



overreact

a tool for creating *ab initio* microkinetic models

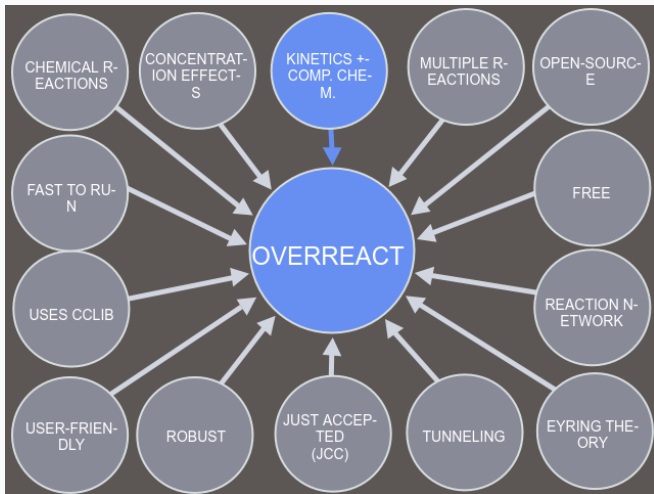
Felipe S. S. Schneider

28th March 2022

Advisor: Prof. Giovanni F. Caramori

Molecular Electronic Structure Group (Chemistry Dept./UFSC)

`schneider.felipe@posgrad.ufsc.br`



The problem in a nutshell

The Challenge of Reproducing with Calculations Raw Experimental Kinetic Data for an Organic Reaction

Raúl Pérez-Soto, Maria Besora,* and Feliu Maseras*



Cite This: *Org. Lett.* 2020, 22, 2873–2877



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Metrics & More

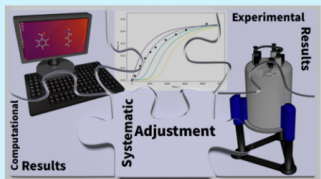


Article Recommendations

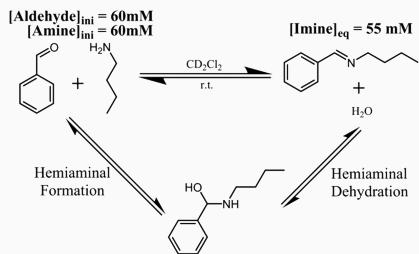


Supporting Information

ABSTRACT: DFT calculations and microkinetic simulations are applied to the reproduction of previously reported experimental results on the evolution of product concentration versus time in the condensation reaction of *n*-butylamine and benzaldehyde. The mechanism is complicated by the role played by water impurities as proton shuttles. Several functionals and other approaches are tested, yet good agreement is only achieved upon the usage of an adjustment consisting of a directed biasing of the computed DFT free energies.

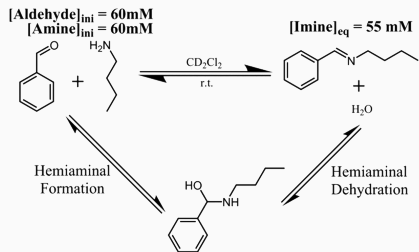


What they did



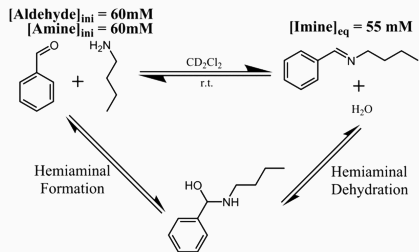
- B3LYP-D3/cc-pVTZ
(Gaussian09)

What they did



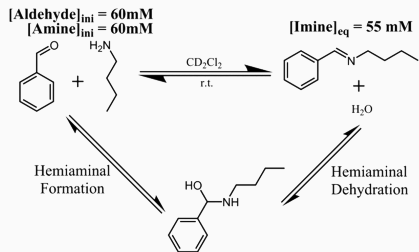
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- *Rigid-Rotor Harmonic Approximation (RRHO)*

What they did



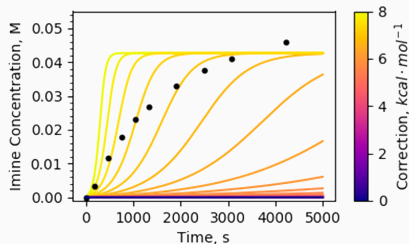
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- *Rigid-Rotor Harmonic Approximation (RRHO)*
- SMD (dichloromethane)

