

Ketohydroperoxide reactions uncovered by KinBot

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Introduction

Kinetic models: hundreds, up to thousands, or even ten-thousands of reactions; many rate coefficients are needed

Use of estimation methods **not always accurate**

Experimental data: **scarce**

High-level theoretical data: **scarce**

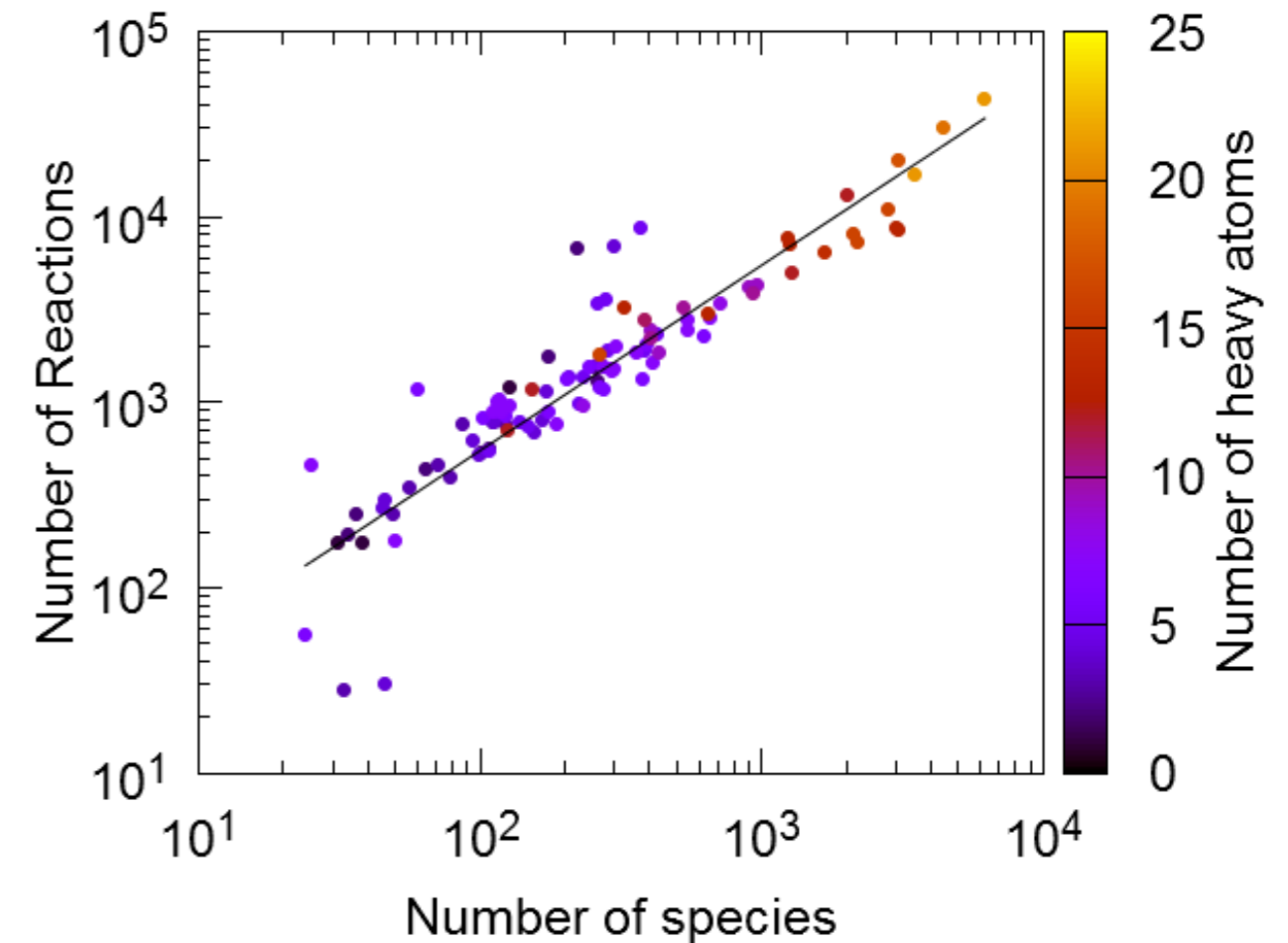
2 challenges with reaction mechanisms and kinetic models:

