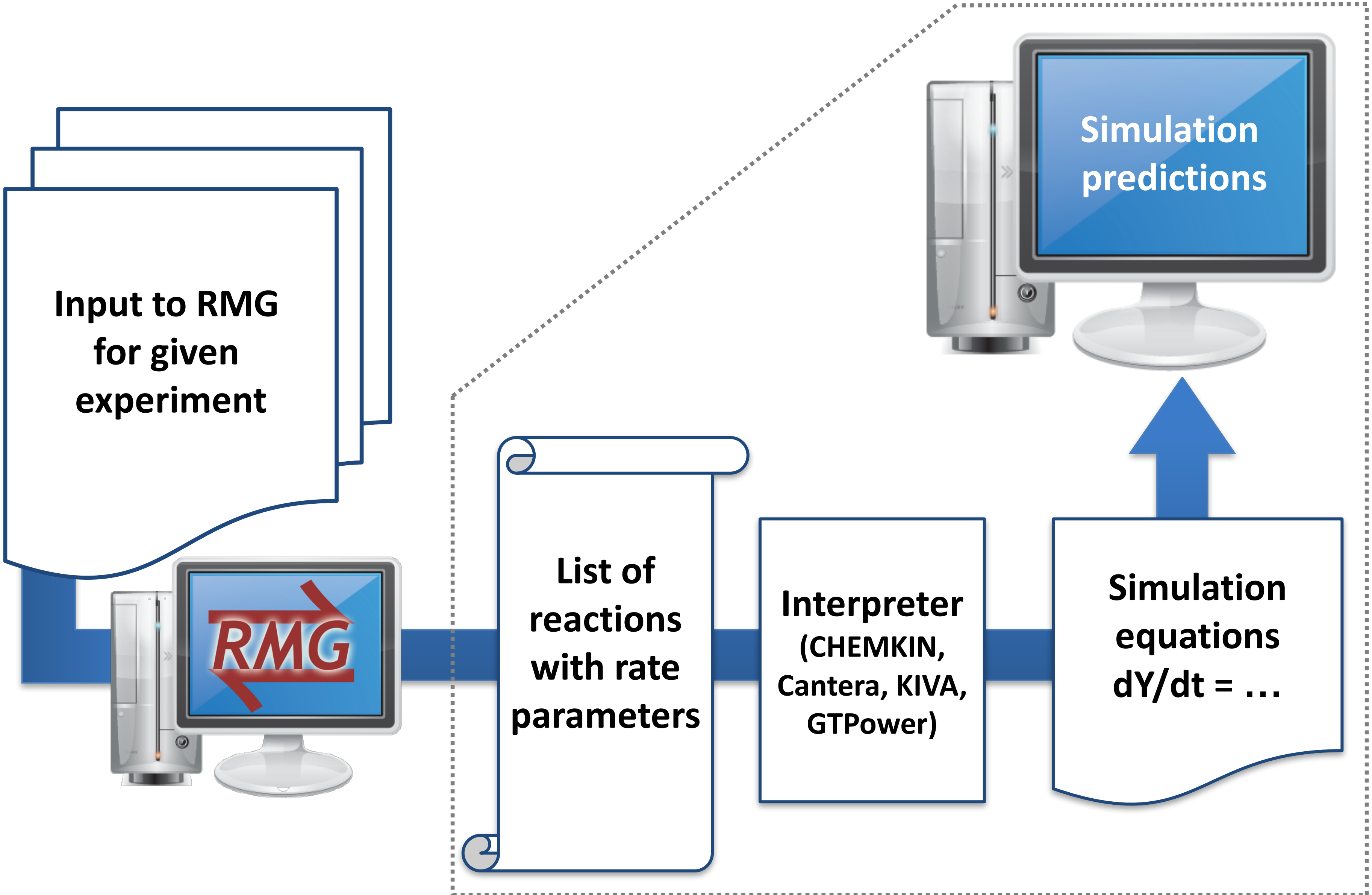
Building Models in RMG – part 2

Shamel Merchant

15th Nov 2013

Ideal world



Input to RMG
for given
experiment

List of
reactions
with rate
parameters

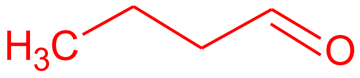
Interpreter
(CHEMKIN,
Cantera, KIVA,
GTPower)