What they did



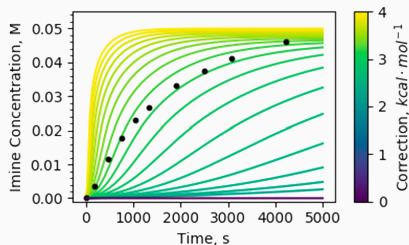
- B3LYP-D3/cc-pVTZ (Gaussian09)
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- SMD (dichloromethane)
- 1 atm \rightarrow 1 M correction

Their results



Two hypotheses:

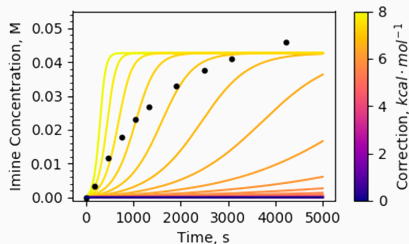
- H1: adjusting transition state energies only



Plus: water impurities (1 mM) should be considered!

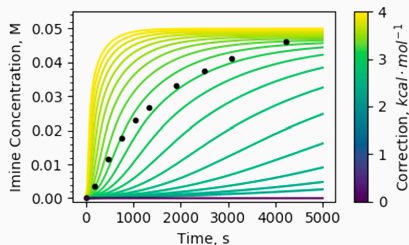
Pérez-Soto, R. et al. *Organic Letters* 2020, 22, 2873–2877

Their results



Two hypotheses:

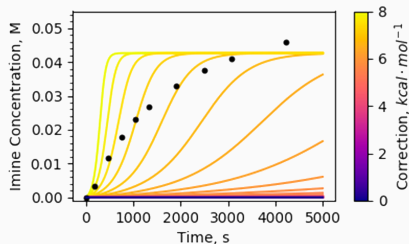
- H1: adjusting transition state energies only
- H2: adjusting *all* structures



Plus: water impurities (1 mM) should be considered!

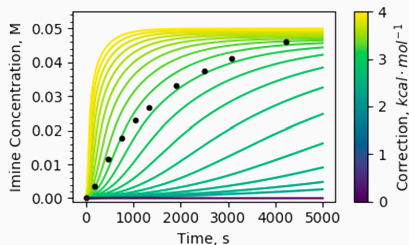
Pérez-Soto, R. et al. *Organic Letters* 2020, 22, 2873–2877

Their results



Two hypotheses:

- H1: adjusting transition state energies only
- H2: adjusting *all* structures
 - 3.2 kcal/mol

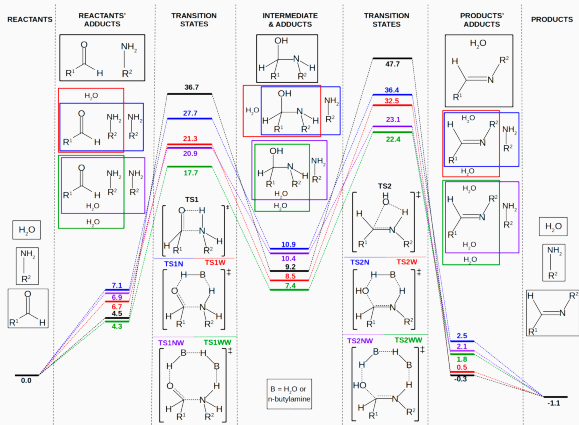


Plus: water impurities (1 mM) should be considered!

Pérez-Soto, R. et al. *Organic Letters* 2020, 22, 2873–2877

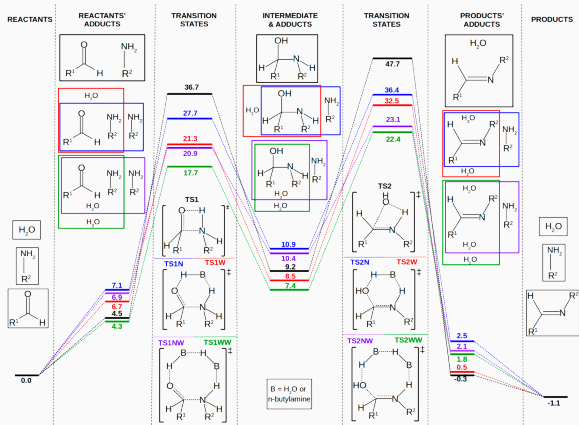
Going forward

- Quantum tunneling?



