Assessing the impact of reaction rate variation on autoignition model performance: butanol

Kyle E Niemeyer
& Morgan Mayer
Oregon State University

Sai Krishna Sirumalla
& Richard West
Northeastern University

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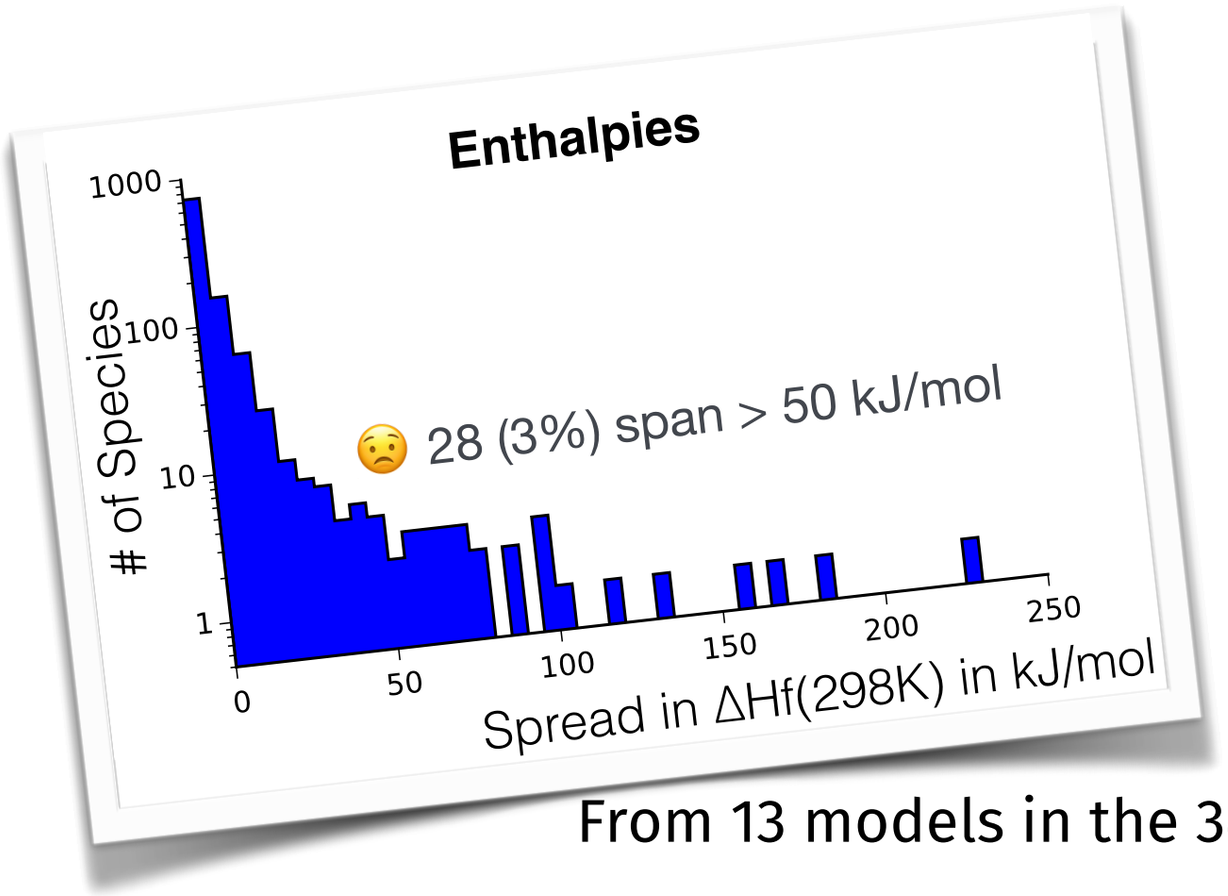
kyle.niemeyer@oregonstate.edu