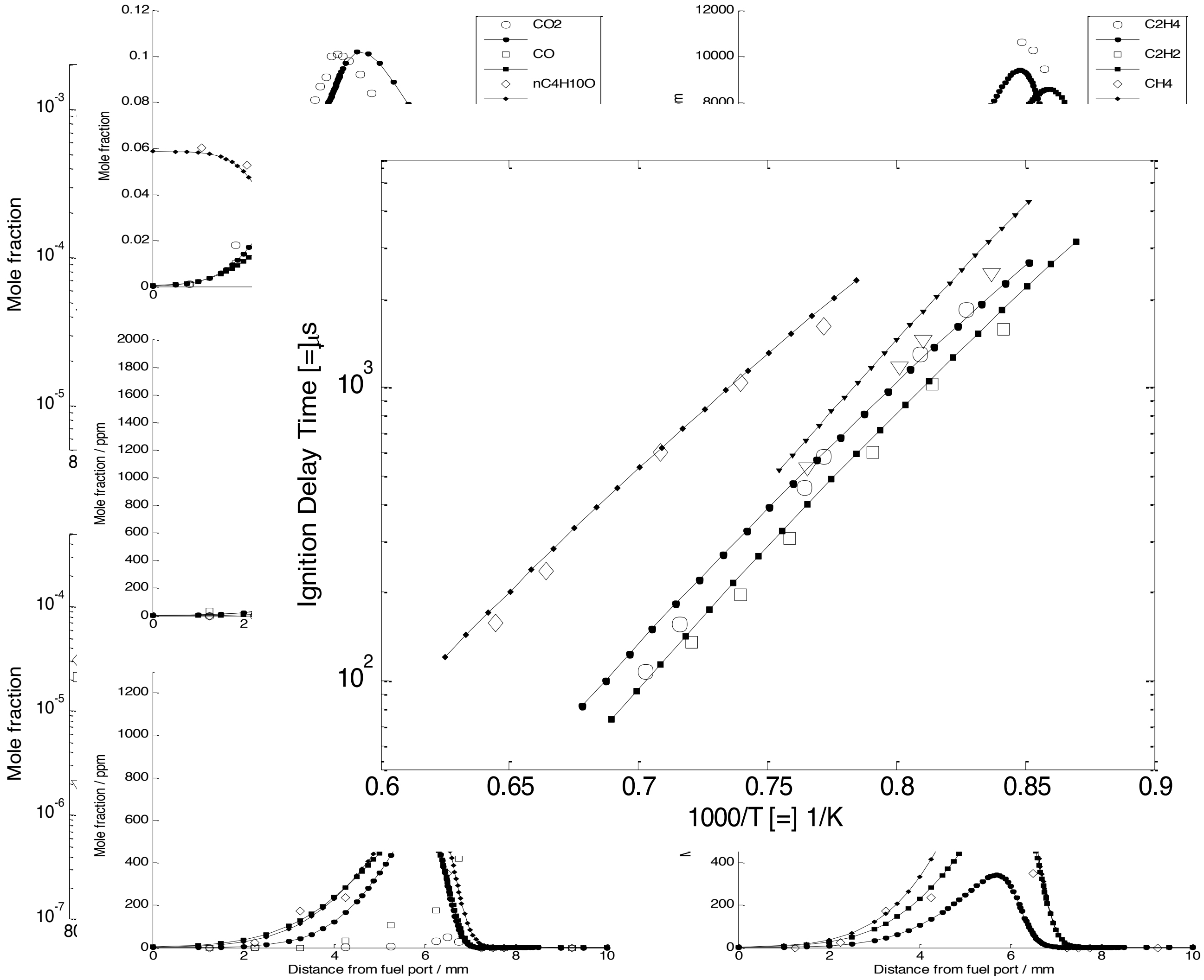
Simulation
equations
dY/dt = …

Simulation
predictions

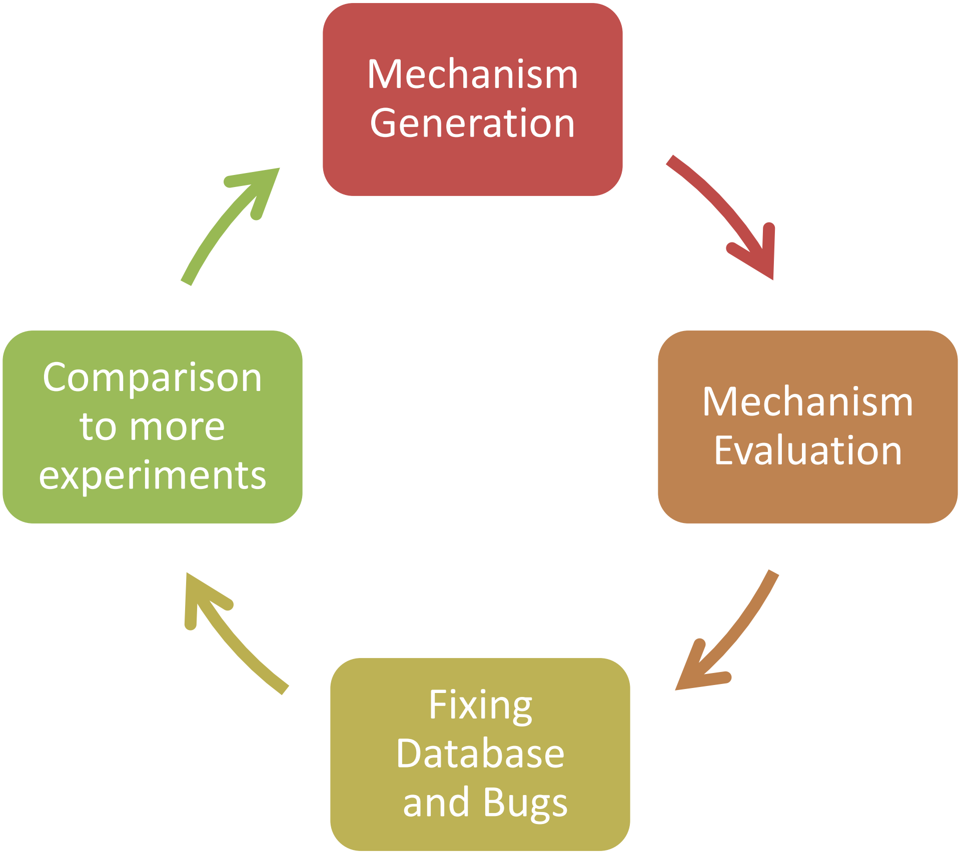
Ideal world

- Pyrolysis
- JSR
  - 1 atm
  - 10 atm
- Opposed-flow flame
- Shock tubes
  - Moss et al.
  - Black et al.
  - Butanal





What really happens …



Mechanism Generation

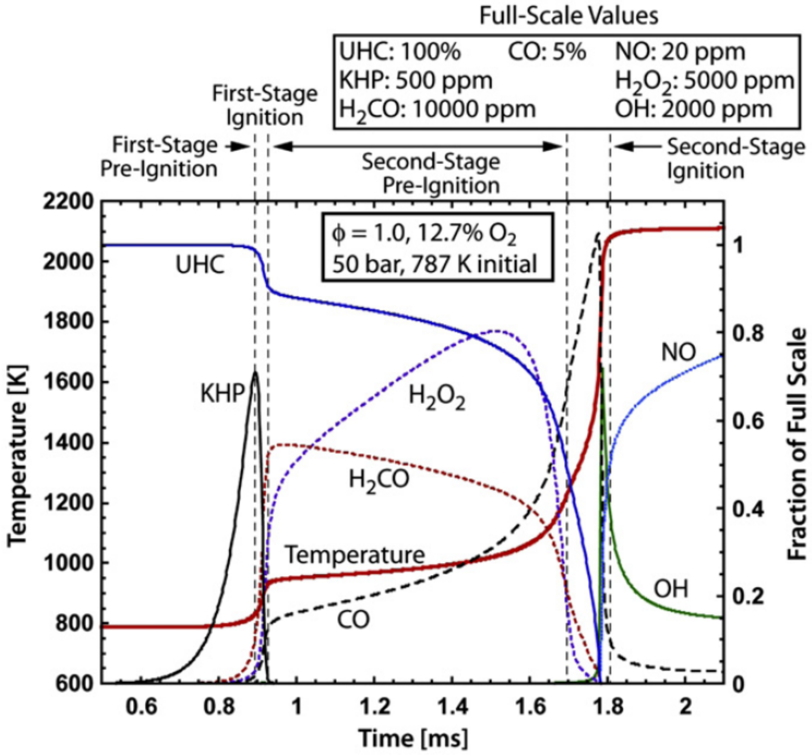
Mechanism Evaluation

Fixing Database and Bugs

Comparison to more experiments

Setting up the input file

1. Try to mimic the experiment you are going to compare against.
   - Model should be valid at equivalence conditions of your experiments
   - JSR and PFR use residence time as the termination criterion
   - RCM and ST are tricky since you have an adiabatic system

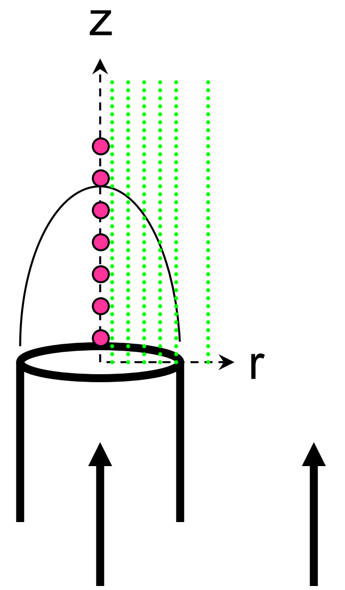


Most of the fuel is being consumed when the T >> $T_{initial}$

Ideally if you have the Experimental Temperature profile vs Time you can use it to determine your termination, initially you can just give
T = 800 K, 1000 K, 2000 K
Conversion = 0.9, 0.9, 0.9

Setting up the input file

1. Try to mimic the experiment you are going to compare against.
   - For flame experiments like doped flame, you can use the restart feature to make your model



Methane
Nitrogen
Argon
Butanol

Air

The flame is broken down into a number of center line zones

1. For each zone we know the residence time from average flow velocity
2. Use experimental data T, P to figure out appropriate initial conditions for each zone. The initial concentration comes from previous zone final species concentration
3. Use the restart to grow the model from one zone to another

Setting up the input file

2. Setting up thermo library

    - Basic Libraries to include

    Primary Thermo Library

    DFT QCI Thermo Library

    - Special Libraries

    Butanol CBS-QB3 calculations

    JP 10 BMK calculations

3. Setting up transport library

    - Basic Library to include

    GRI-Mech 3.0

Setting up the input file

3. Setting up reaction library and seed mechanism

- Oxidation mechanism especially for ignition delay

On the minimum add a small molecule seed currently Shamel recommends the ERC-Mechanism v0.9

- Pyrolysis mechanism

Can run without any seed unless aromatic formation is important

For aromatics special reactions need to be accounted for currently there seems no unified seed

Butanol: Aromatics seed obtained from Sandeeps hexadiene mechanism ++

JP10: Assorted library from various papers

- RL: It is also helpful to have good estimates of H abstraction from parent fuel molecule by OH, CH3, H and HO2. Check RMG prior hand and if it is using estimates do a literature search or quick ab-initio calculations.
- RL: Any special reactions go here, like assisted keto-enol tautomerizations
- Note don't add well skipping reactions in reaction.txt in a reaction library, they will be sent to fame and you will get answers which don't make sense!