Pérez-Soto, R. et al. *Organic Letters* 2020, 22, 2873–2877

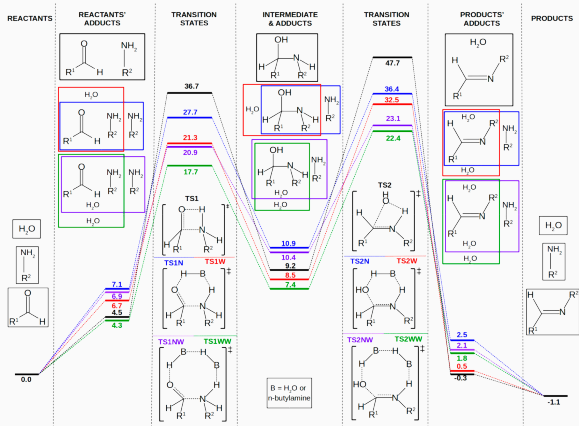
Going forward



- Quantum tunneling?
- Quasi-RRHO?

Pérez-Soto, R. et al. *Organic Letters* 2020, 22, 2873–2877

Going forward



- Quantum tunneling?
- Quasi-RRHO?
- Automation?

	#Constants
25	
26	k00 = 1.1520016141e+08
27	k01 = 2.1243982518e+11
28	k02 = 4.6522262685e+09
29	k03 = 2.1243982518e+11
30	k04 = 2.1243982518e+11
31	k05 = 1.0627425113e+11
32	k06 = 2.3472075016e+08
33	k07 = 2.1243982518e+11
34	k08 = 2.8944452758e+10
35	k09 = 2.1243982518e+11
36	k10 = 1.2474135377e+06
37	k11 = 2.1243982518e+11
38	k12 = 1.2524507574e+09
39	k13 = 2.1243982518e+11
40	k14 = 1.6652981977e+09
41	k15 = 2.1243982518e+11
42	k16 = 2.5518729986e+09

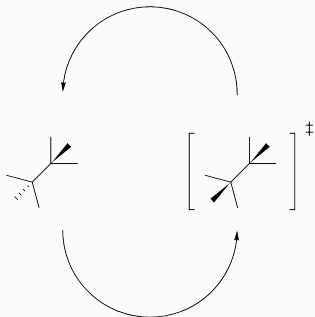
...

Pérez-Soto, R. et al. *Organic Letters* 2020, 22, 2873–2877

The idea

Meet overreact, the tool

```
1 $scheme
2 // Reactions
3 S -> ‡E -> S
4 $end
5
6 $compounds
7 // Species: logfile
8 S: staggered.out‡
9 E: eclipsed.out
10 $end
```

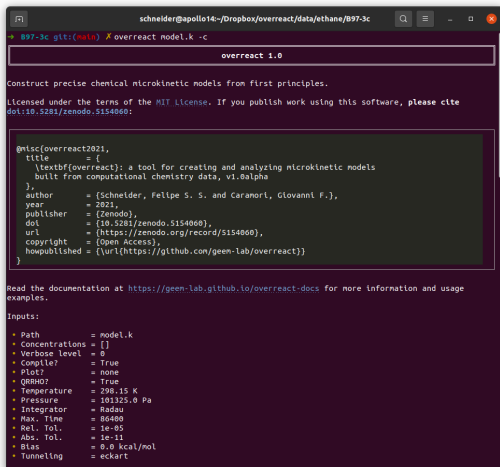


Ethane internal rotation

(B97-3c @ ORCA 4.2.1)

Schneider, F. S. S. and Caramori, G. F. **overreact**, an *in silico* lab: automated quantum chemical microkinetic simulations. *In preparation* 2021.

Meet overreact, the tool: user-friendly



```
schneider@apollo14:~/Dropbox/overreact/data/ethane/B97-3c
→ B97-3c git:(main) ✗ overreact model.k -c

overreact 1.0

Construct precise chemical microkinetic models from first principles.

Licensed under the terms of the MIT License. If you publish work using this software, please cite
doi:10.5281/zenodo.5154060:

@misc{overreact2021,
  title = [
    \textbf{overreact}: a tool for creating and analyzing microkinetic models
    built from computational chemistry data, v1.0alpha
  ],
  author = [Schneider, Felipe S. S. and Caranori, Giovanni F.],
  year = 2021,
  publisher = [Zenodo],
  doi = [10.5281/zenodo.5154060],
  url = [https://zenodo.org/record/5154060],
  copyright = [Open Access],
  howpublished = [\url{https://github.com/veen-lab/overreact}]
}

Read the documentation at https://veen-lab.github.io/overreact-docs for more information and usage
examples.

Inputs:


- Path = model.k
- Concentrations = []
- Verbose level = 0
- Compile? = True
- Plot? = none
- QRHO? = True
- Temperature = 298.15 K
- Pressure = 101325.0 Pa
- Integrator = Radau
- Max. Time = 86400
- Rel. Tol. = 1e-05
- Abs. Tol. = 1e-11
- Bias = 0.0 kcal/mol
- Tunneling = eckart