1. Find all kinetically relevant **reaction pathways**
2. For each pathway, calculate **accurate rate coefficients**

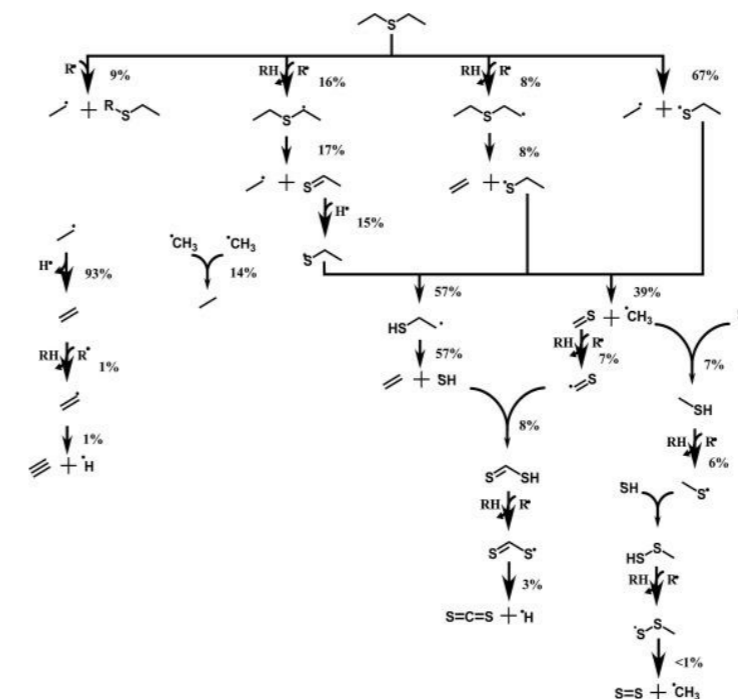
Manually: time-consuming, tedious and not always complete

Automated searches: faster, systematic, less error-prone

Development of the **KinBot** software



Van de Vijver, R. et al.; Int. J. Chem. Kinet. 2015, 47 (4), 199-231.



66 species

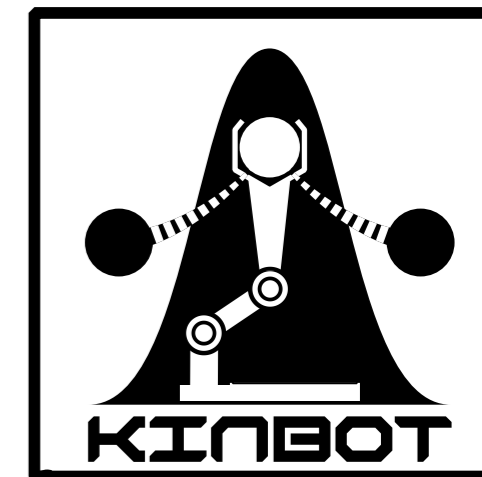
444 reaction

23 rate coefficients from
ab initio

421 rate coefficients
estimated

Van de Vijver, R. et al.; Chem. Eng. J. 2015, 278, 385-393.

KinBot



- Finds all kinetically relevant reaction pathways
- Directly allows the calculation of rate coefficients as a function of pressure, temperature, or internal energy
- Requires no user intervention
- Favorably scales for supercomputers
- Visualizes results
- Is agnostic about quantum chemistry code and level of theory

Core KinBot functionality: Find reactive saddle points

How is it done?

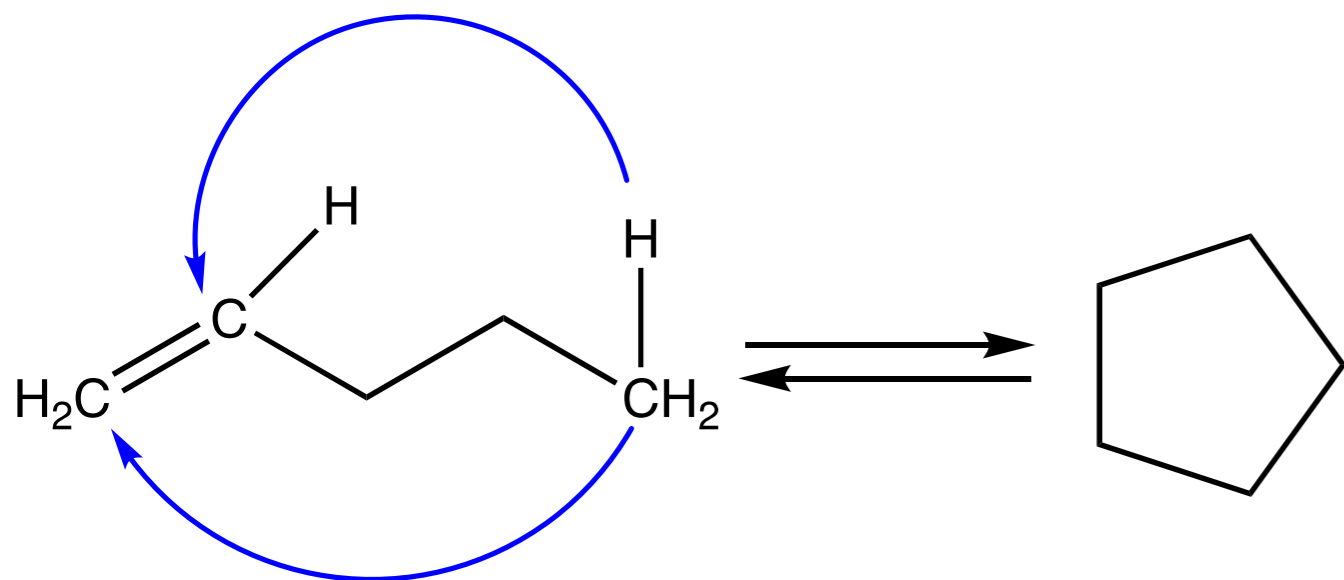
1. Identify the possibility of a reaction
2. Generate very good guess for a conformer of the saddle point
3. Optimize to nearest first-order saddle point