Analyzing the mechanism

1. Comparison to experimental data
2. Reaction flux diagram
3. Sensitivity analysis
4. Parameter analysis or brute force sensitivity analysis

Workflow for constructing the kinetic model upon learning of a new experiment

- Run RMG at relevant T, P, $\underline{C}$ conditions, using previous model as initial "core"
- (Fix RMG bugs, add new features, etc.)
- Run new model in CHEMKIN w/sensitivity analysis
- (Adjust tolerances, discover CHEMKIN cannot cope with CHEB in a CONV simulation, etc.)
- Ask myself "Do I believe these kinetics / thermochemistry that the model is sensitive to?"
- If not, search literature.
- If no values exist in literature, quantum chemistry calculations (CBS-QB3, G3) + TST with 1-d hindered rotor corrections
- Wash, rinse, repeat (new pathways may be explored)

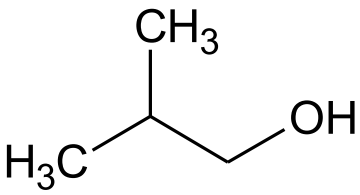
Case Study 1: iso-Butanol

Butanol condition file for oxidation

MaxOxygenNumberPerSpecies: 5

FinishController:
(1) Goal Conversion: iBuOH 0.9
(2) Error Tolerance: 0.1

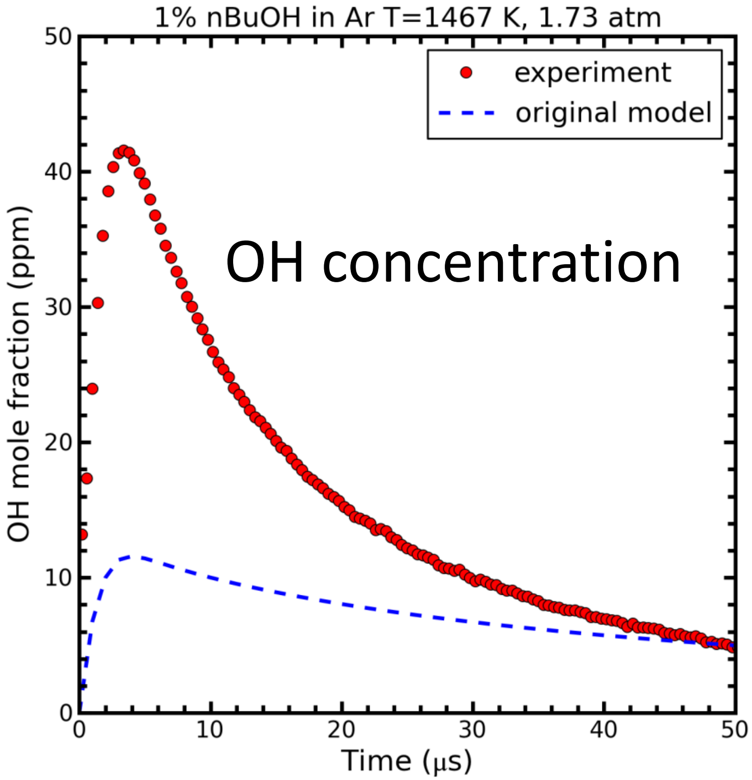
ReactionLibrary:
//Name: aromatics
//Location: aromatics
(This library is special since it has pdep rates at single pressure in reactions.txt and should not be included as a reaction library)



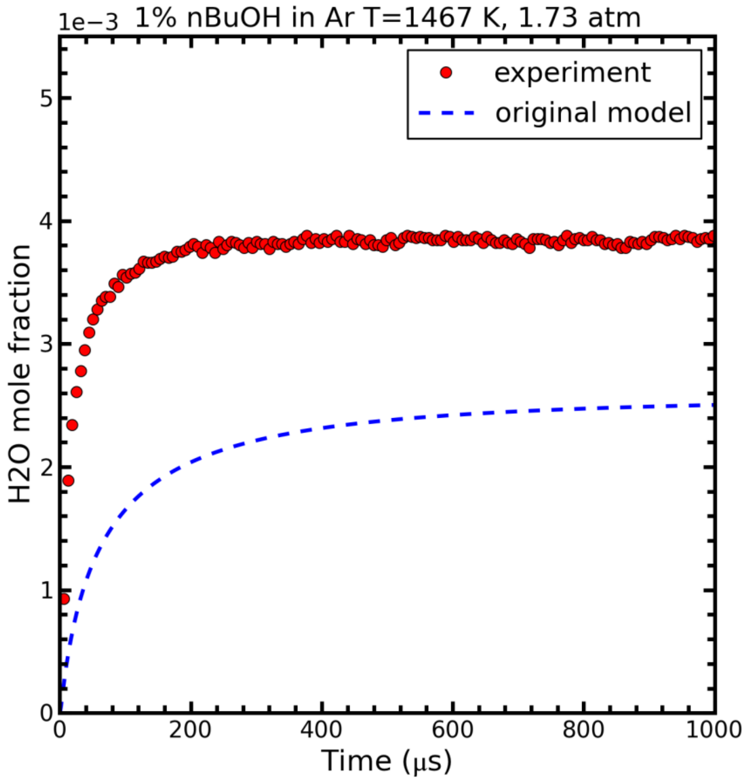
SeedMechanism:
Name: ERC-FoundationFuelv0.9
Location: ERC-FoundationFuelv0.9
GenerateReactions: no
Name: iBuOH_decmp_fromSJK
Location: iBuOH_decmp_fromSJK
GenerateReactions: no
(I tend to use no for small molecule seed because all important pathways have mostly been accounted for ... RMG also gives wild results for ones which are missing)

~1000 K model not quantitative for ~1400 K fast-pyrolysis experiments

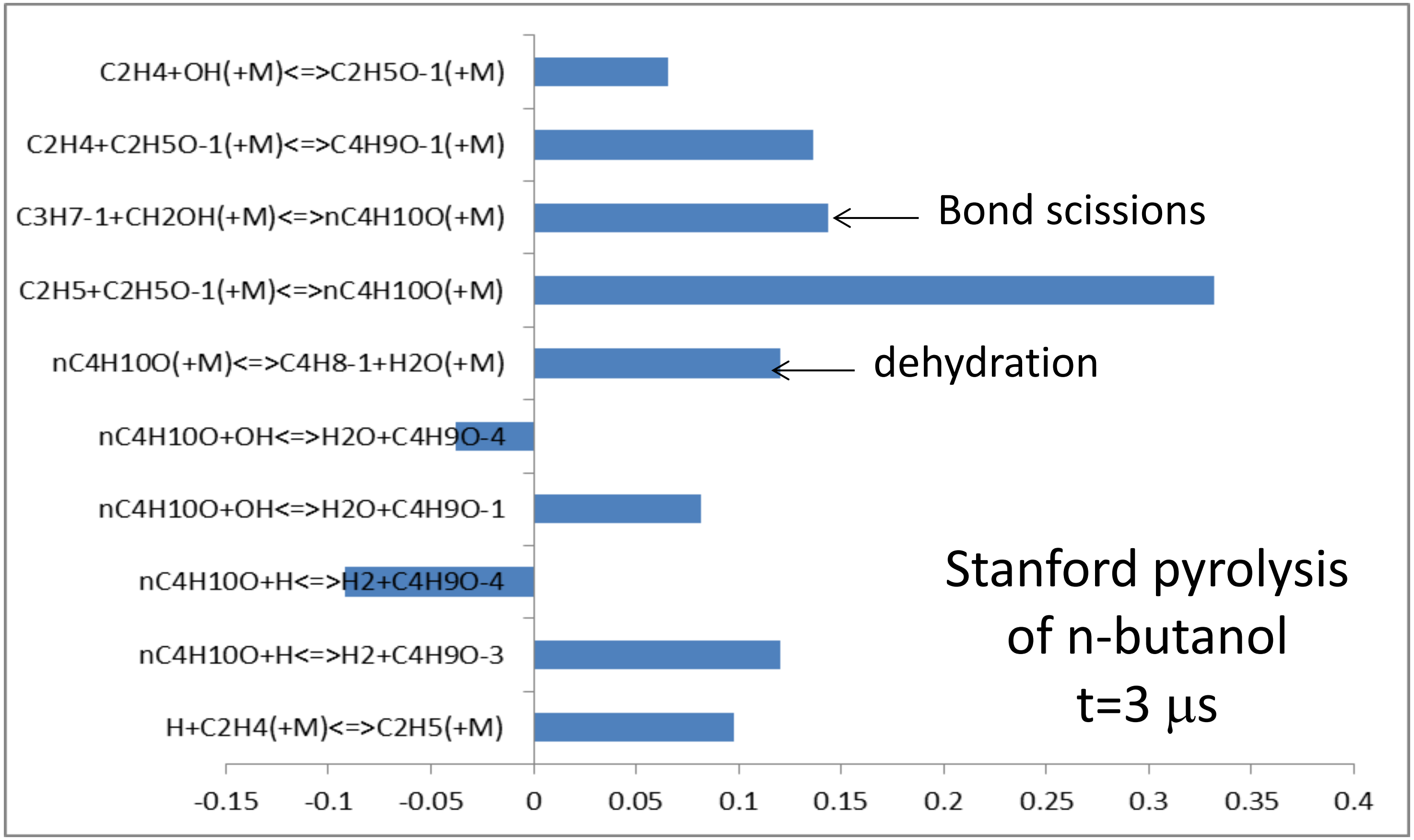
Initial Model Predictions (no quantum calculations)



