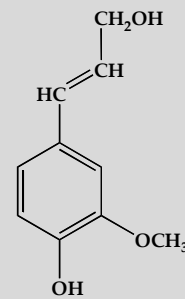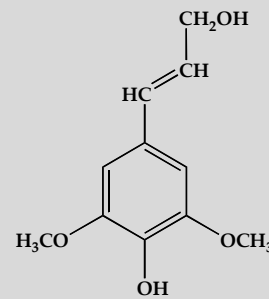
Anisole: Phenoxy Decomposition Competes With Bimolecular Rxns

from Scheer et al. JPCA 114 p9043 (2010)

based on Pecullan et al. JPCA 101 p3305 (1997)
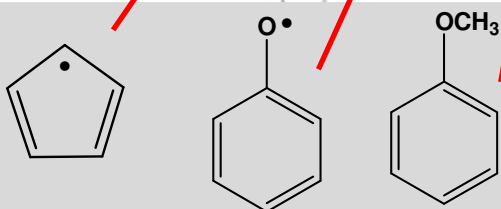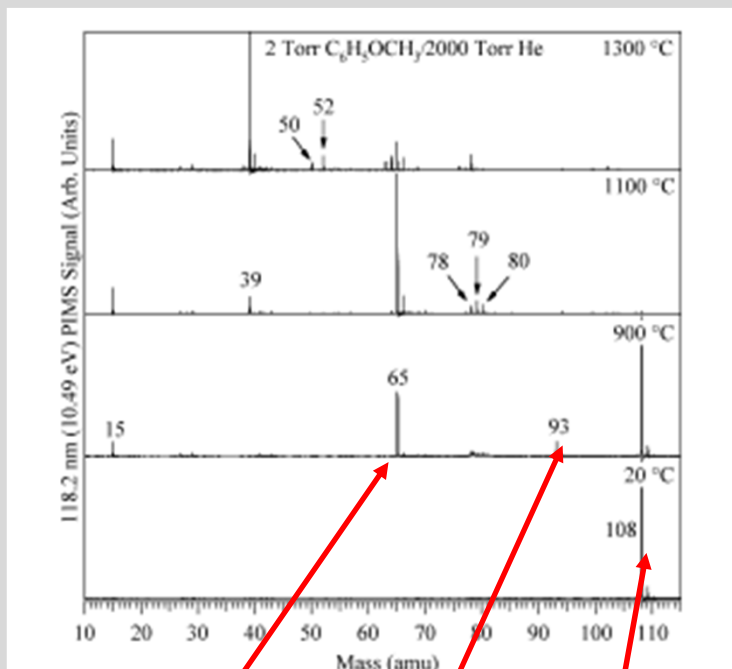
High T, low concentration:
100% CO + cyclopentadienyl channel
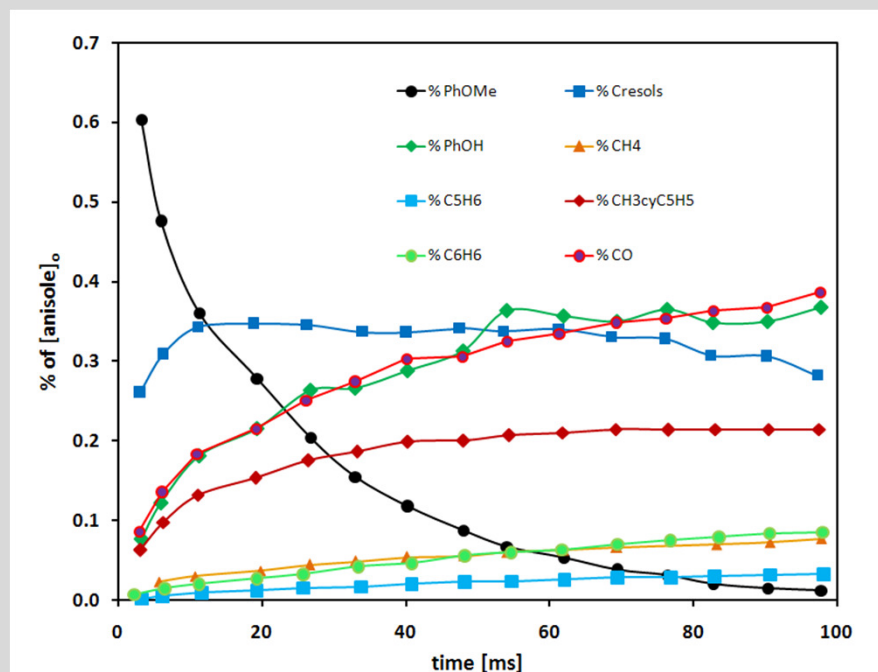
Lower T, high concentration:
CO + cyclopentadienyl channel << 100%
cresole + phenol production dominates
=> requires bimolecular rxns

=> Accurate description of phenoxy decomposition rate constant needed

Experimentally Determined and Calculated Barriers For Phenoxy Decomposition Deviate By 5-10 kcal/mol

Shock tube experiments of anisole provide kinetic data for phenoxy decomposition
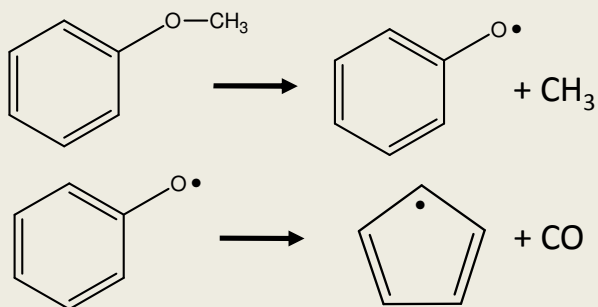
- first step is fast compared to second step
  => CO and cyclopentadienyl formation
     provide info on phenoxy decomposition
- measurements by Lin and Lin yielded
  1985 @ 1010-1430 K and 0.517–0.91 atm Ar
    $k(T) = 1.0E12\ s^{-1} \bullet exp(-47.7 +/- 1.4\ kcal/(mol \bullet RT))$
  1986 @ 1000-1580K and 0.4-0.9 atm Ar
    $k(T) = 2.5E11\ s^{-1} \bullet exp(-43.9 +/- 0.9\ kcal/(mol \bullet RT))$
  1994 Franck et al. confirm Arrhenius slope

Calculations on the PES of this reaction at various levels of theory predict higher barriers

Total barrier in kcal/mol		
This work CBS-QB3	Olivella et al. CASPT2	Liu et al. G2M(rcc,MP2*)
53	54	52

=> Goal of this work: Explain Experiment ⇔ Theory deviations

Lin, C.-Y.; Lin, M. C. *JPC* **1986**, *90*, 425. ; Lin, C.-Y.; Lin, M. C. *IJCK* **1985**, *17*, 1025; Frank_ProcCombustInst **1995** , *25***,** 833.
Olivella, S.; Sol, A.; Garcia-Raso, A. *JPC* **1995**, *99*, 10549.; Liu, R.; Morokuma, K.; Mebel, A. M.; Lin, M. C. *JPC* **1996**, *100*, 9314.