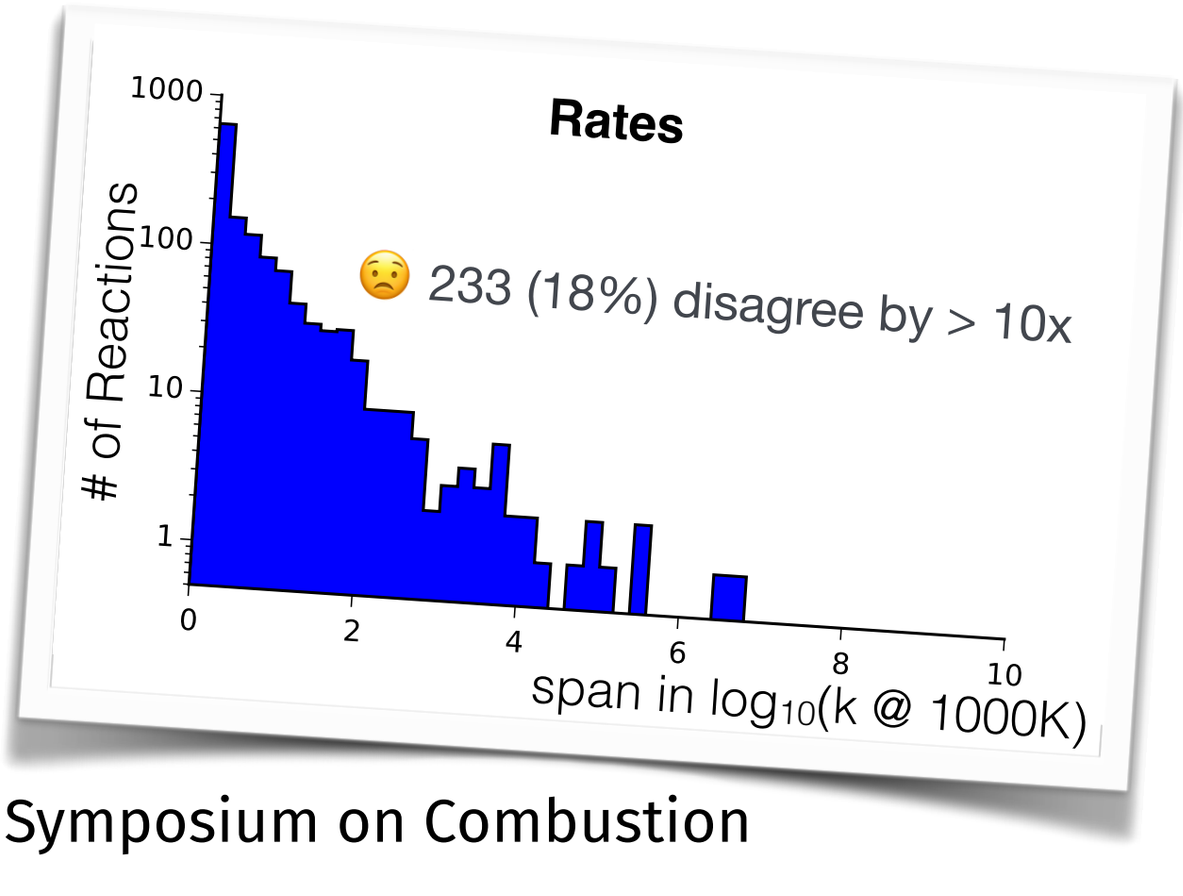
@kyleniemeyer

https://git.io/nrg

NSF grants 1403171 and 1605568

Models contain discrepancies that are hard to detect and quantify



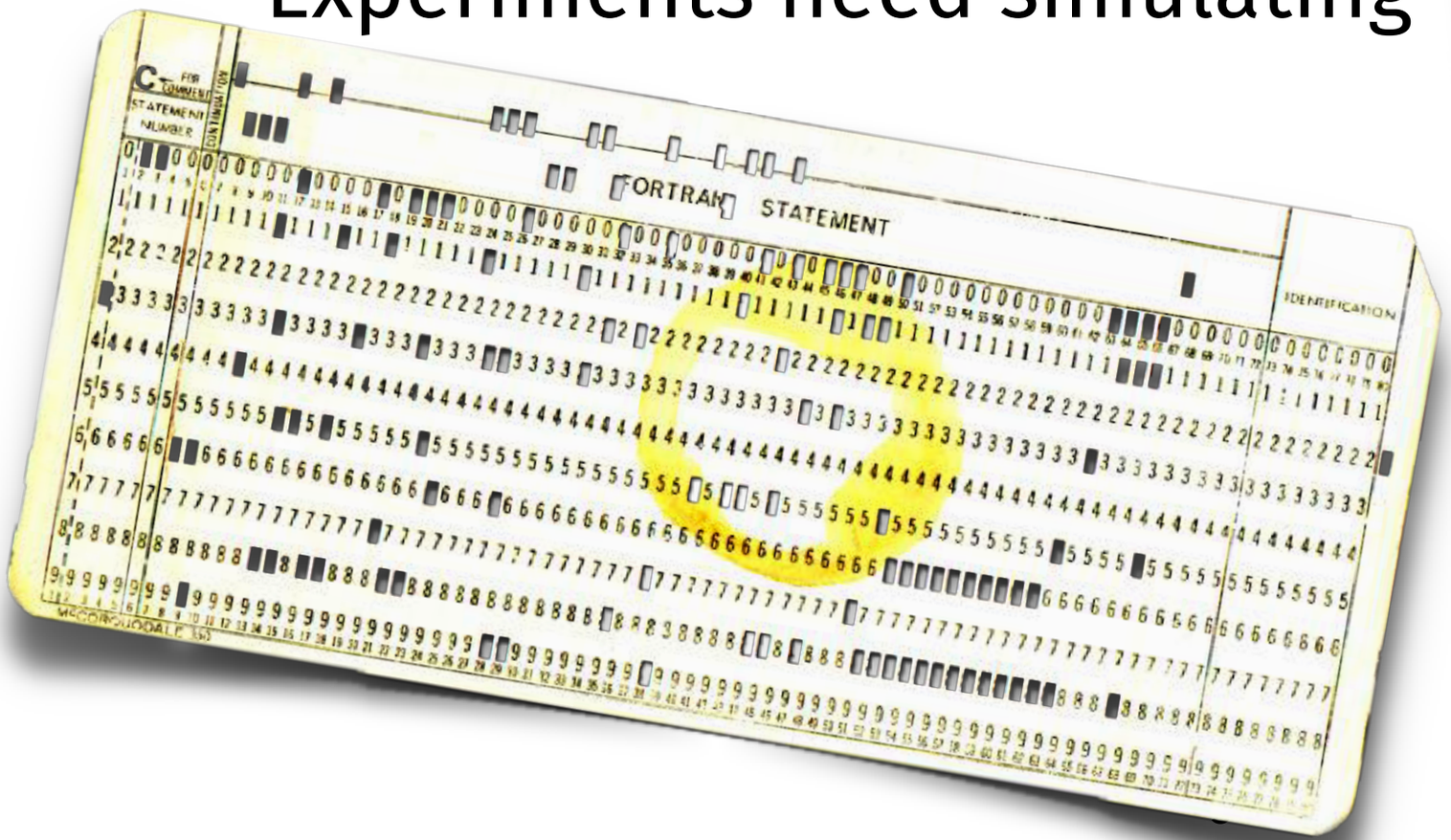


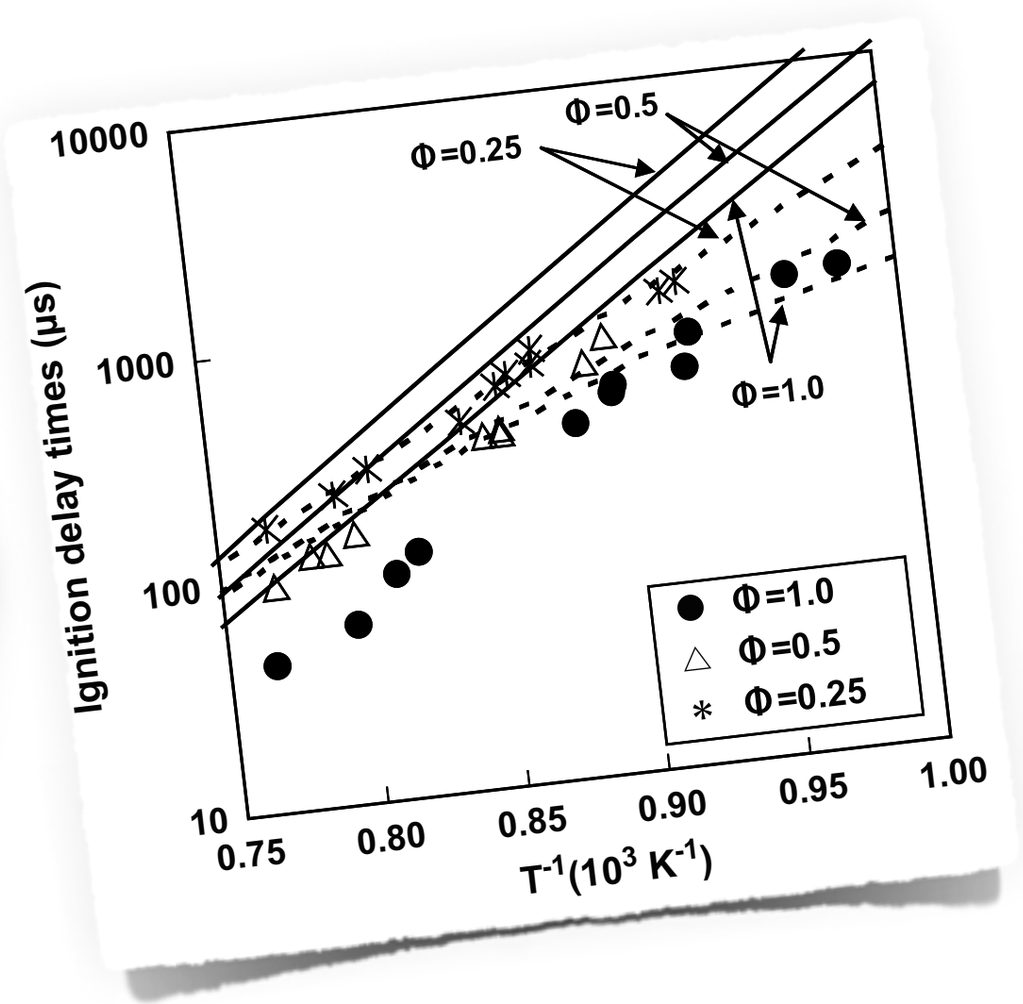
From 13 models in the 34th Symposium on Combustion

But so what?

Comparing models and data is harder than it should be

- Models in “Chemkin” format
- Data reported in PDFs
- Experiments need simulating





Goals

- Common platform for experiments
- Common platform for models
- Tool to make them speak to each other, simplifying “validation” & improvement workflow
- Example: n-butanol

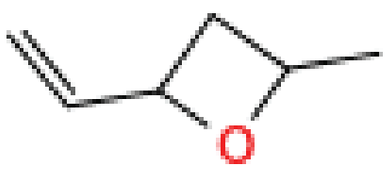
NASA (Chemkin) format is very dense – not much room for species identifiers

Species Name Chemical Formula Parameters for H(T), S(T)