OH concentration



Sensitivity analysis helps to figure out reactions whose rate coefficients you need to improve

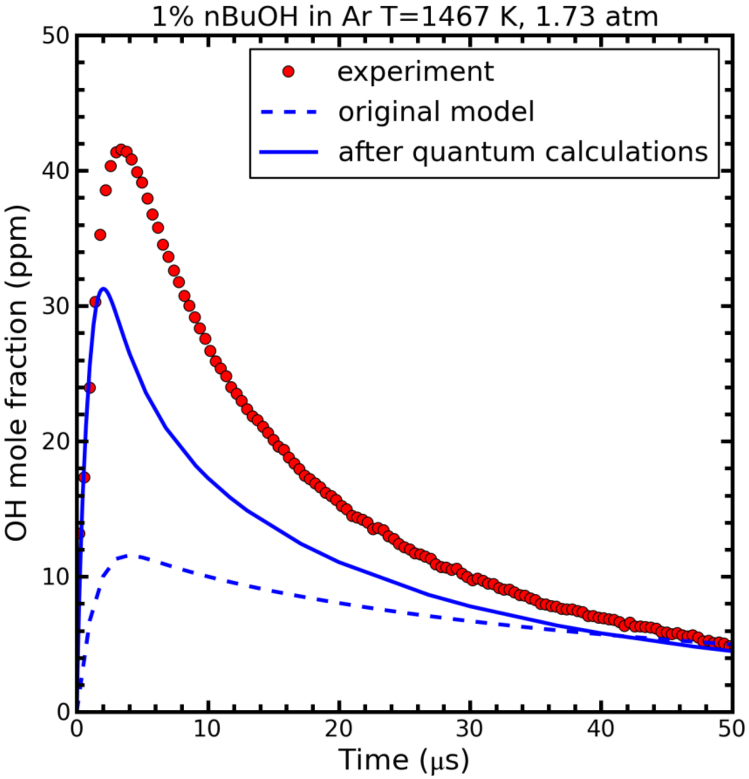


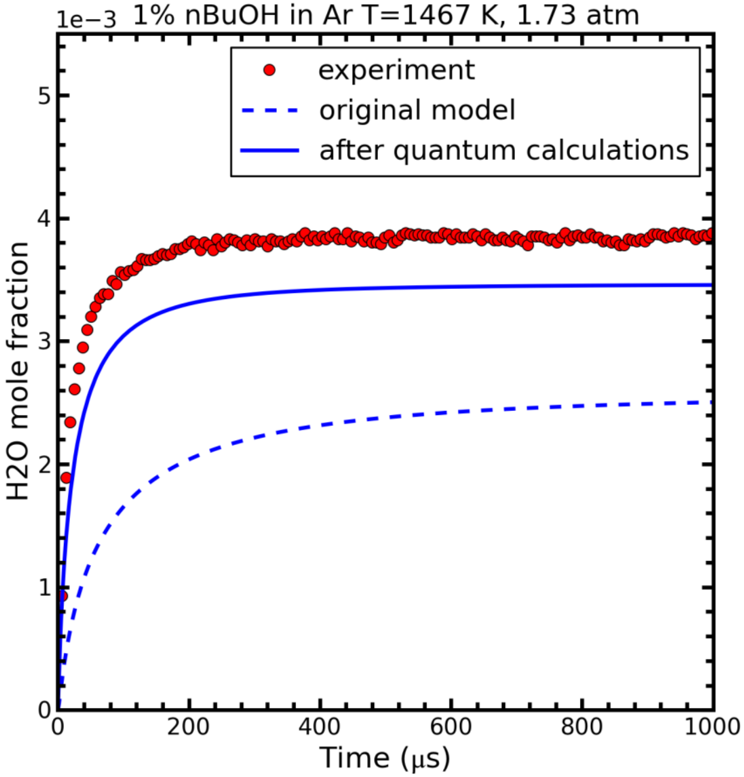
Stanford pyrolysis
of n-butanol
t=3 μs

Improving models by incorporating literature rate constants

Current Model Predictions

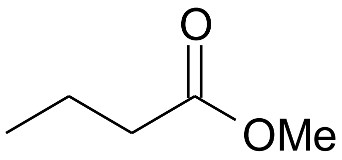
(with literature rate constants included as seed since they are reported as pressure dependent)