Applied Methodology: From QM Calculations To Pressure-Dependent Rate Constants

Gaussian Software®

CBS-QB3 and QCBS-QB3 levels

Geometry, Frequencies, Electronic Energy, …

FANCY

Statistical mechanics

Heat of Formation, Entropy, Heat Capacity, …

TSTdG

Transition state theory

High-pressure Rate Constants $k_\infty(T)$ for Elementary Reactions

CHEMDIS

QRRK / MSC approach

Pressure-dependent Rate Constants $k(T,P)$ for Apparent Reactions
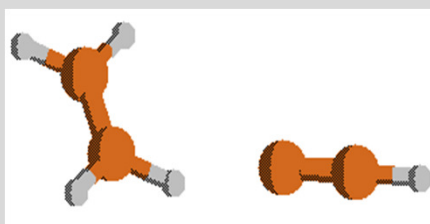
k(T,P)
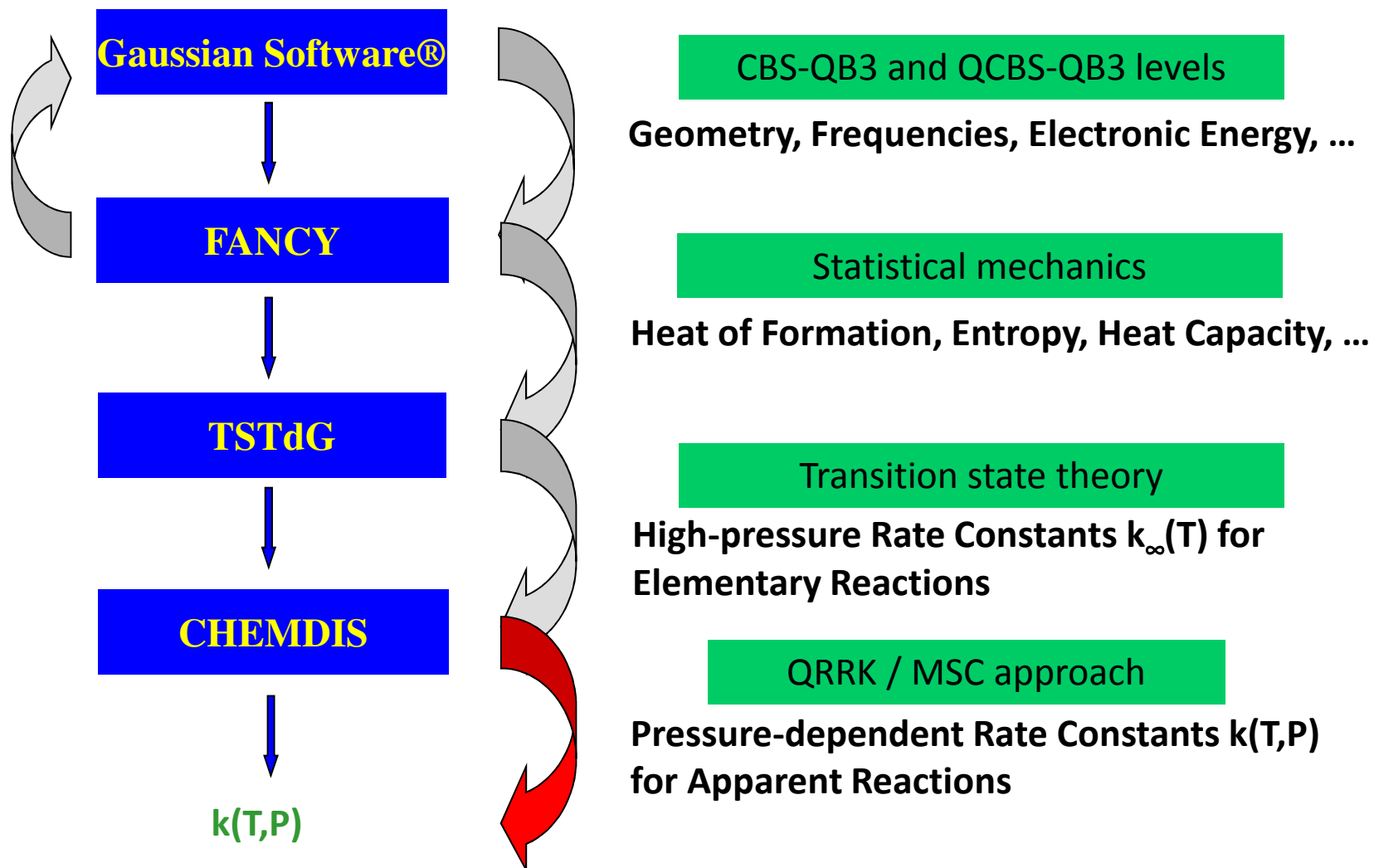
Original vs. Modified CBS-QB3 Methods

CBS-QB3: Geometry/frequencies @ B3LYP/6-311G(d,p) level
"QCBS-QB3": Geometry/frequencies @ QCISD/6-31G(d) level

Cyclopentadienyl thermo

Property	CBSQB3	QCBSQB3	literature
BDE [kcal/mol]	82.7	82.4	81-83 (Roy,NIST)
Entropy [cal/mol•K]	68.4	63.6	63.5 (Kiefer 2001)