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Structure comprehension + motif search (based on 20+ families)



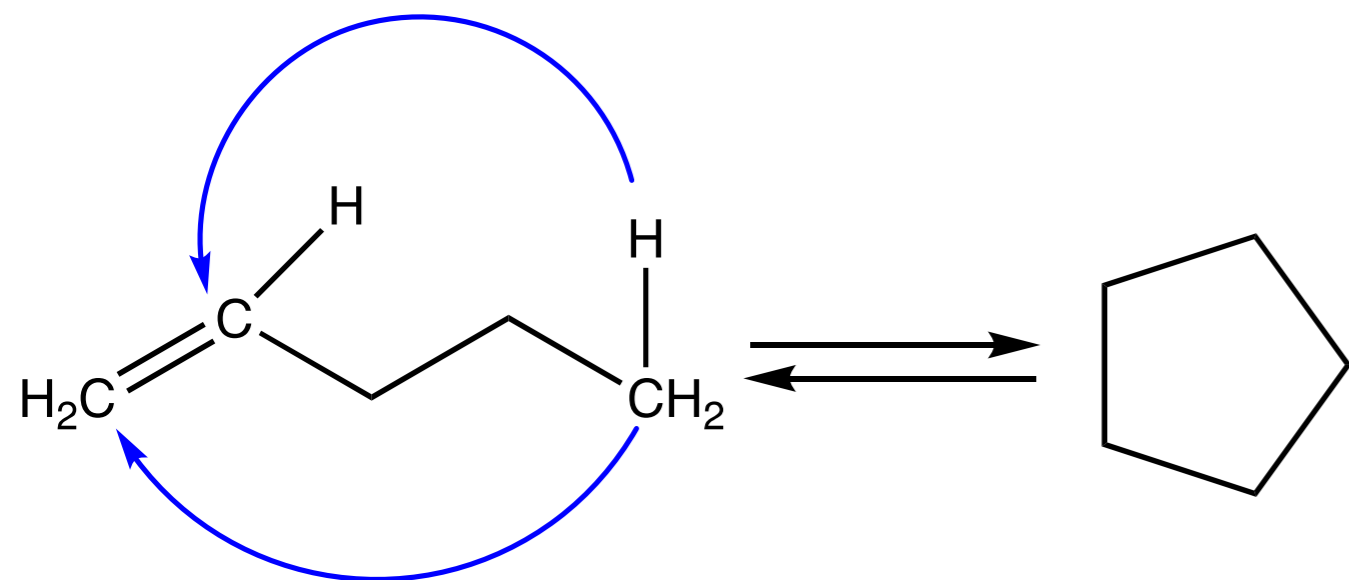
Endocyclic closed-shell cyclization

Core KinBot functionality: Find reactive saddle points

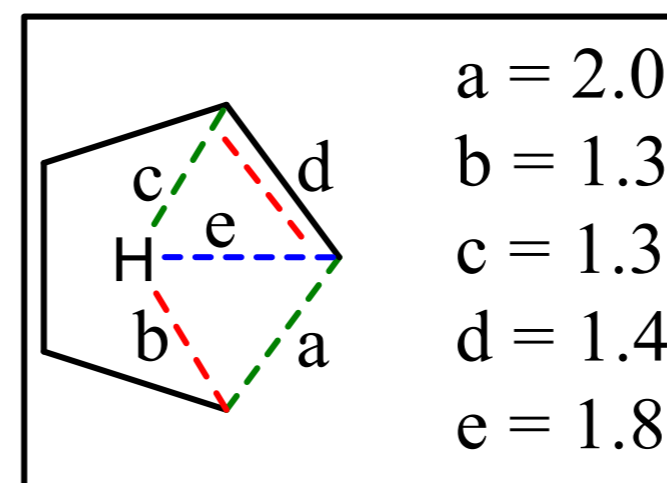
How is it done?