Case Study 2: Methyl Butanoate

Methyl Butanoate condition file for oxidation

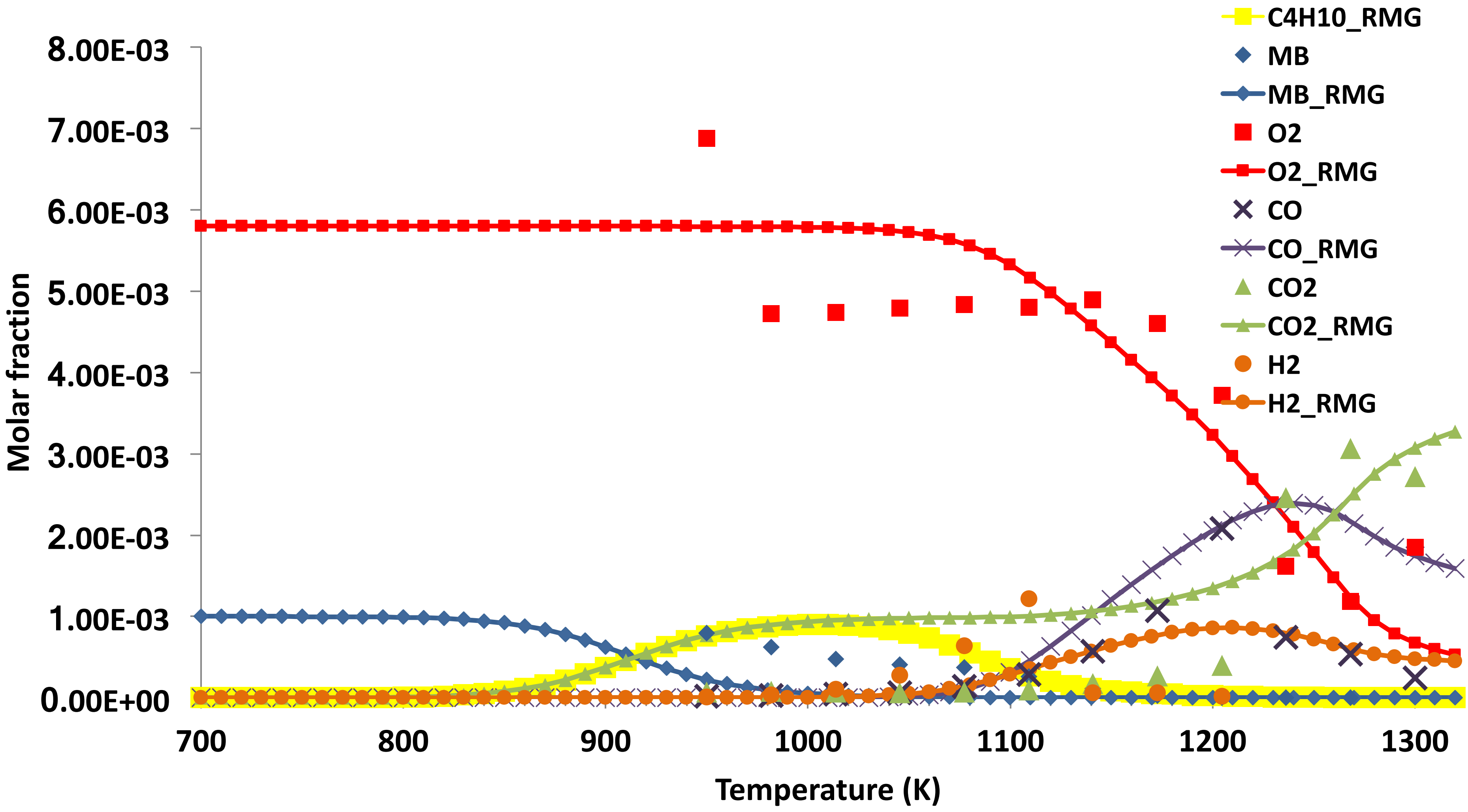


FinishController:
(1) Goal Conversion: mB 0.9
(2) Error Tolerance: 0.1

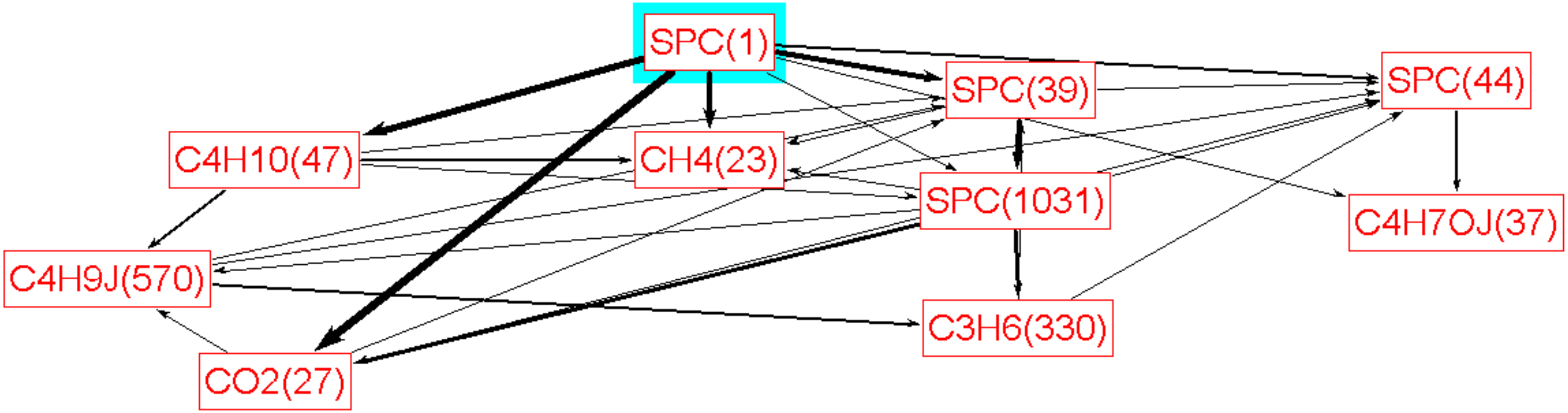
ReactionLibrary:

SeedMechanism:
Name: ERC-FoundationFuelv0.9
Location: ERC-FoundationFuelv0.9
GenerateReactions: no