$C_2H_3 + C_2H_2 => C_2H_4 + C_2H$
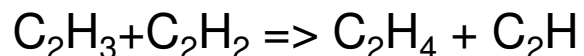
Non-linear C--H--C
@ CBS-QB3

linear C--H--C
@ QCBS-QB3

$C_2H_4 + H => C_2H_5$
high-p rate constant

CBS-QB3

QCBS-QB3

Symbols: literature data
imported from Miller et al. PCCP 6 p1192 (2004)
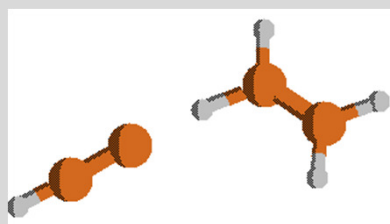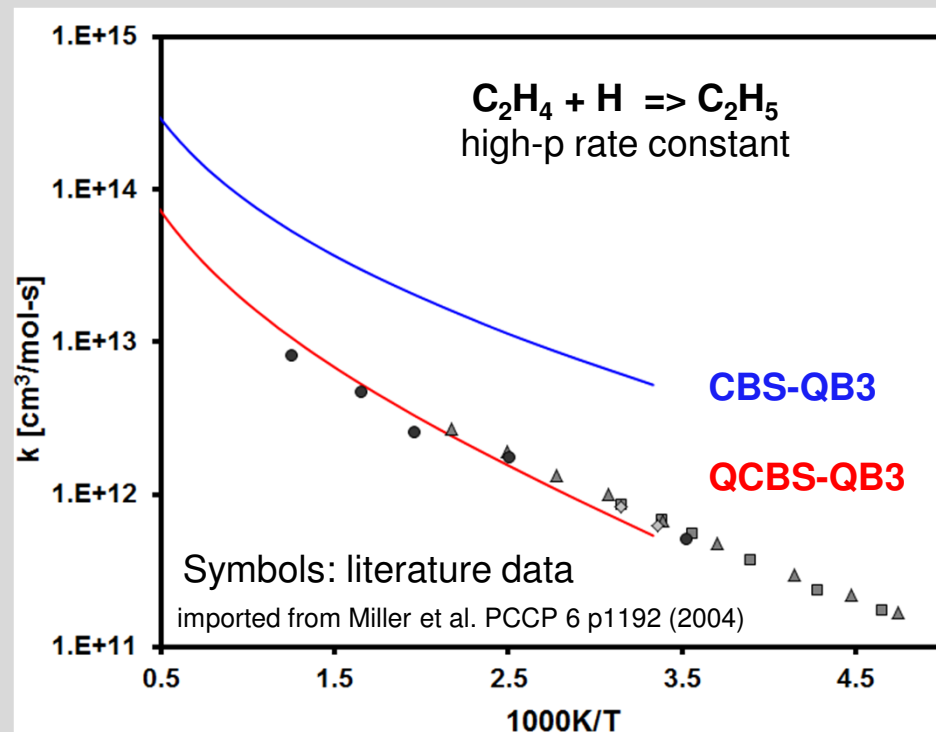
"QCBS-QB3" used to probe reliability of B3LYP structure/frequencies/thermo

Key Features of PES For Phenoxy Decomposition Are Well Established

Δ_fH^{298} / kcal/mol

63.4 (**64.3**)

66.7 (**67.9**)

58.8 (**60.1**)

51.6 (**53.8**)

47.5 (**49.1**)

2

3

38.0 (**38.8**)

+ CO

4

13.3 (**13.7**)

1
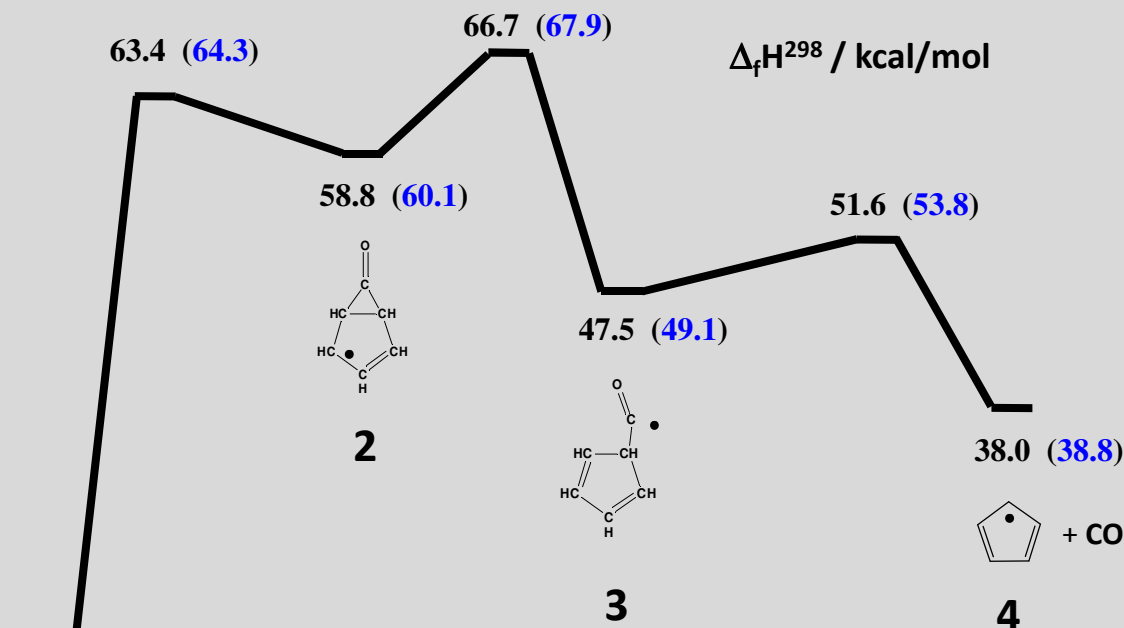
Alternative ring-opening / ring-closing pathway is less favorable and not considered

E [kcal/mol] relative to PhO·	CBS-QB3	QCBS-QB3	Olivella et al. CASPT2	Liu et al. G2M(rcc,MP2*)
TS-1 **1 → 2**	50.1	50.6	51.7	49.3
TS-2 **2 → 3**	53.4	54.2	53.8	52.2
TS-3 **3 → 4**	38.3	40.1	35.4	N/A

=> Good agreement among various methods => no room for large errors in barriers!