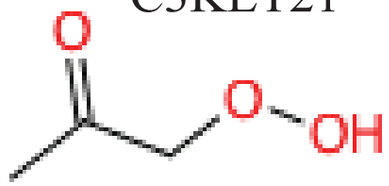
```
ch3chocho 11/14/95 thermc   3h   5o   2    0g   300.000  5000.000 1395.000     21
 1.27827539e+01 1.21529347e-02-4.21228103e-06 6.59844007e-10-3.85228684e-14    2
-2.15946846e+04-3.94512036e+01 5.06096897e-01 4.26121702e-02-3.37628379e-05    3
 1.39422914e-08-2.35317319e-12-1.74952136e+04 2.58742916e+01                   4
ch3chcho  12/ 1/99 thermc   3h   5o   1    0g   300.000  5000.000 1385.000     21
 1.02647528E+01 1.17295061E-02-4.06267561E-06 6.36086751E-10-3.71220190E-14    2
-7.25910488E+03-2.91646638E+01 1.54196914E+00 3.03297391E-02-1.88922690E-05    3
 5.92263358E-09-7.53762316E-13-4.01761098E+03 1.83707011E+01                   4
sc3h5cho   11/15/95 therc   4h   6o   1    0g   300.000  5000.000 1390.000     21
 1.31695904e+01 1.42484434e-02-4.90843998e-06 7.65789041e-10-4.45834896e-14    2
-2.04032613e+04-4.43673205e+01 4.35795171e-01 4.48719314e-02-3.36582931e-05    3
 1.33066870e-08-2.17839128e-12-1.60394651e+04 2.37597452e+01                   4
sc3h5co   11/15/95 thermc   4h   5o   1    0g   300.000  5000.000 1392.000     21
 1.25514754e+01 1.22521948e-02-4.22382101e-06 6.59184896e-10-3.83818826e-14    2
-4.25349795e+03-4.02864145e+01 1.74191343e+00 3.97229536e-02-3.20061901e-05    3
 1.38227925e-08-2.46272017e-12-6.64428100e+02 1.70762023e+01                   4
ic3h6cho   2/22/96 thermc   4h   7o   1    0g   300.000  5000.000 1390.000     31
 1.33102250e+01 1.62097959e-02-5.57575891e-06 8.69003718e-10-5.05554202e-14    2
-7.62177931e+03-4.25050854e+01 5.21481767e-01 4.43114357e-02-2.86617314e-05    3
 9.30319894e-09-1.20761563e-12-2.99677086e+03 2.68182130e+01                   4
c3h6cho-1  9/27/95 thermc   4h   7o   1    0g   300.000  5000.000 1379.000     31
```

Space constraints led to “creative” naming schemes

MVOX

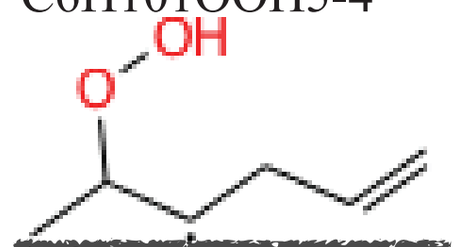


C3KET21



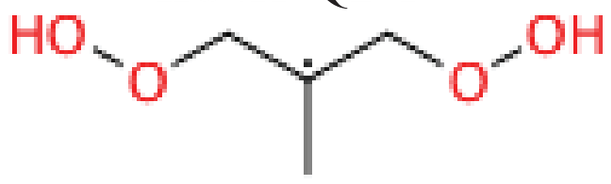
C3H5-A

C6H101OOH5-4

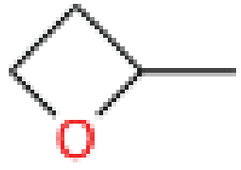


C3H5-S

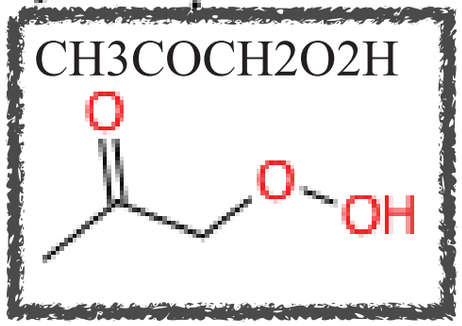
IIC4H7Q2-T



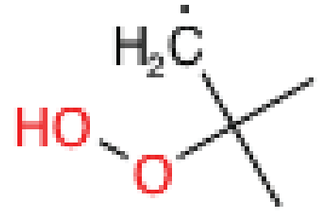
C4H8O1-3



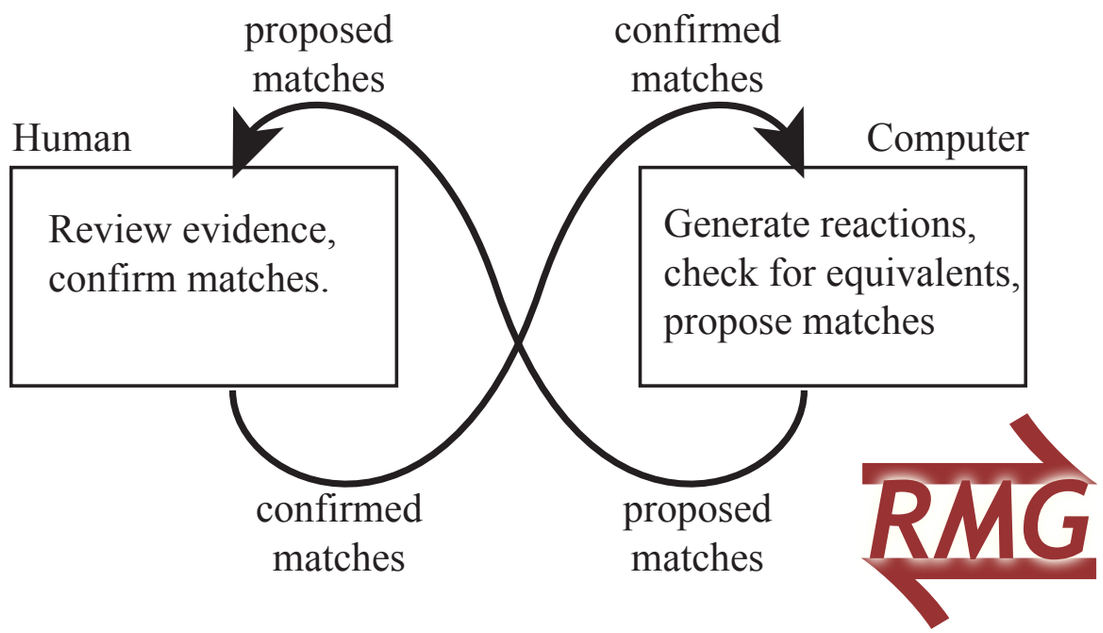
CH3COCH2O2H



TC4H8O2H-I



Our tool uses chemical knowledge from RMG to help interpret mechanism and identify species