```

Meet overreact, the tool: detailed output

```
schneider@apollo14:~/Dropbox/overreact/data/ethane/B97-3c
(parsed) reactions
no reactant(s) via product(s) half equilb.?
0 S Et S No

logfiles
no compound path
0 S staggered.out
1 Et eclipsed.out

compounds
no compound elec. energy spin mult. smallest vibfreqs point group
[Ea] [cm^-1]
0 S -79.788178457691 1 +307.6, +825.4, +826.1 D3d
1 Et -79.783894168233 1 -298.9, +902.2, +902.5 D3h

estimated thermochemistry (compounds)
no compound mass G^corr H^corr H^corr S
[amu] [kcal/mol] [kcal/mol] [kcal/mol] [cal/mol-K]
0 S 30.07 33.01 48.03 49.22 54.40
1 Et 30.07 32.95 48.15 48.74 52.96

estimated (reaction) thermochemistry
no reaction A^mass^* DG^* AE^* AU^* AH^* AS^*
[amu] [kcal/mol] [kcal/mol] [kcal/mol] [kcal/mol] [cal/mol-K]
0 S -> S 0.00 0.00 0.00 0.00 0.00 0.00

estimated (activation) thermochemistry
no reaction A^mass^* DG^‡ AE^‡ AU^‡ AH^‡ AS^‡
[amu] [kcal/mol] [kcal/mol] [kcal/mol] [kcal/mol] [cal/mol-K]
0 S -> S 0.00 2.63 2.08 2.20 2.20 -1.44

estimated reaction rate constants
no reaction half equilb.? k k k k
[M^-1.s^-1] [(cm^3/particle)^-1.s^-1] [atm^-1.s^-1] K
0 S -> S No 8.17e+10 8.17e+10 0.17e+10 1.11

Only in the table above, all Gibbs free energies were biased by 0.0 J/mol.
For half-equilibria, only ratios make sense.
B97-3c, g11, (max)
```

Experimental: $\frac{1}{12 \times 10^{-12}} \text{s}^{-1} = 8.333 \times 10^{10} \text{s}^{-1}$ (ΔG^\ddagger : 2.88 kcal/mol)

Zheng, J. *Science* **2006**, *313*, 1951–1955

Hirota, E. et al. *The Journal of Chemical Physics* **1979**, *71*, 1183–1187

Meet overreact, the tool: indicating solvent

```
1 $scheme
2 NH3(w[?][?])+OH·(w) -> NH3·OH#(w) -> NH2·(w) + H2O(w)
3
4 $compounds
5 NH3(w): NH3.out
6 OH·(w): OH·.out
7 NH2·(w): NH2·.out
8 H2O(w): H2O.out
9 NH3·OH#(w): NH3·OH.out
10 // symmetry=3 // extra symmetries
```



(M062X-D3(0)/6-311++G(d,p)/SMD(water) @ ORCA 4.2.1)

Meet overreact, the tool: results in solvent



	$k \text{ (M}^{-1}\text{s}^{-1}\text{)}$
Hickel and Sehested ¹ (exp.)	9.7×10^7
Men'kin et al. ² (exp.)	7.0×10^7
Neta et al. ³ (exp.)	9.0×10^7
Ours (ORCA 4.2.1)	1.1×10^8
Dzib et al. ⁴ (Gaussian09)	2.3×10^7

```
schneider@apollo14:~/Dropbox/overreact/data/hickel1992/UM06-2X/6-311++G(d,p)
estimated reaction rate constants
no  reaction                half equilb.?      k [M^-1.s^-1]      k [(cm^3/particle)^-1.s^-1]      k [atm^-1.s^-1]      K
0   NH3(w) + OH(w) -> NH2(w) + H2O(w)      No                1.13e+08           1.88e-13            4.62e+06            2.45
Only in the table above, all Gibbs free energies were biased by 0.0 J/mol.
For half-equilibria, only ratios make sense.
6-311++G(d,p) gtt:(mola) /
```

¹Hickel, B.; Sehested, K. *International Journal of Radiation Applications and Instrumentation. Part C. Radiation Physics and Chemistry* **1992**, *39*, 355–357.

²Men'kin, V. et al. *High Energy Chemistry (English Translation)* **1989**, *22*, 333–336.

³Neta, P. et al. *The Journal of Physical Chemistry* **1978**, *82*, 1875–1878.