QCBS-QB3 Leads To Slightly Lower TST Rate Constants

## Transition state theory results

Method / rxn	A [s^{-1}]	n	E[kcal/mol]	k(900K) [s^{-1}]	k(1100K) [s^{-1}]
CBS-QB3					
1 → 2	2.25E+012	0.45	50.5	2.65E+1	4.98E+3
2 → 3	1.35E+013	0.07	8.19	2.22E+11	5.18E+11
3 → prod	8.48E+012	0.32	4.66	5.37E+12	9.30E+12
QCBS-QB3					
1 → 2	3.97E+012	0.32	51.02	1.39E+1	2.67E+3
2 → 3	4.63E+012	0.14	7.90	1.41E+11	3.25E+11
3 → prod	3.08E+012	0.46	5.04	4.23E+12	7.84E+12

⇒ CBS-QB3 and QCBS-QB3 based rate constants agree within factor of 2
⇒ Geometry/frequency calculation part seems reliable within expected uncertainty limits

Experimental Data Appear To Follow Simple Arrhenius Expression
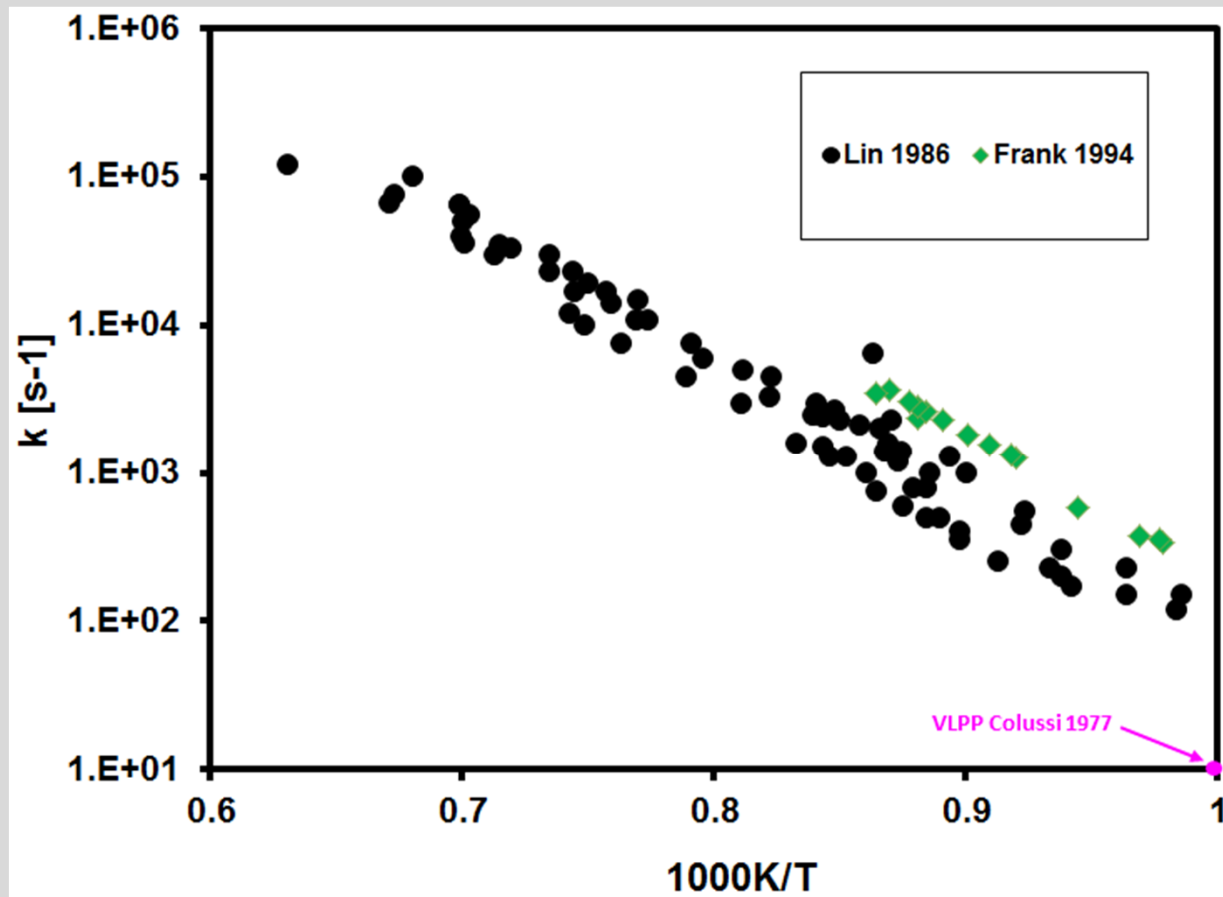
Lin & Lin 1986
Incident shock tube
CO monitored (< 100% seen)
0.40 - 0.9 atm
0.1-0.8% Anisole/Ar
fit to set of 4 reactions

Frank et al. 1994
Reflected shock tube
CO monitored (~ 100% seen)
0.0025-0.09% $ArOCH_3$/Ar
single reaction step

Colussi 1977
VLPP experiment
k(1000 K) estimated 10s^{-1}
(no pressure given)

⇒ Plot of experimental data suggest that measurements might be done at high pressure limiting conditions