Identifying ‘sc3h5co’ from its reactions

R1 sc3h5cho + o2 ⇌ sc3h5co + ho2

R2 sc3h5cho + oh ⇌ sc3h5co + h2o

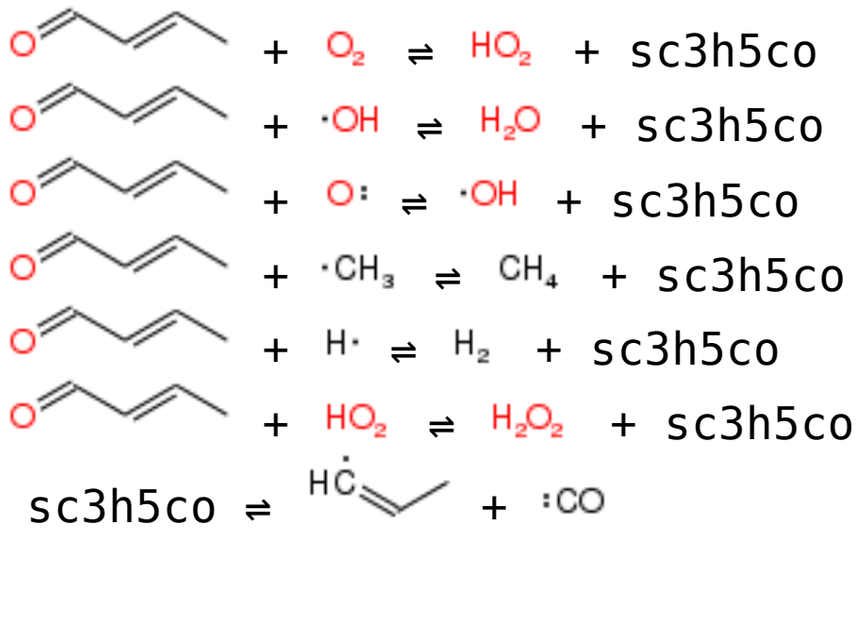
R3 sc3h5cho + o ⇌ sc3h5co + oh

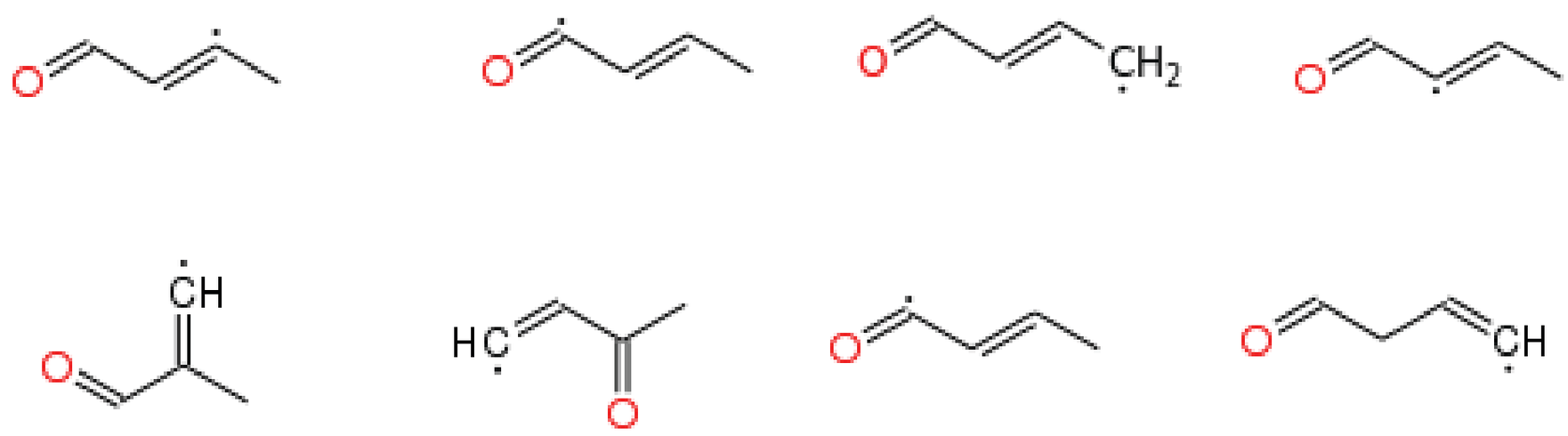
R4 sc3h5cho + ch3 ⇌ sc3h5co + ch4

R5 sc3h5cho + h ⇌ sc3h5co + h2

R6 sc3h5cho + ho2 ⇌ sc3h5co + h2o2

R7 sc3h5co ⇌ c3h5-s + co





Identifying ‘sc3h5co’ from its reactions

R1 sc3h5cho + o2 ⇌ sc3h5co + ho2

R2 sc3h5cho + oh ⇌ sc3h5co + h2o

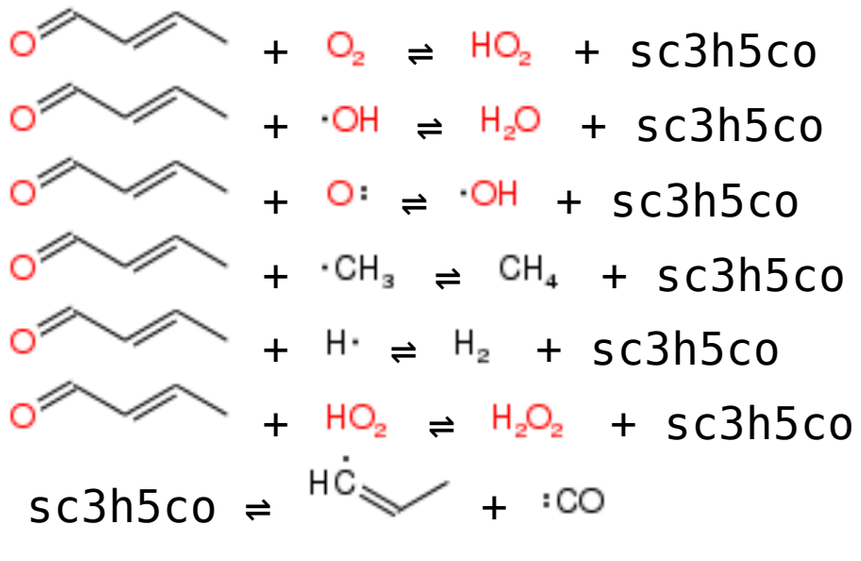
R3 sc3h5cho + o ⇌ sc3h5co + oh

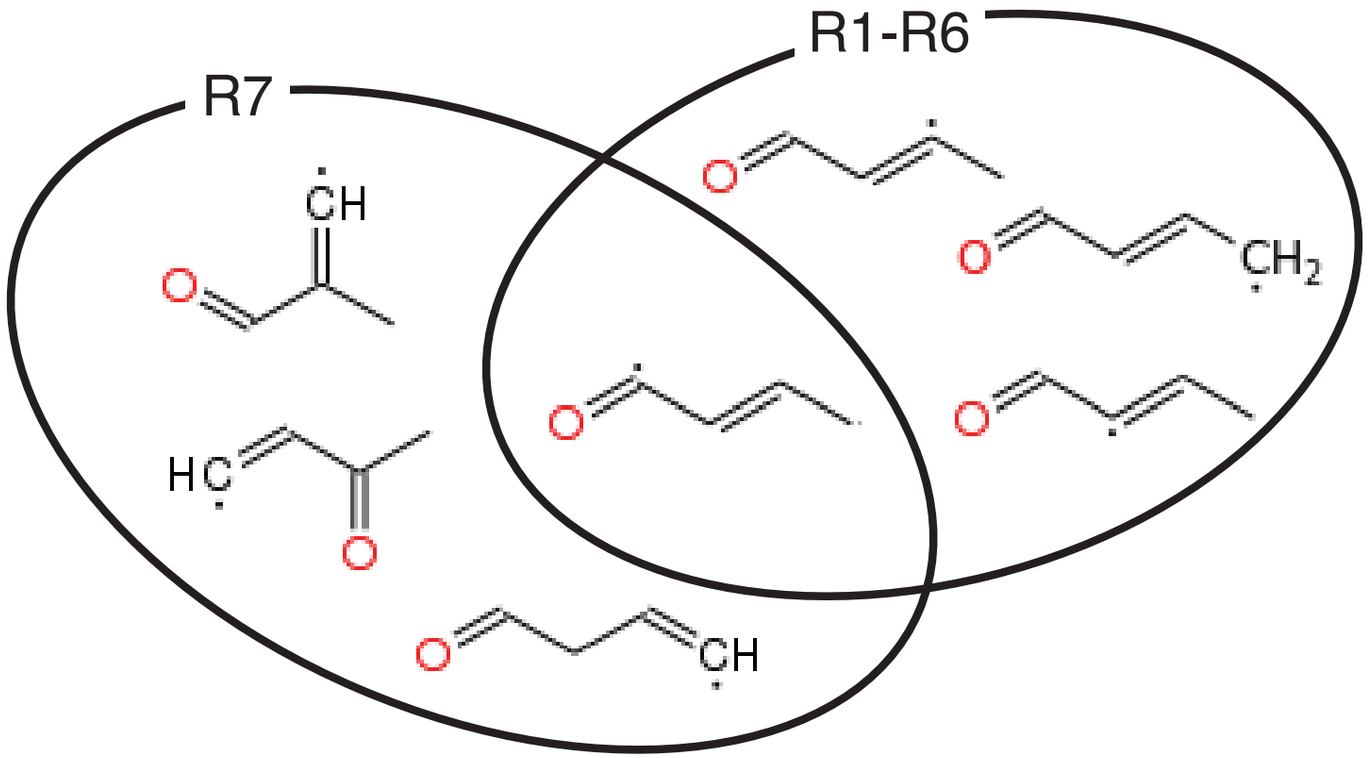
R4 sc3h5cho + ch3 ⇌ sc3h5co + ch4

R5 sc3h5cho + h ⇌ sc3h5co + h2

R6 sc3h5cho + ho2 ⇌ sc3h5co + h2o2

R7 sc3h5co ⇌ c3h5-s + co





‘sc3h5co’ is but-2-enoyl

Over 70 models collected from published Chemkin files

Combustion and Flame, Symposium Proceedings, Institutional Websites, email…

PCI2013/353-Malewicki
PCI2017/037-Sakai
PCI2017/032-Cheng
PCI2017/082-Hemken
PCI2017/111-Jin
PCI2017/052-Stagni
PCI2017/022-Thion
PCI2017/052-Li
PCI2017/058-Sun
PCI2017/024-Bohon
PCI2017/145-Sun
PCI2017/051-Pelucchi
PCI2017/012-Felsmann
PCI2017/047-Rodriguez
PCI2017/038-Labbe-Zhao(30Torr-10Atm)
PCI2017/087-Tran
PCI2017/036-Rashidi
PCI2017/025-Sudholt
EL24115
CombFlame2013/2712-Sarathy
CombFlame2013/1958-Zhao
CombFlame2013/487-Schenk
CombFlame2013/1541-Zhang
CombFlame2013/17-Malewicki
CombFlame2013/1315-Chang
CombFlame2013/1939-Cai
CombFlame2013/2291-Somers
CombFlame2013/1609-Veloo
CombFlame2013/2680-Vranck
MB-Dooley
Narayanaswamy
Shamel-Propane
Reduced-DRG-GRI-mech
PCI2015/0409-Zhang
PCI2015/0325-Nawdiyal
PCI2015/0153-Marshall
AramcoMech_1.3
USC_Mech_ii
n-Heptane
CombFlame2015/3755-Konnov
Chernov
MB-Farooq
GRI-mech-3.0
CombFlame2014/405-Cai
CombFlame2014/65-Darcy
CombFlame2014/885-Xiong
CombFlame2014/1135-Dames
CombFlame2014/84-Wang
CombFlame2014/657-Jin
CombFlame2014/798-Cai
CombFlame2014/818-Zhang
AramcoMech_2.0
Biomass
MB-Fisher
MatheuCH4
Gasoline_2
GRI-17-species-mech
Gasoline_Surrogate
IJCK2013/638-Metcalfe
PCI2013/269-Matsugi
PCI2013/401-Liu
PCI2013/335-Wang
PCI2013/325-Husson
PCI2013/297-Herbinet
PCI2013/361-Malewicki
PCI2013/599-Veloo
PCI2013/259-Labbe
PCI2013/225-Somers
PCI2013/527-Sheen
PCI2013/411-Darcy
PCI2013/289-Dagaut