⁴Dzib, E. et al. *International Journal of Quantum Chemistry* **2018**, *119*, e25686.

Meet overreact, the tool: equilibria

```
1 $scheme
2 NH3(w[[]])+OH.(w) -> NH3.OH#(w) -> NH2.(w) + H2O(w)
3 NH4+(w) <=> NH3(w) + H+(w) // pK = 9.25
4
5 $compounds
6 NH3(w): NH3.out
7 OH.(w): OH.out
8 NH2.(w): NH2.out
9 H2O(w): H2O.out
10 NH3.OH#(w): NH3.OH.out
11 // symmetry=3 // extra symmetries
12 NH4+(w): NH4+.out
13 H+(w):
14 // energy=0.0
15 // energy=-1112525.6 // J == -265.9 kcal/mol (proton solvation from doi:10.1021/jp810292n)
16 energy=-1094746.6 // J == -261.7 kcal/mol (the value that adjusts the pK)
17 mult=1
18 atomnos=[1]
19 atommasses=[1.008]
20 atomcoords=[[0.0, 0.0, 0.0]]
```

no	reaction	half equilb.?	k [M ⁻ⁿ .s ⁻¹]	k [(cm ³ /particle) ⁿ⁻¹ .s ⁻¹]	k [atn ⁻ⁿ .s ⁻¹]	κ
0	NH3(w) + OH.(w) -> NH2.(w) + H2O(w)	No	1.13e+08	1.88e-13	4.62e+06	2.45
1	NH4+(w) -> NH3(w) + H+(w)	Yes	1	1	1	
2	NH3(w) + H+(w) -> NH4+(w)	Yes	1.79e+09	2.97e-12	7.3e+07	

Only in the table above, all Gibbs free energies were biased by 0.0 J/mol.
For half-equilibria, only ratios make sense.
=> 0-311++G(d,p) g1c:(cm^3) /

Meet overreact, the library



overreact

- Parsing of **multiple reactions**



¹Brown, R. *JOURNAL OF RESEARCH of the National Bureau of Standards* **1981**, 86, 357

²Bell, R. P. *Transactions of the Faraday Society* **1959**, 55, 1

Meet overreact, the library



overreact

- Parsing of **multiple reactions**



- Rigid rotor-harmonic oscillator approximation (**RRHO**)

¹Brown, R. *JOURNAL OF RESEARCH of the National Bureau of Standards* **1981**, 86, 357

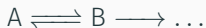
²Bell, R. P. *Transactions of the Faraday Society* **1959**, 55, 1

Meet overreact, the library



overreact

- Parsing of **multiple reactions**



- Rigid rotor-harmonic oscillator approximation (**RRHO**)
- **Automatic** 1 atm \rightarrow 1 M correction

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²Bell, R. P. *Transactions of the Faraday Society* **1959**, 55, 1

Meet overreact, the library



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- Parsing of **multiple reactions**



- Rigid rotor-harmonic oscillator approximation (**RRHO**)
- **Automatic** 1 atm \rightarrow 1 M correction
- Eyring-Evans-Polanyi equation

¹Brown, R. *JOURNAL OF RESEARCH of the National Bureau of Standards* **1981**, 86, 357

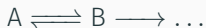
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Meet overreact, the library



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- Parsing of **multiple reactions**



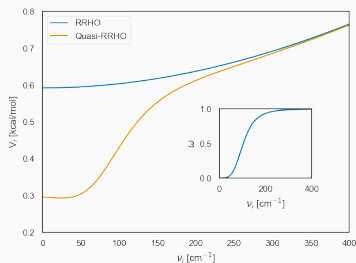
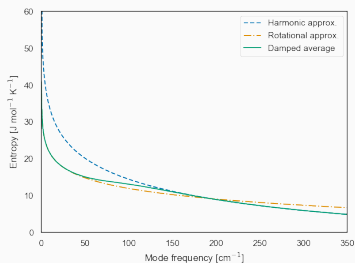
- Rigid rotor-harmonic oscillator approximation (**RRHO**)
- **Automatic** 1 atm \rightarrow 1 M correction
- Eyring-Evans-Polanyi equation
- **Eckart¹transmission coefficients**
(Wigner²also implemented)

¹Brown, R. *JOURNAL OF RESEARCH of the National Bureau of Standards* **1981**, 86, 357