# Predicted Pressure-Dependent Rate Constants Agree Well With Data

QRRK/MSC predictions with a rather high ΔE_{all} value reproduce experimental data
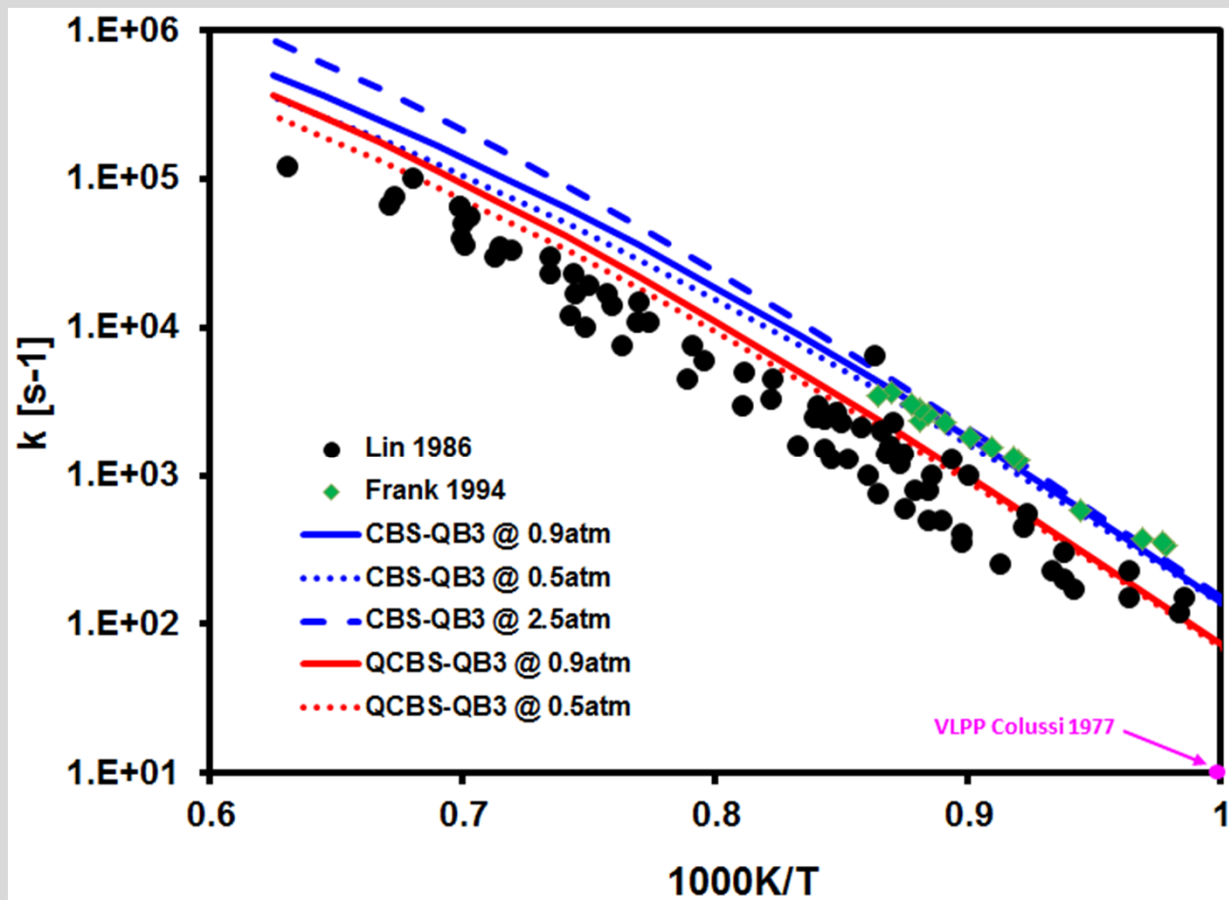
- Below T =1100 K no significant Pres. effect

- At high T predictions for p=0.5 atm agree better (consistent with (T,P) sets in experiment)

- Colussi's results is clearly at very low P (not shown: calcs for 0.001 and 0.0001atm bracket this value)

$\Rightarrow$ Good agreement between CBS-QB3 data and Franck et al.
$\Rightarrow$ QCBS-QB3 predictions agree better with Lin and Lin data
$\Rightarrow$ Quantitative Agreement with experiments despite higher barriers in the PES!