55k instances of 13k rates for 6k reactions in 74 models

ChemKED kinetics experiment data format written in YAML

Human- ***AND*** machine-readable!

Parsers and libraries for nearly every programming language!

```yaml
file-author:
  name: Kyle E Niemeyer
  ORCID: 0000-0003-4425-7097
file-version: 0
chemked-version: 0.0.1
reference:
  doi: 10.1016/j.ijhydene.2007.04.008
  authors:
    - name: N. Chaumeix
    - name: S. Pichon
    - name: F. Lafosse
    - name: C.-E. Paillard
  journal: International Journal of Hydrogen Energy
  year: 2007
  volume: 32
  pages: 2216-2226
  detail: Fig. 12., right, open diamond
experiment-type: ignition delay
apparatus:
  kind: shock tube
  institution: CNRS-ICARE
  facility: stainless steel shock tube
common-properties:
  pressure: &pres
    - 220 kilopascal
```

Ref: [1]

ChemKED schema is free & libre, PyKED software enforces it

- The ChemKED schema is also a YAML-formatted file
- PyKED ensures required data are present, have appropriate units and bounded values, etc.
- Ensures reference information is correct if DOI is provided

```yaml
# Common reference for authors' information
author: &author
  type: dict
  required: true
  isvalid_orcid: true
  schema:
    ORCID:
      type: string
    name:
      required: true
      type: string
#
# Common reference for value-unit schema
value-with-uncertainty: &value-with-uncertainty
  isvalid_uncertainty: true
  items:
    - type: string
    - type: dict
      schema:
        uncertainty-type:
          required: true
          type: string
          allowed:
            - absolute
            - relative
        uncertainty:
          required: true
          anyof_type:
            - string
            - float
          excludes:
            - upper-uncertainty
            - lower-uncertainty
        upper-uncertainty:
          required: true
          anyof_type:
            - string
            - float
          excludes:
            - uncertainty
```

PyTeCK: **P**ython tool for **Te**sting **C**hemical **K**inetics

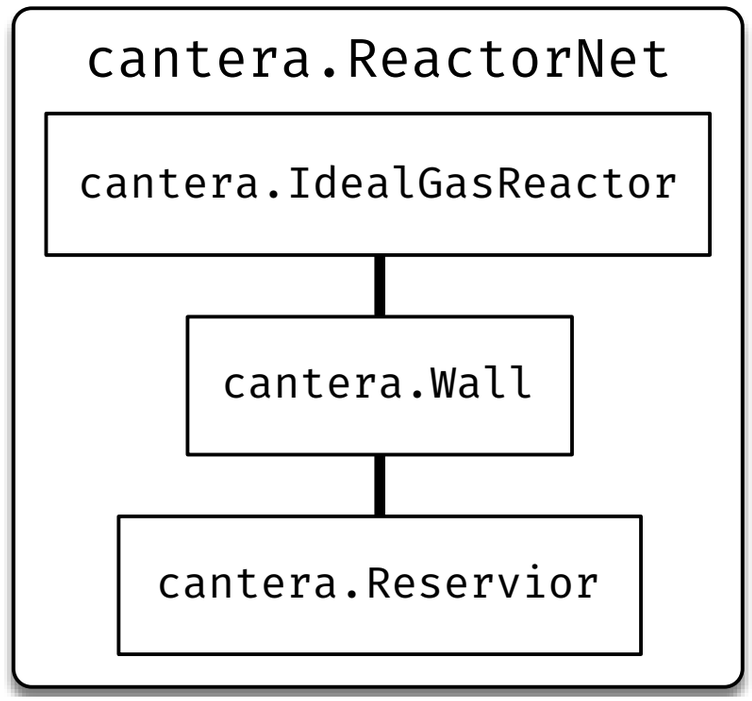
- Reads ChemKED experimental data
- Imports Cantera kinetic model
- Runs (autoignition) simulations
- Quantifies error of model

Refs: [2]

Straightforward autoignition simulations (for now)