²Bell, R. P. *Transactions of the Faraday Society* **1959**, 55, 1

Meet overreact, the library: quasi-RRHO

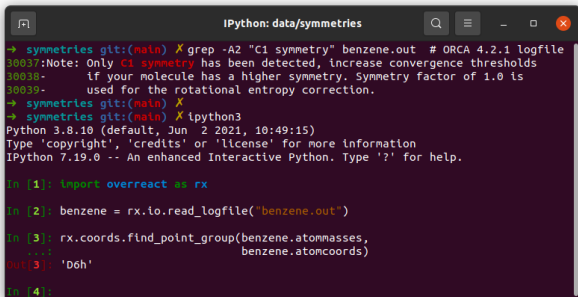
- Quasi-RRHO for both vibrational entropies¹ and enthalpies²



¹Grimme, S. *Chemistry - A European Journal* **2012**, *18*, 9955–9964.

²Li, Y.-P. et al. *The Journal of Physical Chemistry C* **2015**, *119*, 1840–1850.

Meet overreact, the library: symmetries



```
IPython: data/symmetries
→ symmetries git:(main) X grep -A2 "C1 symmetry" benzene.out # ORCA 4.2.1 logfile
30037:Note: Only C1 symmetry has been detected, increase convergence thresholds
30038-   if your molecule has a higher symmetry. Symmetry factor of 1.0 is
30039-   used for the rotational entropy correction.
→ symmetries git:(main) X
→ symmetries git:(main) X !python3
Python 3.8.10 (default, Jun 2 2021, 10:49:15)
Type 'copyright', 'credits' or 'license' for more information
IPython 7.19.0 -- An enhanced Interactive Python. Type '?' for help.

In [1]: import overreact as rx

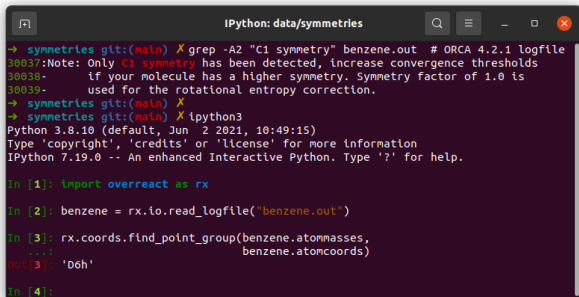
In [2]: benzene = rx.io.read_logfile("benzene.out")

In [3]: rx.coords.find_point_group(benzene.atommasses,
    ...                             benzene.atomcoords)
Out[3]: 'D6h'

In [4]:
```

- Robust code for the determination of point groups and rotational symmetry numbers

Meet overreact, the library: symmetries



```
IPython: data/symmetries
→ symmetries git:(main) X grep -A2 "C1 symmetry" benzene.out # ORCA 4.2.1 logfile
30037:Note: Only C1 symmetry has been detected, increase convergence thresholds
30038-   if your molecule has a higher symmetry. Symmetry factor of 1.0 is
30039-   used for the rotational entropy correction.
→ symmetries git:(main) X
→ symmetries git:(main) X ipython3
Python 3.8.10 (default, Jun 2 2021, 10:49:15)
Type 'copyright', 'credits' or 'license' for more information
IPython 7.19.0 -- An enhanced Interactive Python. Type '?' for help.

In [1]: import overreact as rx

In [2]: benzene = rx.io.read_logfile("benzene.out")

In [3]: rx.coords.find_point_group(benzene.atommasses,
    ...                             benzene.atomcoords)
Out[3]: 'D6h'

In [4]:
```

- Robust code for the determination of point groups and rotational symmetry numbers
- (The above implies an error of $RT \ln\left(\frac{12}{1}\right) \approx 1.5$ kcal/mol @ 25°C)

Meet overreact, the library



overreact

- Automatic generation of the required differential equations

$$\frac{dy}{dt} = f(t, y)$$

¹Virtanen, P. et al. *Nature Methods* **2020**, *17*, 261–272

²O'boyle, N. M. et al. *Journal of Computational Chemistry* **2008**, *29*, 839–845

Meet overreact, the library



overreact

- Automatic generation of the required differential equations

$$\frac{dy}{dt} = f(t, y)$$

- Solution via standard methods (via `scipy`¹)

¹Virtanen, P. et al. *Nature Methods* **2020**, *17*, 261–272

²O'boyle, N. M. et al. *Journal of Computational Chemistry* **2008**, *29*, 839–845

Meet overreact, the library



overreact

- Automatic generation of the required differential equations

$$\frac{dy}{dt} = f(t, y)$$

- Solution via standard methods (via `scipy`¹)
- Compatible with **many** packages (via `cclib`²)