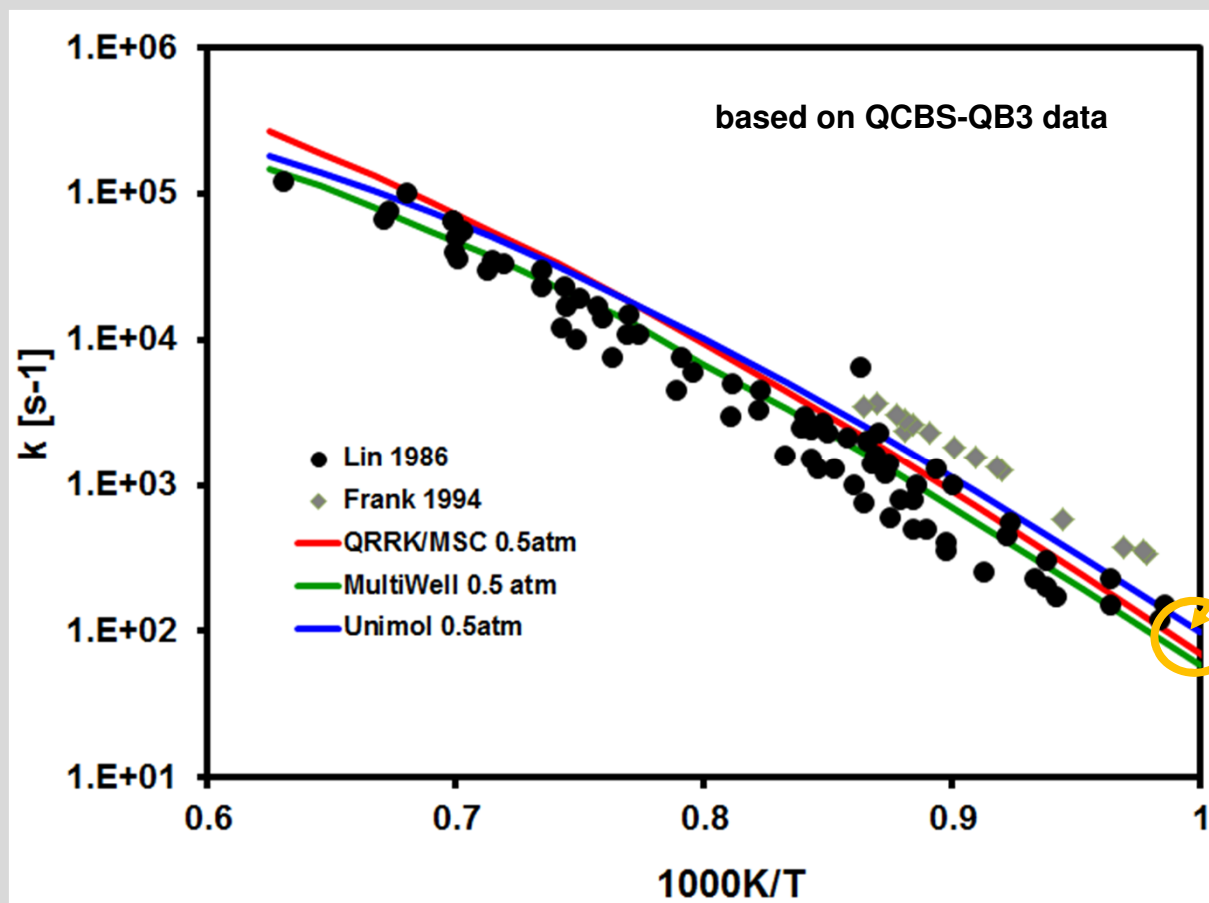# 3-Step Process Can be Approximated As Single Step Reaction
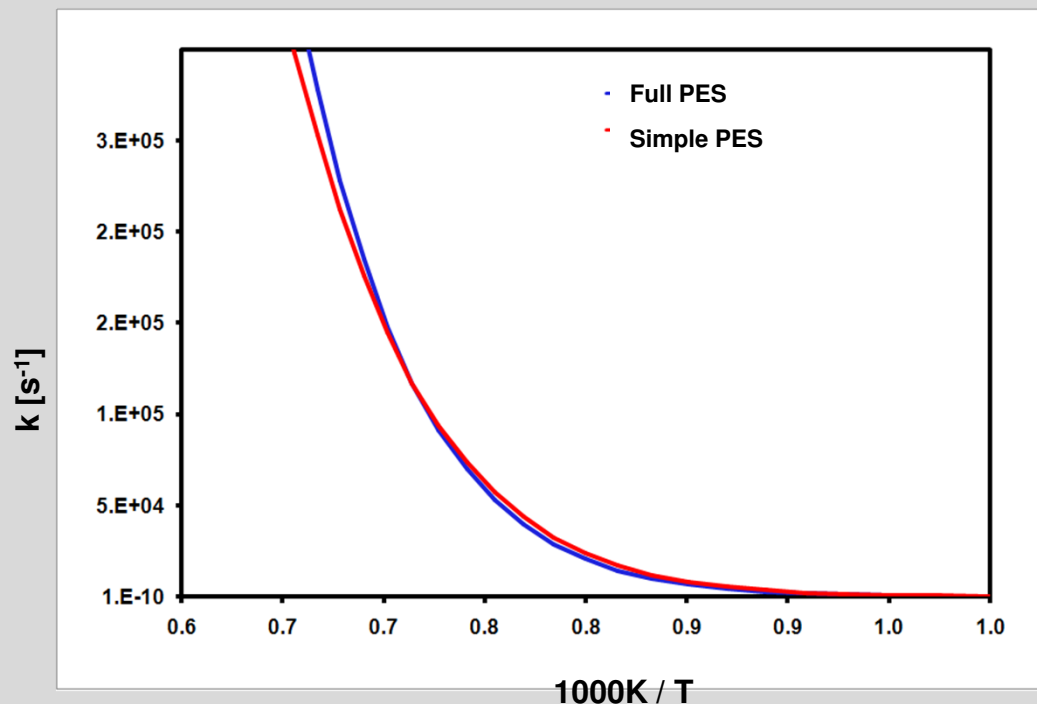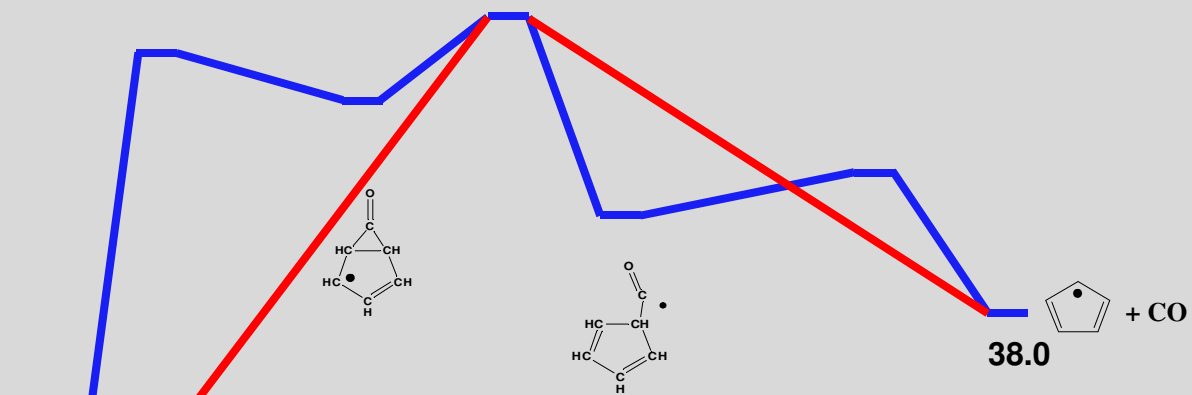
⇒ Analysis based on simplified PES yields essentially the same rate constants
  ● allows more efficient studies of substituted phenoxy systems in the future
  ● allows the use of Unimol (single well code) to validate results

Good Agreement Between QRRK/MSC and RRKM/ME Methods

Different Codes for Fall-off analysis lead essentially to the same results

based on QCBS-QB3 data

Legend:
- Lin 1986
- Frank 1994
- QRRK/MSC 0.5atm
- MultiWell 0.5 atm
- Unimol 0.5atm

Axes: k [s-1] vs 1000K/T

Had a smaller ΔE_{all} for QRRK/ MSC analysis been used, even better agreement would have been achieved!

Small deviations in k_{inf} caused by slight differences in the calcs:
+ Hindered rotors
+ k(T) input format
   ILT vs direct count
+ 3-step vs. 1-step
…

MultiWell: stochastic time integration
Unimol: deterministic steady-state RRKM/ME code
QRRK/MSC: deterministic steady state modified strong collisions approach
$\Rightarrow$ all treatments essentially give the same answer!