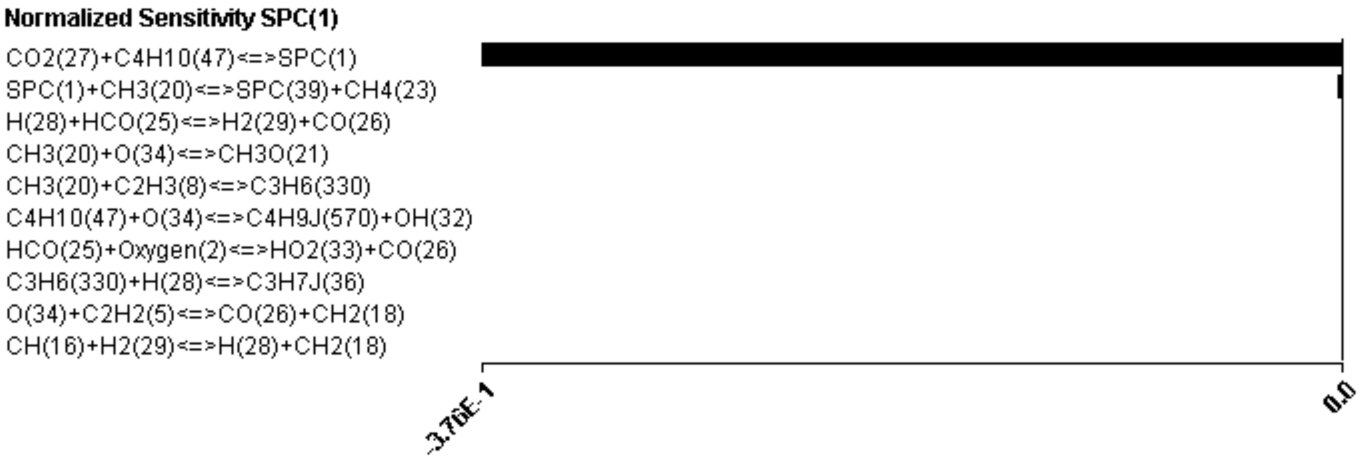
Methyl Butanoate decomposing too fast



Flux analyzer shows methyl butanoate quickly breaks down to give butane and CO2

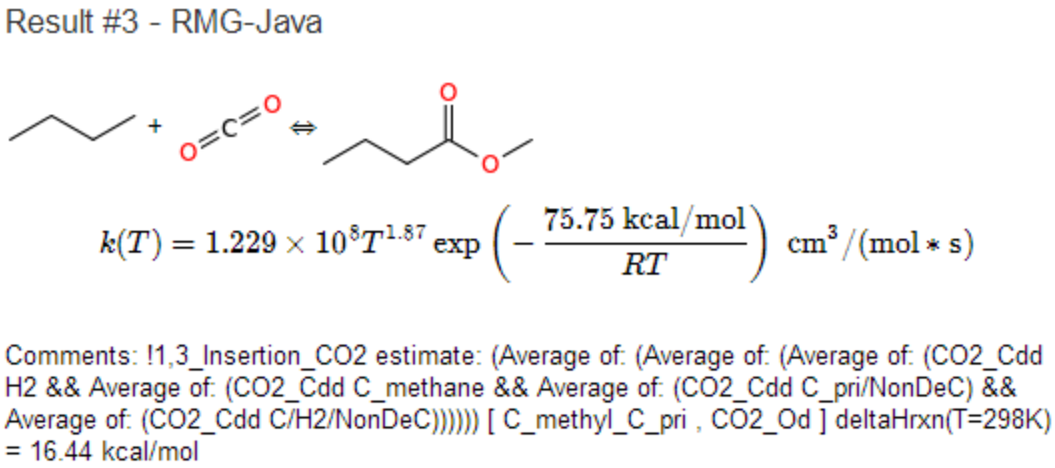


(39) - C5H9O2J
(44) – C5H9O2J
(1031) – C4H6O2



900 K

Improving methyl butanoate network



Result #3 - RMG-Java

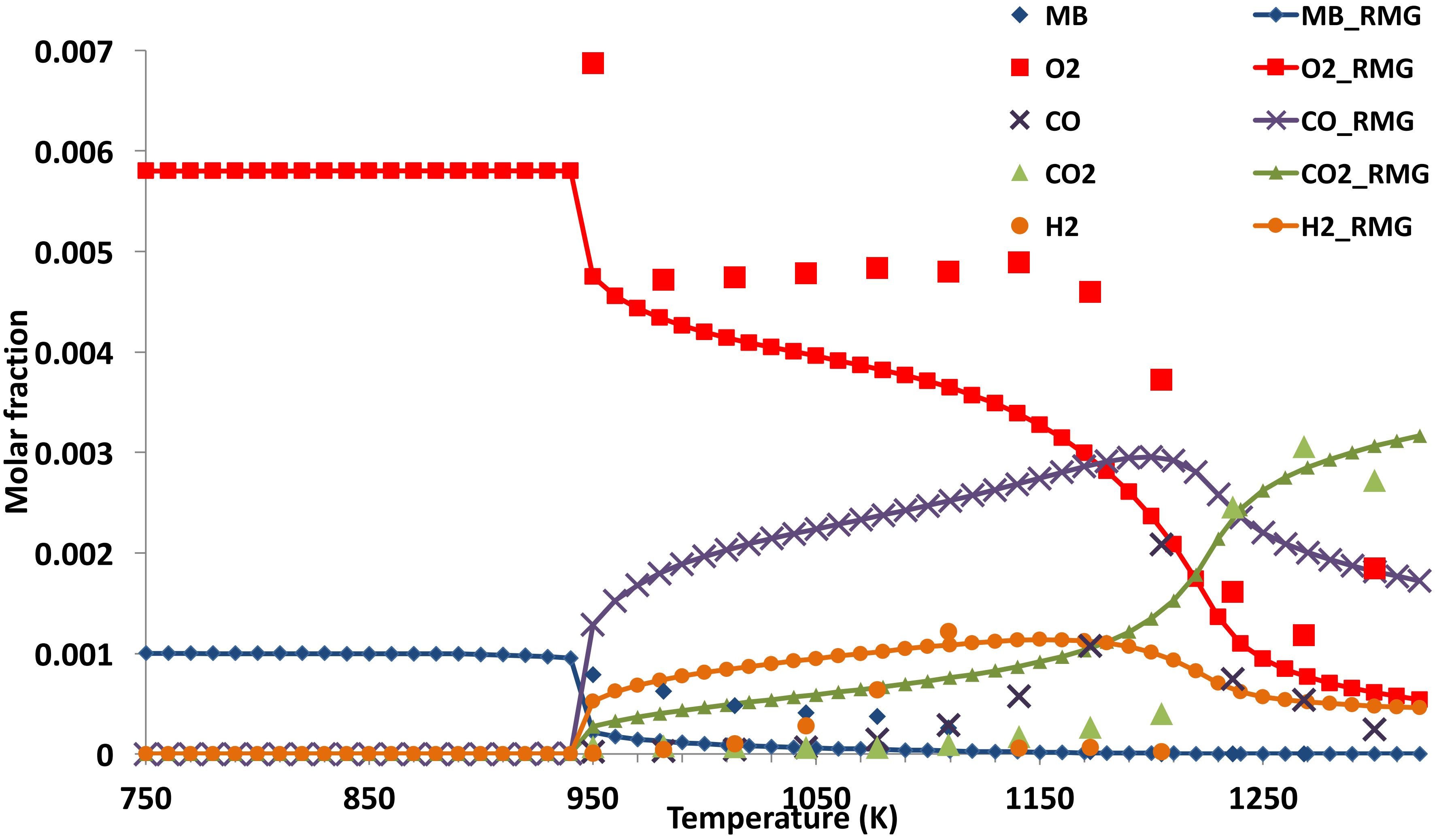
$$k(T) = 1.229 \times 10^{8} T^{1.87} \exp\left(-\frac{75.75\ \mathrm{kcal/mol}}{RT}\right)\ \mathrm{cm^3/(mol*s)}$$

Comments: !1,3_Insertion_CO2 estimate: (Average of: (Average of: (Average of: (CO2_Cdd H2 && Average of: (CO2_Cdd C_methane && Average of: (CO2_Cdd C_pri/NonDeC) && Average of: (CO2_Cdd C/H2/NonDeC)))))) [C_methyl_C_pri , CO2_Od] deltaHrxn(T=298K) = 16.44 kcal/mol

1. The rate constant is an average of average estimate which usually indicates it can be way off.
2. At this point do a literature search, for this reactions we could not find an estimate
3. Perform a fast quantum calculation to get sense of the rate constant – even without rotors on a low level theory can be very helpful

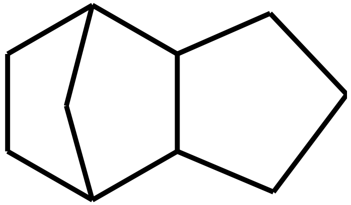
k = 7.3E1 * T^3.13 * exp(-118 kcal/mol /RT) cm3/(mol*s)

Improved predictions for methyl butanoate decomposition



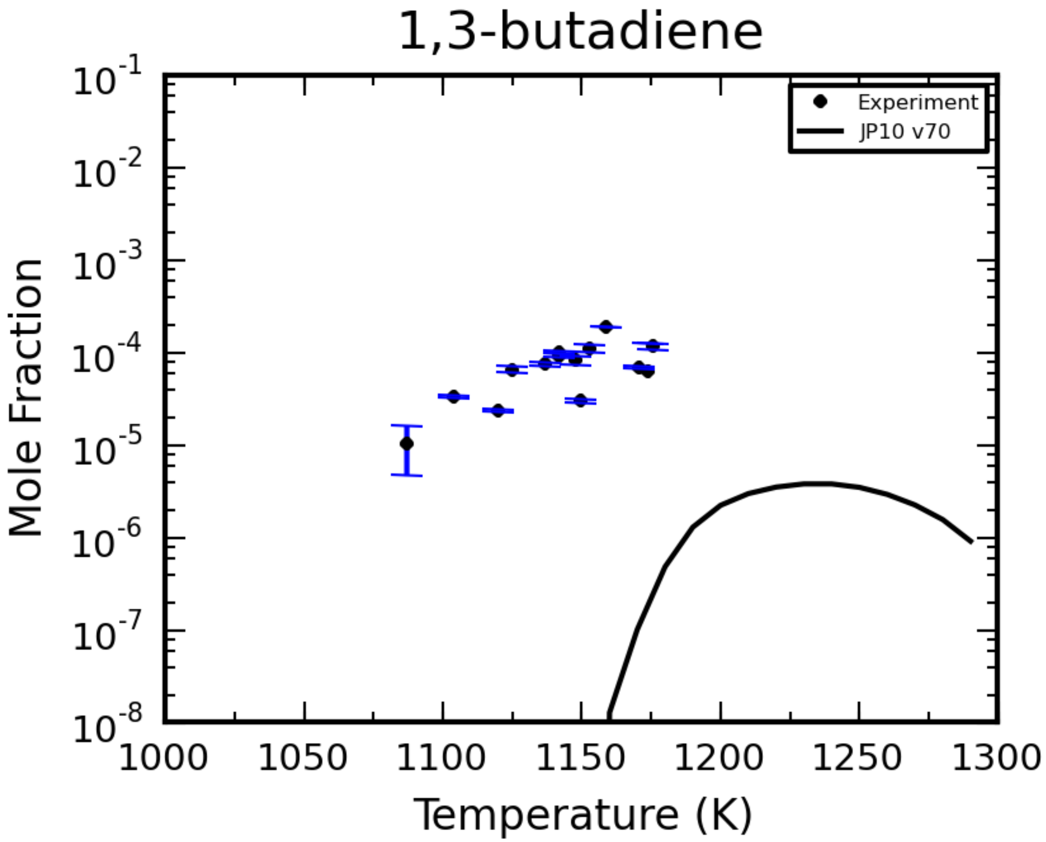
Case Study 3: JP 10

JP-10 condition file for pyrolysis



```
MaxCarbonNumberPerSpecies: 10
MaxRadicalNumberPerSpecies: 2
MaxHeavyAtomPerSpecies: 12

ThermoMethod: Hybrid mopac
MaxRadNumForQM: 0
CheckConnectivity: confirm
KeepQMFiles: no

FinishController:
(1) Goal Conversion: JP10 0.95
(2) Error Tolerance: 0.05

ReactionLibrary:
Name: JP10BetaScission
Location: JP10BetaScission
Name: JP10seed
Location: JP10seedmech
Name: JP10
Location: JP10
//Name: CombustionCorev5
//Location: combustion_core/version5
END


SeedMechanism:
END
```

1,3- Butadiene is not correctly predicted by initial JP-10 model

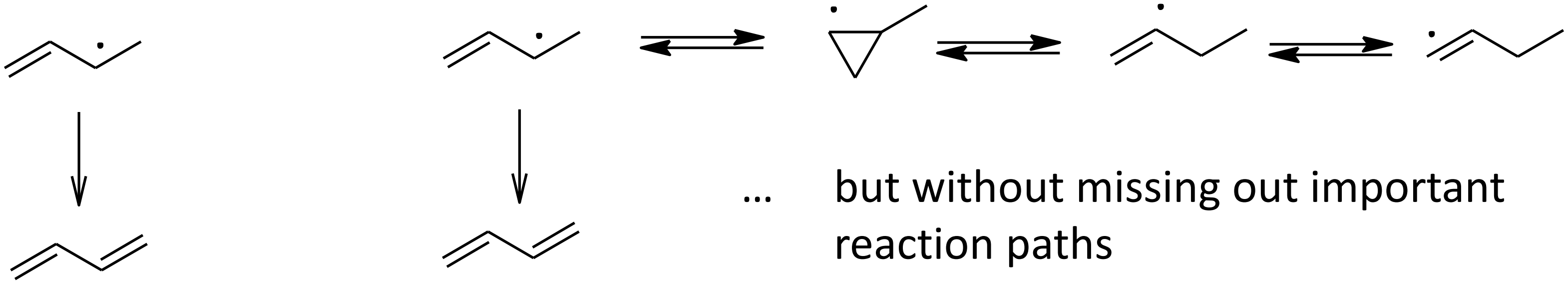


Note: Comparison against speciation experimental data is often more helpful then composite targets like ignition delays and flame speeds, I will often start with JSR and PFR dataset while making a new model.