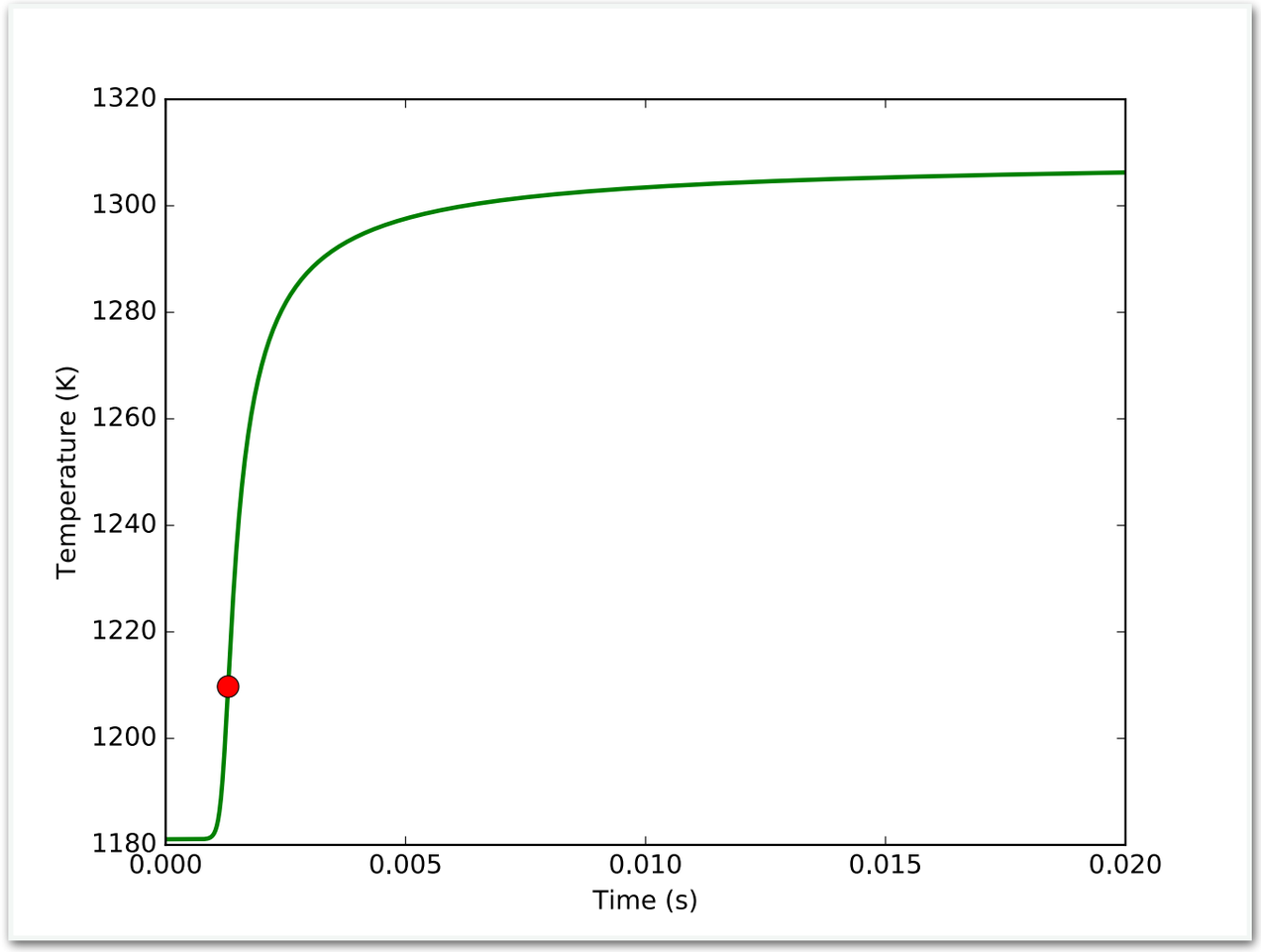
$$\frac{dT}{dt} = \frac{-1}{c_v}\left(\sum_{i=1}^{N_{\mathrm{sp}}} e_i \frac{dY_i}{dt} + p\frac{dv}{dt}\right)$$

$$\frac{dY_i}{dt} = \frac{1}{\rho} W_i \dot{\omega}_i \quad i = 1, \ldots, N_{\mathrm{species}}$$



`Simulation.process_results()`

- Have: time history (HDF5)
- Need: ignition delay time
- `detect_peaks`
- Options:
  - Max, d/dt max
  - P, T, OH, CH



Error function

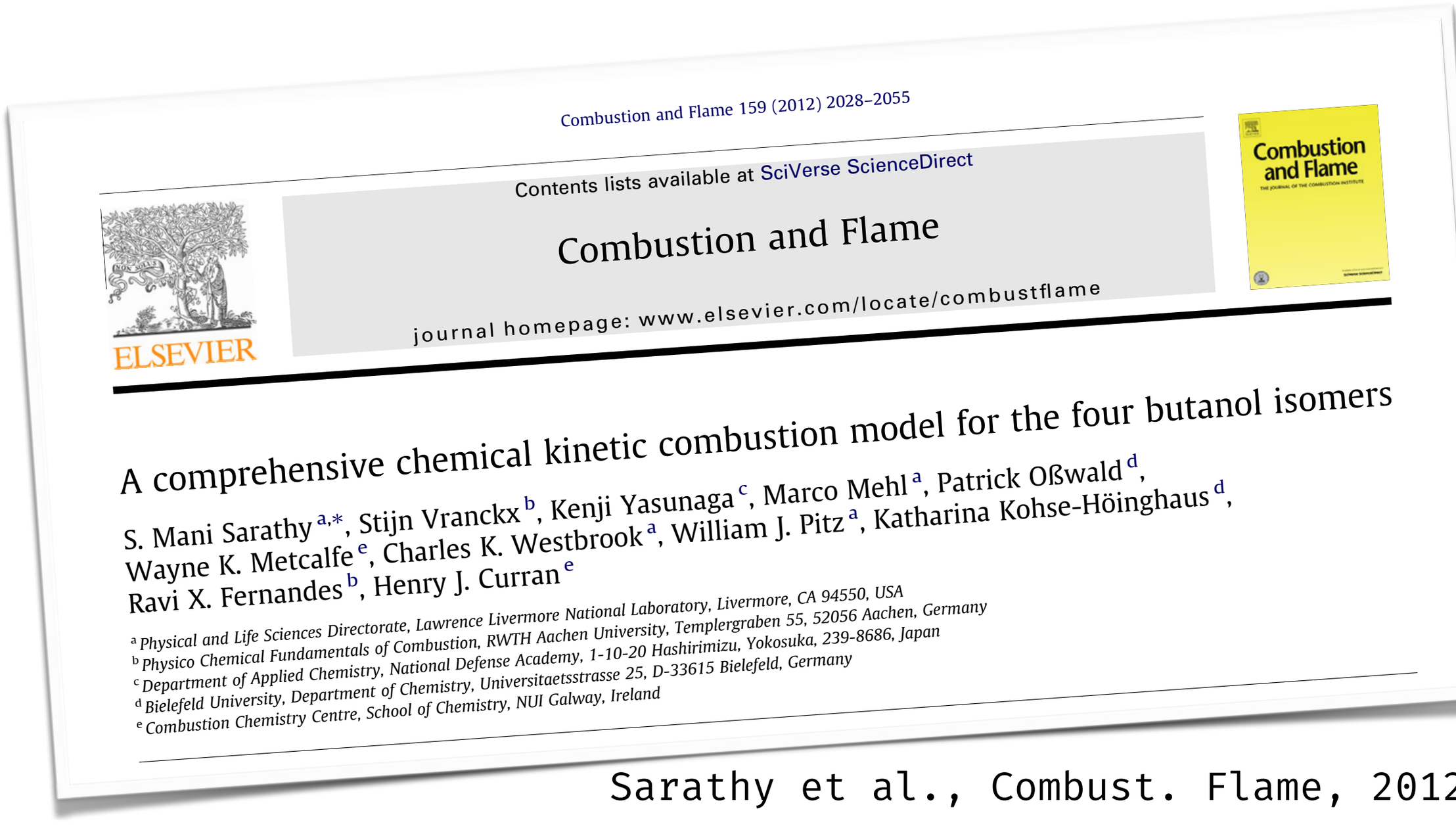
Dataset error function: $$E_i = \frac{1}{N_i} \sum_{j=1}^{N_i} \left(\frac{\log \tau_{ij}^{\mathrm{exp}} - \log \tau_{ij}^{\mathrm{sim}}}{\sigma(\log \tau_{ij}^{\mathrm{exp}})} \right)^2$$

Overall error function: $$E = \frac{1}{N} \sum_{i=1}^{N} E_i$$

Lower is better, 1.0 is perfect.