Use of High Pressure Rate Constant has Impact at High AND Low T
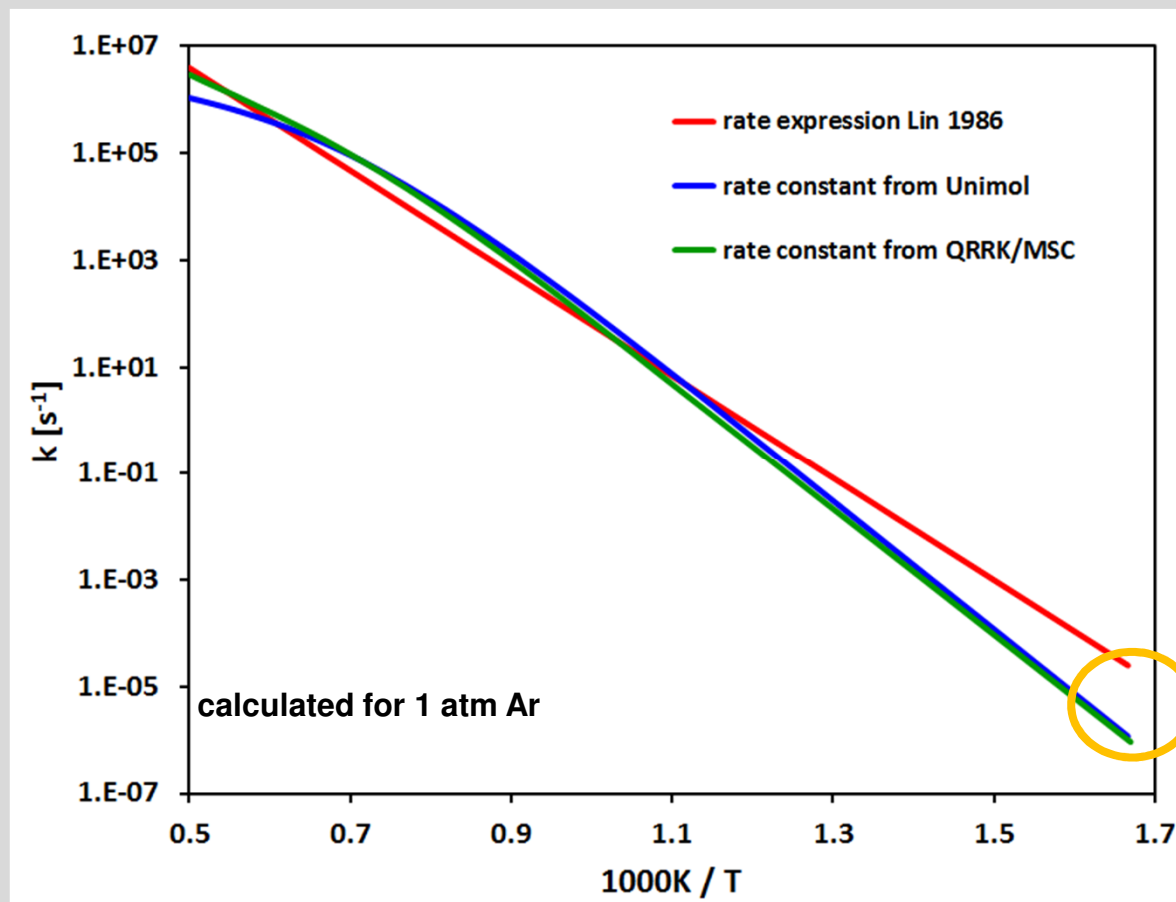
> ➤ Extrapolation to high T over-estimates the rate constant (too little fall-off)
> ➤ Extrapolation to low T over-estimates the rate constant (Ea too small)
> ➤ this might explain problems with modeling anisole product yields at low T

Carstensen/Dean Phenoxy Decomposition ICCK 2011

Substituted Phenoxy Radicals Relevant To Lignin Chemistry Dissociate More Slowly Due To Higher Barriers
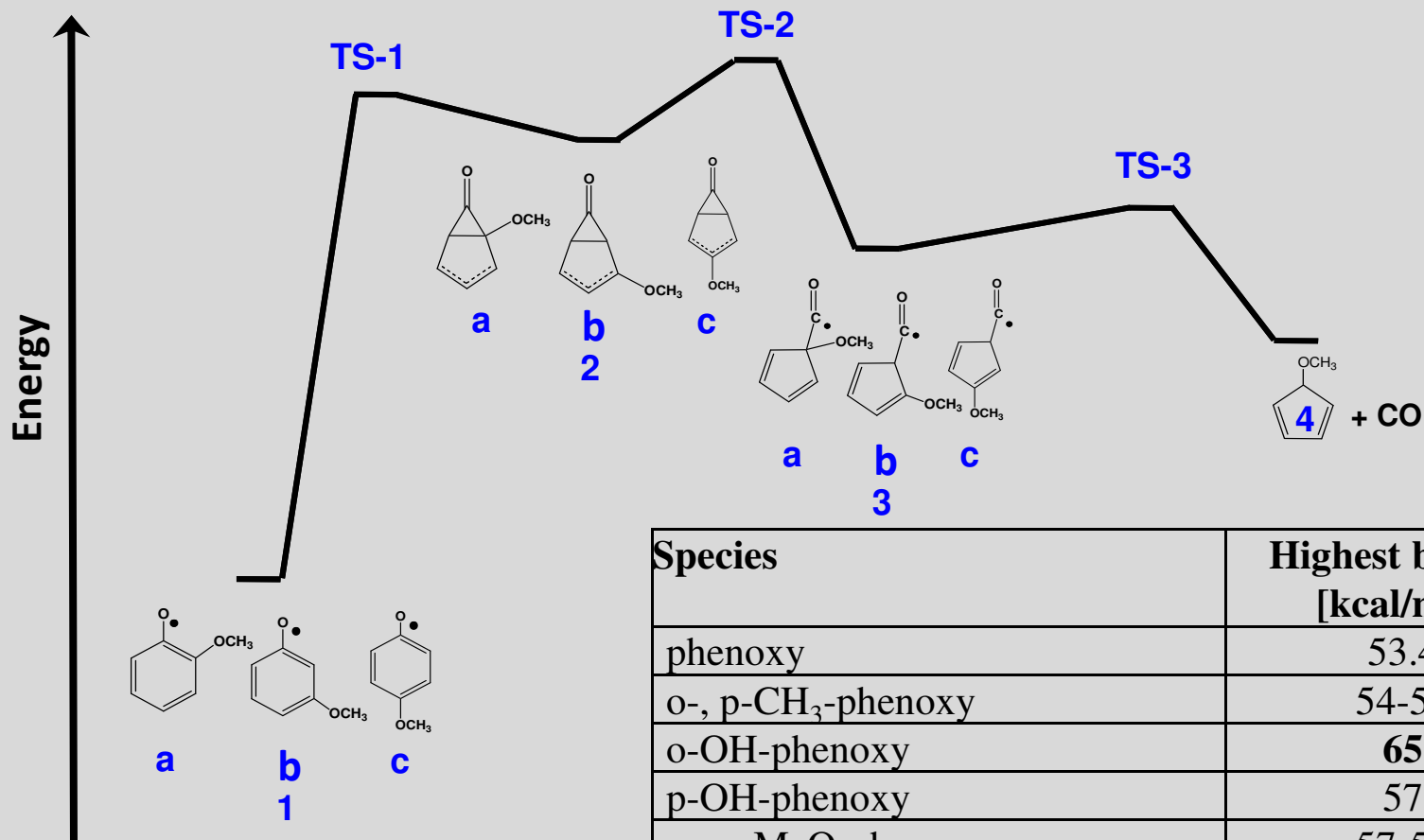
Species	Highest barrier [kcal/mol]
phenoxy	53.4
o-, p-CH$_3$-phenoxy	54-55
o-OH-phenoxy	**65**
p-OH-phenoxy	57
o-, p-MeO-phenoxy	57-58
o-OH-,m-MeO-phenoxy	~ 61
o-OH,o-MeO-phenoxy	~ 69