Generating a better network for JP-10

How to recognize a good network?

accurate and to the point



… but without missing out important reaction paths

Depth first search vs broader search

- Depth first strategy (combustion and pyrolysis): shut down all intramolecular isomerizations
- Generally gives you a good idea of what the main products will look like (beta network in cracking)

Generating a better network for JP-10

1	JP10(1)	1.1933E-07	-1.3609E-03
76	BR1(76)	2.5443E-15	-2.9012E-11
104	MA110(104)	1.7662E-10	6.0465E-06
39	BR3(39)	1.5458E-15	-1.7627E-11
100	C10H16JJ(100)	2.0085E-14	-2.2904E-10
105	C10H16(105)	2.0959E-10	8.5514E-05
68	ethene(68)	1.6835E-09	9.3189E-04
122	C8H12JJ(122)	9.6949E-17	5.3475E-12
207	C8H12(207)	8.5303E-14	4.7053E-09
210	C8H12(210)	4.7308E-10	1.7248E-04
143	C10H16(143)	1.2843E-10	5.3377E-05
84	BR5(84)	1.4308E-16	-1.6316E-12
149	C8H12JJ(149)	1.8605E-16	2.9111E-11
362	C8H12(362)	3.4032E-10	1.4145E-04
112	C5H9J(112)	5.5400E-13	2.2465E-08
32	CPTyl(32)	6.1125E-12	1.1509E-06
404	C5H9J(404)	3.1802E-14	1.2967E-09
33	Allyl(33)	3.4224E-10	1.6826E-04
416	C5H7J(416)	1.1068E-10	2.3561E-05
2	H(2)	2.0681E-10	7.1855E-05
412	C5H6(412)	6.2866E-10	4.9132E-04
540	H2(540)	6.0793E-10	5.5211E-04
535	C5H7J(535)	5.4443E-15	1.1590E-09
22	JP10R8(22)	2.7754E-14	9.7008E-09
23	JR8BS1(23)	1.5858E-14	5.4714E-09
36	cyclopentene(36)	2.6759E-10	2.1631E-04
35	cyclopentenyl(35)	9.4529E-13	2.9405E-07
1191	C10H15J(1191)	1.7326E-14	6.1093E-09

Healthy: random numbering, not focussing on one reaction path and doing what it should be doing

Unhealthy: RMG is focussed on one path, something probably messing op the generation

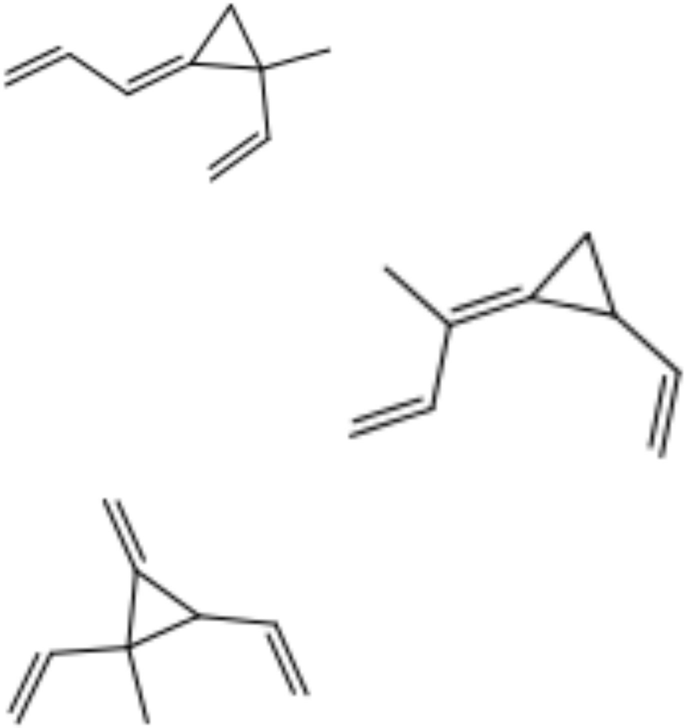
2912	C9H12(2912)	4.3690E-17	3.2748E-11
2914	C9H12(2914)	2.5747E-17	1.9298E-11
2915	C9H12(2915)	4.0336E-18	3.0234E-12
2943	C9H12(2943)	3.7032E-12	2.8893E-06
2913	C9H12(2913)	4.9126E-13	3.7099E-07
2916	C9H12(2916)	6.8833E-12	5.7107E-06
2917	C9H12(2917)	1.1991E-12	9.1401E-07
2945	C9H12(2945)	2.7898E-12	2.2254E-06

Generating a better network for JP-10

Use Connie's visualizer to see what species are getting formed!

Unhealthy: RMG is focussed on one path, something probably messing op the generation

2912	C9H12(2912)	4.3690E-17	3.2748E-11
2914	C9H12(2914)	2.5747E-17	1.9298E-11
2915	C9H12(2915)	4.0336E-18	3.0234E-12
2943	C9H12(2943)	3.7032E-12	2.8893E-06
2913	C9H12(2913)	4.9126E-13	3.7099E-07
2916	C9H12(2916)	6.8833E-12	5.7107E-06
2917	C9H12(2917)	1.1991E-12	9.1401E-07
2945	C9H12(2945)	2.7898E-12	2.2254E-06

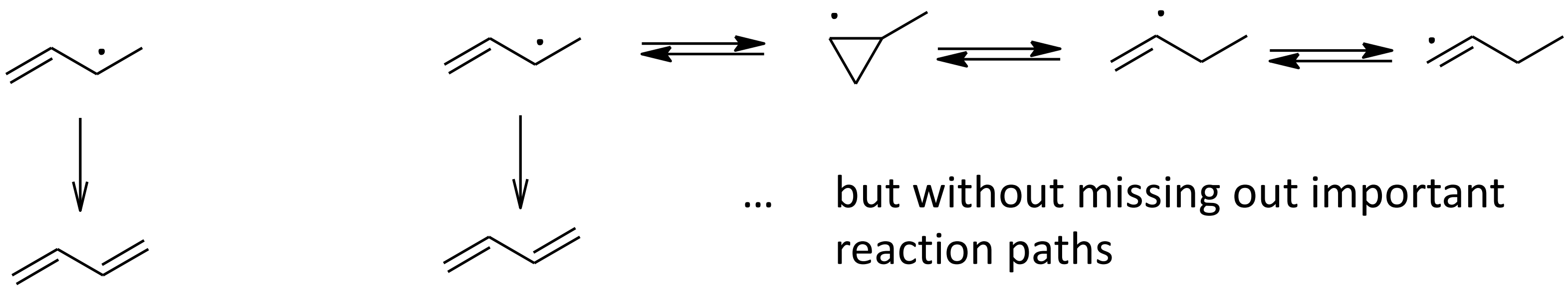


24

Generating a better network for JP-10

How to recognize a good network?

accurate and to the point



… but without missing out important reaction paths

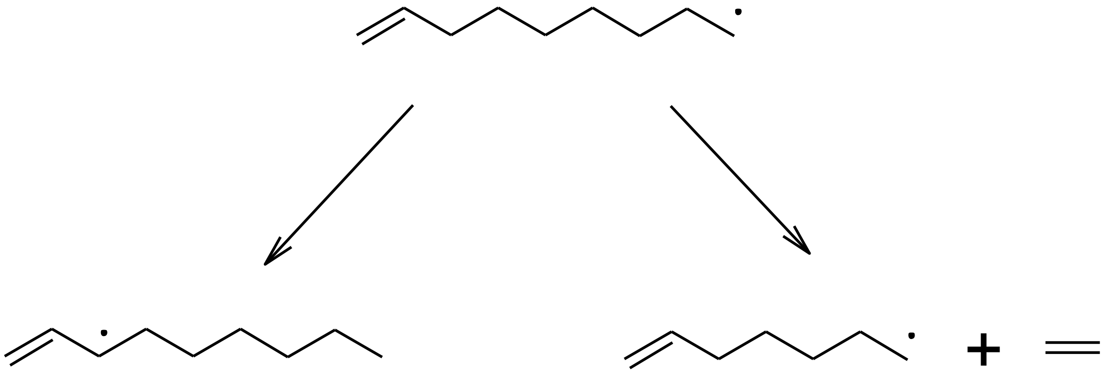
Depth first search vs broader search

- Depth first strategy (combustion and pyrolysis): shut down all intramolecular isomerizations
- Generally gives you a good idea of what the main products will look like (beta network in cracking)

Generating a better network for JP-10

Beta network assumption: β-scission >> intramolecular rearrangements for large species

- Seems to be working quite well, but might be problematic for unsaturated components



- Mainly used as first check for reasonable rate coefficients (network can be used as seed for the broader search)

Hints to generate better networks

How to recognize the problem?