Refs: [3,4]

Base model for butanol: comprehensive and well validated



Combustion and Flame 159 (2012) 2028–2055

Contents lists available at SciVerse ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

A comprehensive chemical kinetic combustion model for the four butanol isomers

S. Mani Sarathy [a,*], Stijn Vranckx [b], Kenji Yasunaga [c], Marco Mehl [a], Patrick Oßwald [d], Wayne K. Metcalfe [e], Charles K. Westbrook [a], William J. Pitz [a], Katharina Kohse-Höinghaus [d], Ravi X. Fernandes [b], Henry J. Curran [e]

[a] Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA
[b] Physico Chemical Fundamentals of Combustion, RWTH Aachen University, Templergraben 55, 52056 Aachen, Germany
[c] Department of Applied Chemistry, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka, 239-8686, Japan
[d] Bielefeld University, Department of Chemistry, Universitaetsstrasse 25, D-33615 Bielefeld, Germany
[e] Combustion Chemistry Centre, School of Chemistry, NUI Galway, Ireland

Sarathy et al., Combust. Flame, 2012

Ref: [5]

1,606 alternate models generated by “fuzzing” parameters

- Original model: 431 species and 2346 reactions

- Feasible swap:
  any rate appearing in 2+ other models

- 784 reactions with feasible swaps
  (484 with 2+ swaps), total 1281 kinetic variations

- Only one swap at a time (for now)

- Likewise 325 thermochemistry variations

Initial screen to select 20 interesting candidate models

- 6,424 ignition simulations
- 1606 variants x 4 isomers (n-, sec-, tert-, iso-butanol)
- All at P=42 atm, T=1200K, ϕ=1

	Kinetics	Thermo
Speed up n-butanol	5	5
Slow down n-butanol	5	5

10 rate substitutions

Rxn.sub	Reaction	#	Models using alternative
273.2	ch2cho + o2 <=> ch2o + co + oh	7	MB-Farooq, MB-Dooley, MB-Fisher, PCI2013/353-Malewicki, Shamel-Propane, CombFlame2013/17-Malewicki, PCI2013/361-Malewicki
145.2	ch3 + ho2 <=> ch3o + oh	6	PCI2013/325-Husson, PCI2013/297-Herbinet, Chernov, PCI2017/047-Rodriguez, CombFlame2013/487-Schenk, PCI2015/0325-Nawdiyal
145.1	ch3 + ho2 <=> ch3o + oh	7	CombFlame2013/1939-Cai, USC_Mech_ii, CombFlame2014/1135-Dames, CombFlame2014/84-Wang, PCI2013/527-Sheen, CombFlame2014/657-Jin, CombFlame2013/1958-Zhao
146.1	ch3 + ho2 <=> ch4 + o2	9	CombFlame2013/1609-Veloo, CombFlame2013/1939-Cai, CombFlame2014/84-Wang, GRI-17-species-mech, USC_Mech_ii, CombFlame2014/1135-Dames, PCI2013/259-Labbe, PCI2013/527-Sheen, GRI-mech-3.0
334.2	c2h3 + o2 <=> ch2cho + o	7	CombFlame2013/1939-Cai, USC_Mech_ii, CombFlame2014/1135-Dames, CombFlame2014/84-Wang, PCI2013/527-Sheen, CombFlame2014/657-Jin, CombFlame2013/1958-Zhao
302.2	c2h4 + oh <=> c2h3 + h2o	9	Gasoline_Surrogate, PCI2013/335-Wang, PCI2017/038-Labbe-Zhao(30Torr-10Atm), CombFlame2013/1541-Zhang, PCI2013/353-Malewicki, n-Heptane, Shamel-Propane, CombFlame2013/17-Malewicki, PCI2013/361-Malewicki
269.2	ch2cho <=> ch2co + h	4	Gasoline_Surrogate, PCI2013/335-Wang, CombFlame2013/1541-Zhang, n-Heptane
577.1	c3h5-a + ho2 <=> c3h5o + oh	5	PCI2017/082-Hemken, PCI2017/052-Li, PCI2017/036-Rashidi, AramcoMech_2.0, PCI2017/087-Tran
128.2	ch3 + h <=> ch4	4	CombFlame2014/405-Cai, CombFlame2013/2680-Vranckx, PCI2017/025-Sudholt, Narayanaswamy
302.1	c2h4 + oh <=> c2h3 + h2o	11	CombFlame2013/1609-Veloo, CombFlame2013/1939-Cai, PCI2017/111-Jin, PCI2015/0409-Zhang, PCI2013/599-Veloo, CombFlame2014/84-Wang, USC_Mech_ii, PCI2013/527-Sheen, CombFlame2014/657-Jin, CombFlame2013/1958-Zhao, GRI-mech-3.0

10 thermochemistry substitutions

Sp.sub	Species	#	Models using alternative
40.2	c2h3	8	MB-Farooq,MB-Fisher,PCI2015/0325-Nawdiyal,CombFlame2013/487-Schenk,PCI2013/353-Malewicki,CombFlame2013/17-Malewicki,PCI2013/361-Malewicki,CombFlame2013/1315-Chang
50.1	ch2co	14	Gasoline_Surrogate,MB-Farooq,MB-Dooley,PCI2013/335-Wang,PCI2013/361-Malewicki,MB-Fisher,CombFlame2013/487-Schenk,CombFlame2013/1541-Zhang,PCI2013/353-Malewicki,n-Heptane,PCI2015/0325-Nawdiyal,CombFlame2013/17-Malewicki,GRI-
264.1	c4h7oh1-4	2	CombFlame2013/1939-Cai,CombFlame2014/657-Jin
50.2	ch2co	8	CombFlame2013/1939-Cai,PCI2017/111-Jin,PCI2015/0409-Zhang,CombFlame2014/84-Wang,USC_Mech_ii,PCI2013/527-Sheen,CombFlame2014/657-Jin,CombFlame2013/1958-Zhao
29.1	ch3o2	5	MB-Farooq,MB-Fisher,PCI2013/353-Malewicki,CombFlame2013/17-Malewicki,PCI2013/361-Malewicki
46.2	ch3co	8	PCI2017/051-Pelucchi,MB-Farooq,CombFlame2014/405-Cai,MB-Fisher,PCI2013/289-Dagaut,PCI2013/353-Malewicki,CombFlame2013/17-Malewicki,PCI2013/361-Malewicki
65.1	c2h3o1-2	12	Gasoline_Surrogate,MB-Farooq,MB-Dooley,PCI2013/335-Wang,MB-Fisher,PCI2013/599-Veloo,CombFlame2013/1541-Zhang,PCI2013/353-Malewicki,n-Heptane,PCI2013/401-Liu,CombFlame2013/17-Malewicki,PCI2013/361-Malewicki
40.1	c2h3	15	CombFlame2013/1609-Veloo,CombFlame2013/1939-Cai,PCI2017/111-Jin,PCI2015/0409-Zhang,CombFlame2014/405-Cai,CombFlame2014/1135-Dames,CombFlame2014/84-Wang,USC_Mech_ii,PCI2013/259-Labbe,PCI2017/038-Labbe-
90.1	c3h6	11	CombFlame2013/1939-Cai,PCI2017/111-Jin,PCI2015/0409-Zhang,CombFlame2014/1135-Dames,CombFlame2014/84-Wang,USC_Mech_ii,PCI2013/259-Labbe,CombFlame2013/487-Schenk,PCI2013/527-Sheen,CombFlame2014/657-
232.1	c3h5oh	14	CombFlame2013/1939-Cai,Gasoline_Surrogate,MB-Farooq,PCI2013/335-Wang,PCI2017/111-Jin,PCI2017/022-Thion,PCI2015/0409-Zhang,MB-Fisher,CombFlame2013/1541-Zhang,MB-Dooley,n-Heptane,CombFlame2014/657-