- `ADF` (versions 2007 and 2013)
- `DALTON` (versions 2013 and 2015)
- `Firefly`, formerly known as PC GAMESS (version 8.0)
- `GAMESS (US)` (versions 2014 and 2017)
- `GAMESS-UK` (versions 7.0 and 8.0)
- `Gaussian` (versions 09 and 16)
- `Jaguar` (versions 7.0 and 8.3)
- `Molcas` (version 18.0)
- `Molpro` (versions 2006 and 2012)
- `MOPAC` (version 2016)
- `NWChem` (versions 6.0, 6.1, 6.5 and 6.6)
- `ORCA` (versions 4.0 and 4.1)
- `Psi4` (versions 1.0 and 1.2.1)
- `Q-Chem` (versions 4.2 and 5.1)
- `Turbomole` (versions 5.9 and 7.2)

¹Virtanen, P. et al. *Nature Methods* **2020**, *17*, 261–272

²O'boyle, N. M. et al. *Journal of Computational Chemistry* **2008**, *29*, 839–845

Meet overreact, the library



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- Automatic generation of the required differential equations

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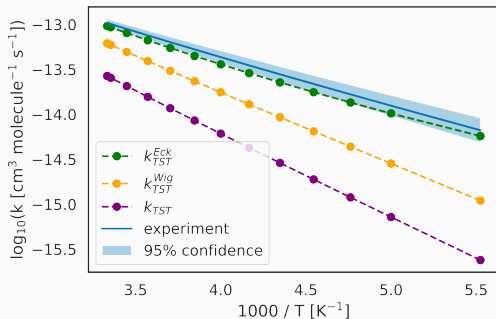
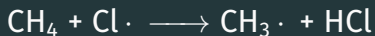
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- `Turbomole` (versions 5.9 and 7.2)

- **Microkinetic modelling**

¹Virtanen, P. et al. *Nature Methods* **2020**, *17*, 261–272

²O'boyle, N. M. et al. *Journal of Computational Chemistry* **2008**, *29*, 839–845

Two solved problems



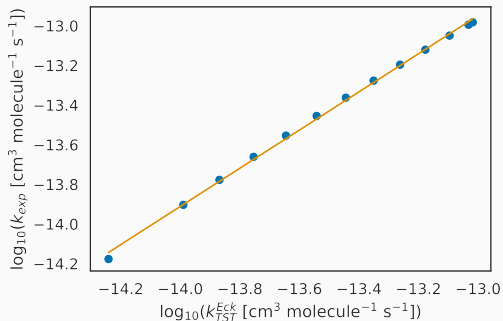
$$k^{exp} = 1.03 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

$$k^{UMP2/cc-pVTZ} = 9.29 \times 10^{-14} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

Burkholder, J. et al. *Chemical kinetics and photochemical data for use in atmospheric studies; evaluation number 19*, tech. rep.; Pasadena, CA: Jet Propulsion Laboratory, National Aeronautics and Space Agency, 2020

Tanaka, N. et al. *Journal of Atmospheric Chemistry* 1996, 23, 37-49

Jupyter notebook: <https://git.io/JBjLB>

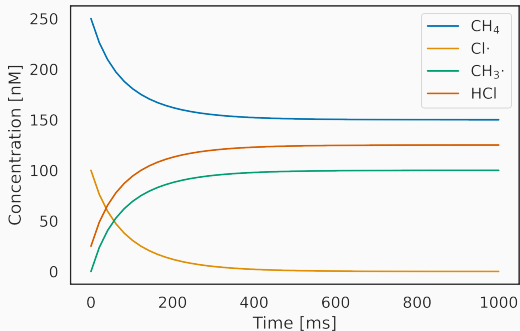


$$\log_{10} k^{exp} = 0.9633 \times \log_{10} k^{UMP2/cc-pVTZ} - 0.4256 \quad (r^2 = 0.9984)$$

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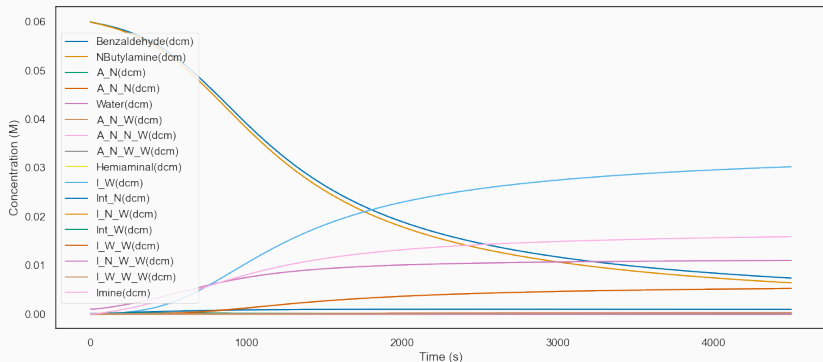
(Arbitrarily) starting from:

$$y_0^{\text{Cl}\cdot} = 1 \times 10^{-7} \text{M}, \quad y_0^{\text{CH}_4} = 2.5y_0^{\text{Cl}\cdot}, \quad y_0^{\text{HCl}} = 0.25y_0^{\text{Cl}\cdot}$$