1. CH$_3$, OH, OCH$_3$ substituents in o, p- position lead to higher total barriers; H-bonding increases barriers (m-substituted phenoxy radicals have generally lower barriers than analogous o, p derivatives)
2. Methoxy and OH substituted phenoxy radicals are intermediates in guaiacol, syringol , ... pyrolysis

Decomposition of Substituted Phenoxy Radicals
Show Similar P-dependence
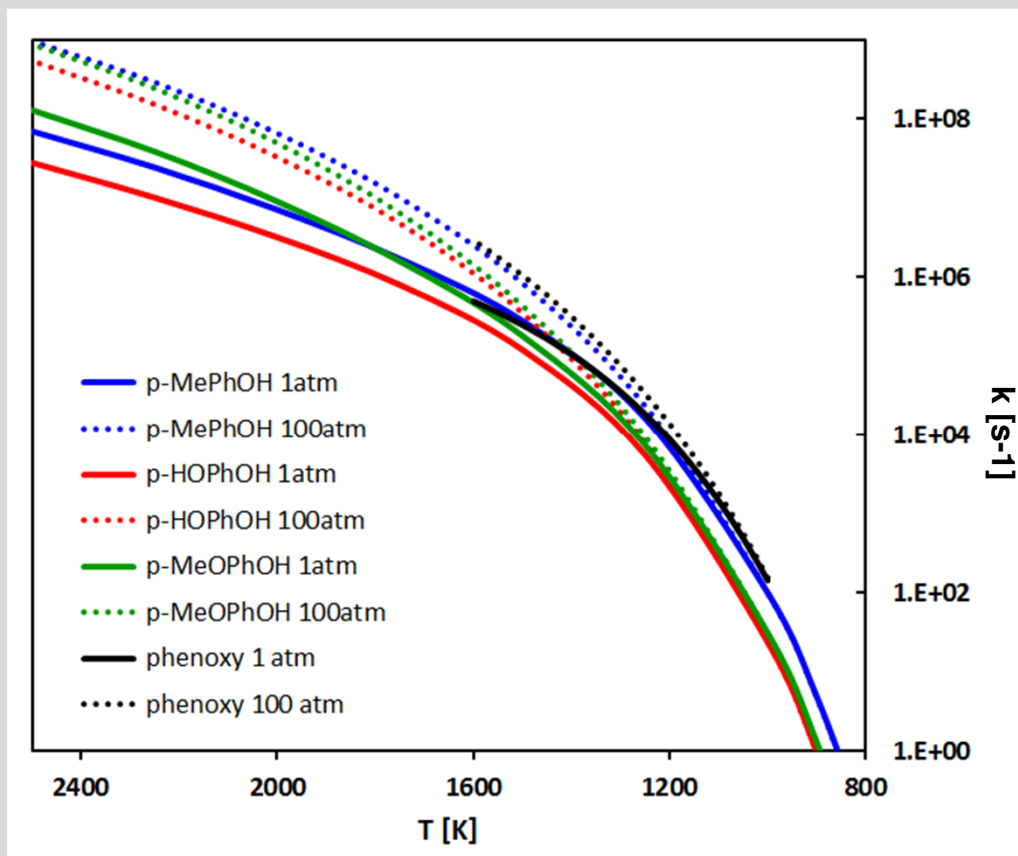
- ➤ Fall-off behavior of substituted phenoxy radicals similar to phenoxy
- ➤ For modeling: Estimating k(T) using of Lin's rate expression for phenoxy would lead to severe errors at low T

Summary / Conclusions

- Thermal decomposition of phenoxy radicals studied with CBS-QB3 and QCBS-QB3 methods
    - overall barrier is ~ 54 kcal/mol
      => 10 kcal/mol higher than reported experimental barrier of ~ 44 kcal/mol
    - similar results with B3LYP and QCISD optimized structures

- Good agreement between predicted and measured rate constants when pressure-dependence is included
    - QRRK/MSC approach yields accurate apparent rate constants
    - Results reveal that experiments did NOT reach high pressure limiting conditions
    - Fall-off reduces the decomposition rate constants and leads to lower apparent barrier
    - RRKM/ME methods confirm this; good agreement between different methods

- Substituted phenoxy radicals show similar k(T,P) behavior
  (assuming other reaction pathways are not competitive)

- Two CBS-QB3 methods used:
  regular CBS-QB3 supports Frank et al. data
  "QCBS-QB3" results are closer to Lin and Lin's measurements
  The current calculations can't resolve this difference.

Acknowledgements

Program manager: Dr. Mark Nimlos
Dr. David Robichaud

Thank you for your attention!
Questions?