n-Butanol: data input from 4 papers

716–1711 K, 0.91–45.12 atm, ϕ: 0.25–3.34

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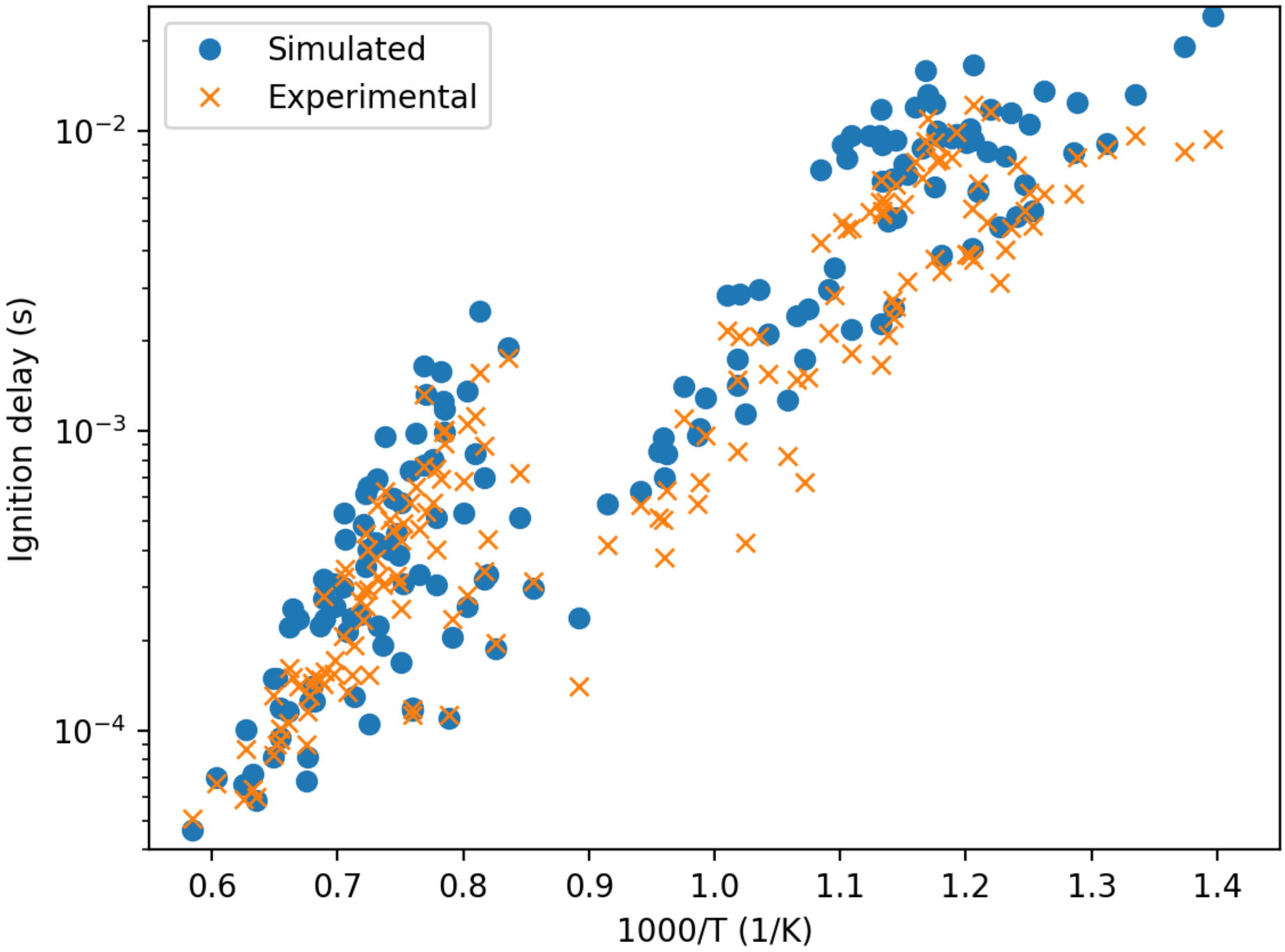
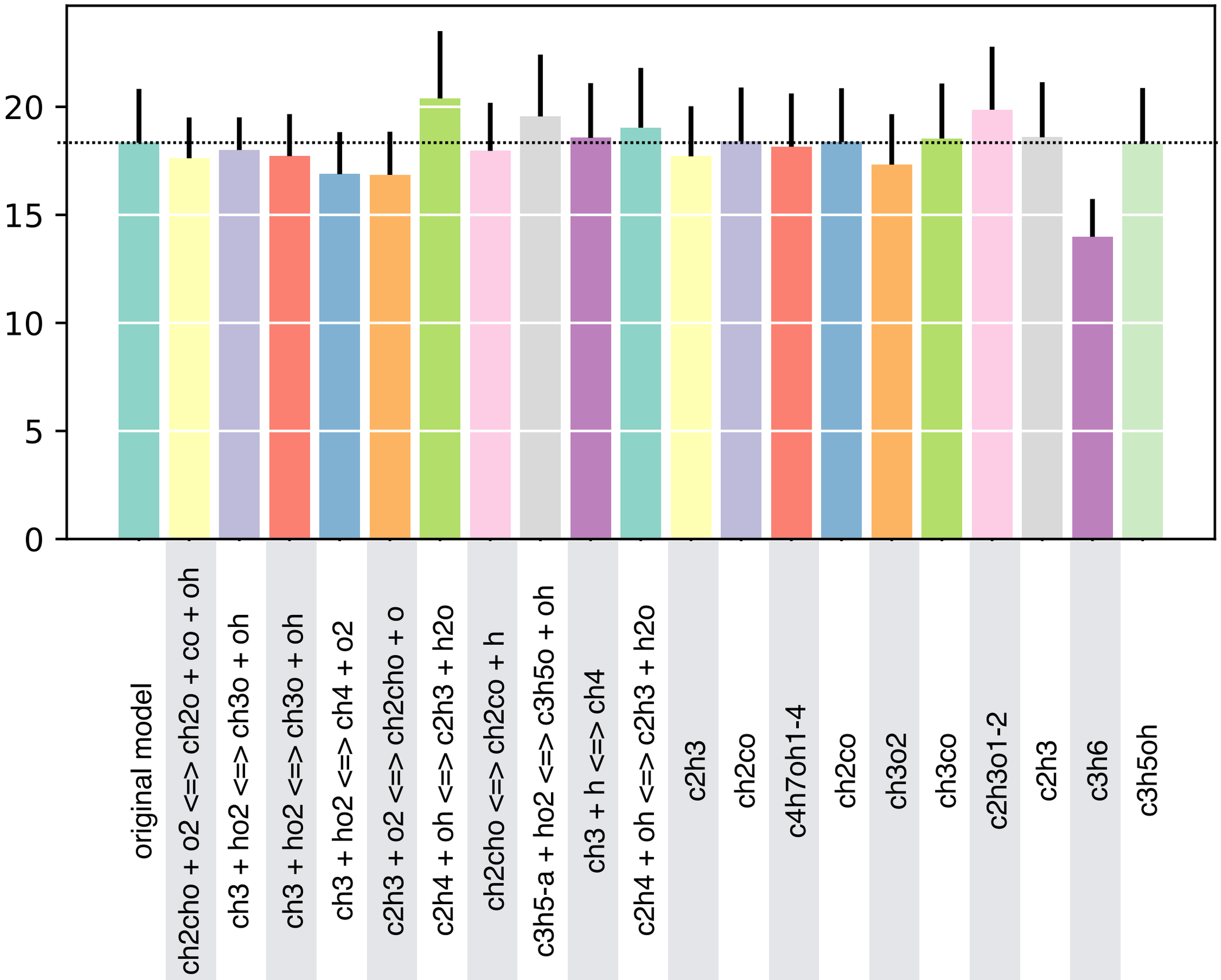
The 20 variations have varying effects on different experimental data points



Some have much bigger effects than others



Prometheus

- Goal: community database for experimental data, models, and calculations

- ***Initial*** team:
  - Kyle Niemeyer (Oregon State)
  - Bryan Weber (Univ. Connecticut)
  - Richard West (Northeastern)
  - Nicole Labbe (CU Boulder)
  - Growing!

https://pr.omethe.us/

https://github.com/pr-omethe-us

Contributions

- Common platform for experiments
- Common platform for models
- Tool to make them speak to each other, simplifying “validation” workflow
- Example: butanol
- Data and code: https://github.com/pr-omethe-us

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