Jupyter notebook: <https://git.io/JBjLQ>

Reproducing the work of Pérez-Soto et al.

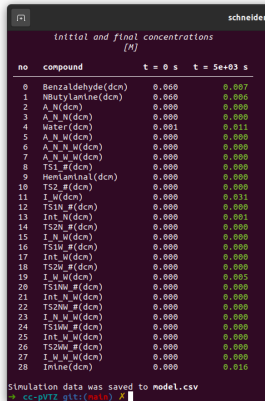
```
1 $ overreact model.k "Benzaldehyde(dcm): 0.06" "NButylamine(dcm) : 0.06" 'Water(dcm): 0.001' \  
2 --bias=3.2 --plot=active --max-time 5000
```



Pérez-Soto, R. et al. *Organic Letters* 2020, 22, 2873–2877

Reproducing the work of Pérez-Soto et al.

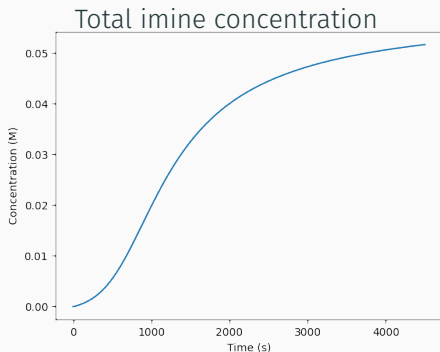
```
1 $ overreact model.k "Benzaldehyde(dcm): 0.06" "NButylamine(dcm) : 0.06" 'Water(dcm): 0.001' \  
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```



Terminal window showing simulation results for initial and final concentrations of various compounds. The window title is "schneider". The output is titled "Initial and final concentrations [M]".

no	compound	t = 0 s	t = 5e+03 s
0	Benzaldehyde(dcm)	0.060	0.007
1	NButylamine(dcm)	0.060	0.006
2	A_N(dcm)	0.000	0.000
3	A_N_N(dcm)	0.000	0.000
4	Water(dcm)	0.001	0.011
5	A_N_W(dcm)	0.000	0.000
6	A_N_N_W(dcm)	0.000	0.000
7	A_N_W_W(dcm)	0.000	0.000
8	TS1_#(dcm)	0.000	0.000
9	Henlamlal(dcm)	0.000	0.000
10	TS2_#(dcm)	0.000	0.000
11	I_W(dcm)	0.000	0.031
12	TS1N_#(dcm)	0.000	0.000
13	Int_N(dcm)	0.000	0.001
14	TS2N_#(dcm)	0.000	0.000
15	I_N_W(dcm)	0.000	0.000
16	TS1W_#(dcm)	0.000	0.000
17	Int_W(dcm)	0.000	0.000
18	TS2W_#(dcm)	0.000	0.000
19	I_W_W(dcm)	0.000	0.005
20	TS1NW_#(dcm)	0.000	0.000
21	Int_N_W(dcm)	0.000	0.000
22	TS2NW_#(dcm)	0.000	0.000
23	I_N_N_W(dcm)	0.000	0.000
24	TS1NW_W(dcm)	0.000	0.000
25	Int_W_W(dcm)	0.000	0.000
26	TS2NW_W(dcm)	0.000	0.000
27	I_W_W_W(dcm)	0.000	0.000
28	Imine(dcm)	0.000	0.016

Simulation data was saved to model.csv
cc-pVTZ_g15:(mol) /



Pérez-Soto, R. et al. *Organic Letters* 2020, 22, 2873–2877

Perspectives

- Improved tunneling corrections

¹Tanaka, N. et al. *Journal of Atmospheric Chemistry* **1996**, *23*, 37–49.

²Garza, A. J. *Journal of Chemical Theory and Computation* **2019**, *15*, 3204–3214.

Future work

- Improved tunneling corrections
- **Kinetic isotope effects (KIE)¹**

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- **Time-resolved spectroscopy**

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Questions?

<https://geem-lab.github.io/overreact-docs/>