Species list:
C10H16(1)
C10H16(2)
C10H16(3)
C10H16(4)
C10H16(5)
C10H16(6)
C10H16(7)
C10H16(8)
C10H16(9)
….

Species list:
C10H15J(1)
C10H15J(2)
C10H15J(3)
C10H15J(4)
C10H15J(5)
C10H15J(6)
C10H15J(7)
C10H15J(8)
C10H15J(9)
….

Species list:
C10H14JJ(1)
C10H14JJ(2)
C10H14JJ(3)
C10H14JJ(4)
C10H14JJ(5)
C10H14JJ(6)
C10H14JJ(7)
C10H14JJ(8)
C10H14JJ(9)
….

Excessive broadening of the network on a certain level (C count) → inclusion of excessive species can lead to memory issues later on

Hints to generate better networks

How to recognize the problem?

Species list:
C10H16(1)
C10H16(2)
C10H16(3)
C10H16(4)
C10H16(5)
C10H16(6)
C10H16(7)
C10H16(8)
C10H16(9)
….

Check rates!

Species list:
C10H15J(1)
C10H15J(2)
C10H15J(3)
C10H15J(4)
C10H15J(5)
C10H15J(6)
C10H15J(7)
C10H15J(8)
C10H15J(9)
….

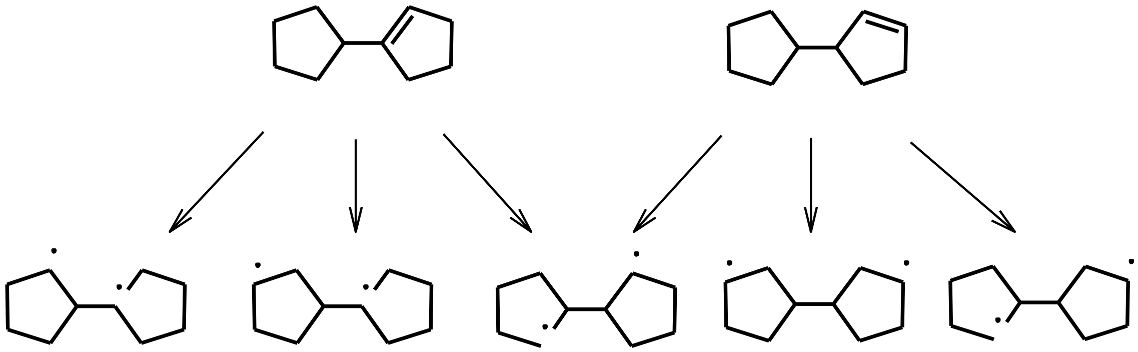
Radical decomposition path might include a few isomerizations, if unwanted amount of species added can be reduced by adding the correct path

Species list:
C10H14JJ(1)
C10H14JJ(2)
C10H14JJ(3)
C10H14JJ(4)
C10H14JJ(5)
C10H14JJ(6)
C10H14JJ(7)
C10H14JJ(8)
C10H14JJ(9)
….

Check thermo and rates!

Intramolecular disproportionation gone wild

Species list:
C10H16(1)
C10H16JJ(2)
C10H16(3)
C10H16(4)
C10H16JJ(5)
C10H16JJ(6)
C10H16JJ(7)
C10H16JJ(8)
C10H16JJ(9)
….



Solved by decreasing the rate for intramolecular disproportionation by a factor of 100 to 1000. This is okay to do till the time we are consistent and fill in the rule by calculation later. It is best to modify a rule then to use reaction libraries

Case Study 4: Disulfide pyrolysis

Thermo Libraries:

- primaryThermoLibrary,
- SulfurLibrary,
- DFT_QCI_thermo,
- GRI-Mech

Quantum Calculations: off

- We can turn this on if RMG predicts weird cyclic species

PressureDependence: off (high pressure system)

FinishController:

- Goal Conversion: 80% of disulfide
- Error Tolerance: 0.25
- The tolerance should be tightened if mechanism is too small and misses important products, or loosened if mechanism doesn’t converge.
- Can also try lower goal conversion

ReactionLibrary:

- Sulfur/Sendt, Sulfur (small-molecule sulfur chemistry libraries)
- Other libraries exist for specific sulfur compounds in kinetic_libraries/Sulfur/

SeedMechanism: none (for now)

kinetics_groups/families.txt:

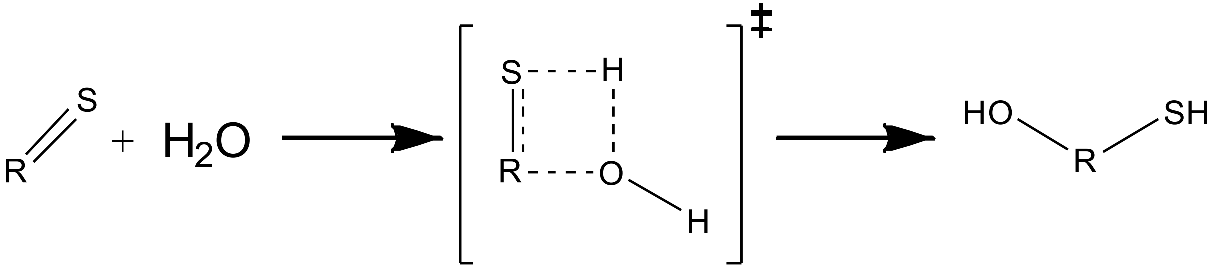
Turn off families with O reactions

Cyclic_Ether_Formation, intra_OH_migration, 1,3_Insertion_CO2, 1,3_Insertion_ROR, 2+2_cycloaddition_CO, 2+2_cycloaddition_CCO, HO2_Elimination_from_PeroxyRadical, Substitution_O,

1,2_shiftS (poorly populated)

When generating sulfur mechanism with water

- Most of the condition file will be the same.
- Need to turn on 1 or more reaction families:
  - 1,3_Insertion_ROR



  - Don’t expect much other oxygen chemistry, so other oxygen families will stay *off* for now

General guide line for running RMG

1. Error tolerances
    1. For C4 to C5 systems 0.1 is reasonable
    2. For C6 to C10 system need to work with 0.5 to 0.25, before it overwhelms the memory

2. For bigger molecules you can limit the C and O number
    1. Limiting the C number prevents adduct growth … be aware that this actually happens in real system.
    2. For low temperature (600 – 800 K) oxidation you should allow for at a minimum of 4 + no of oxygen atoms present in the fuel to allow for peroxy chemistry to occur
    3. Limiting the Pdep to 12 heavy atoms is an option to avoid bigger networks

3. For cyclic species its important to run thermo estimation with QMTP

4. Good seed mechanism will help converge model quickly

5. Initially it might make sense to close down certain families inorder to do depth first search rather than let RMG explore broader networks

6. For missing species, I sometimes include them in condition file with zero concentrations and most of pathway leading upto that species to coax RMG. I personally think this is because of poor estimates of rate coefficients

7. Its okay to use chemkin files for unconverged models, but please check the flux analyzer for dead ends … rmg exploring an insensible pathway is often the reason for this

General guide line for running RMG

8. Closing down reaction family
    1. Close down suspected families to allow RMG to go depth first rather than breadth first initially, this will help you get sense of correct mechanism.
    2. This sub-mechanism can also be used as a seed for another run.
    3. However my personal opinion is that closing down families indicate that the estimates for your system are very in accurate. Stop! Fix family is a better approach.