1. Identify the possibility of a reaction
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Use template + modify dihedrals, angles and bond lengths



Endocyclic closed-shell cyclization



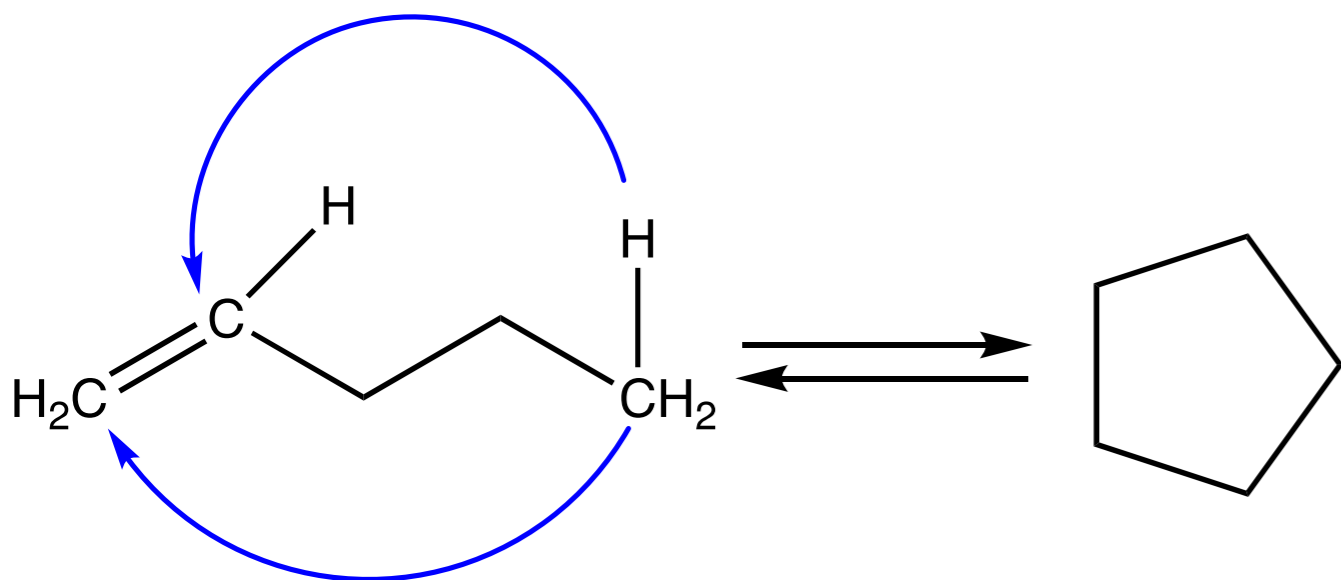
Series of constrained optimizations at a low level of theory (e.g., AM1)

github.com/zadorlab/kinbot
kinbot.sandia.gov

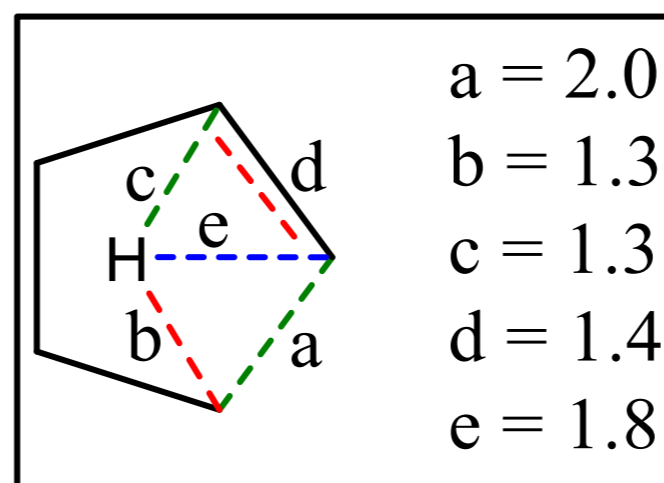
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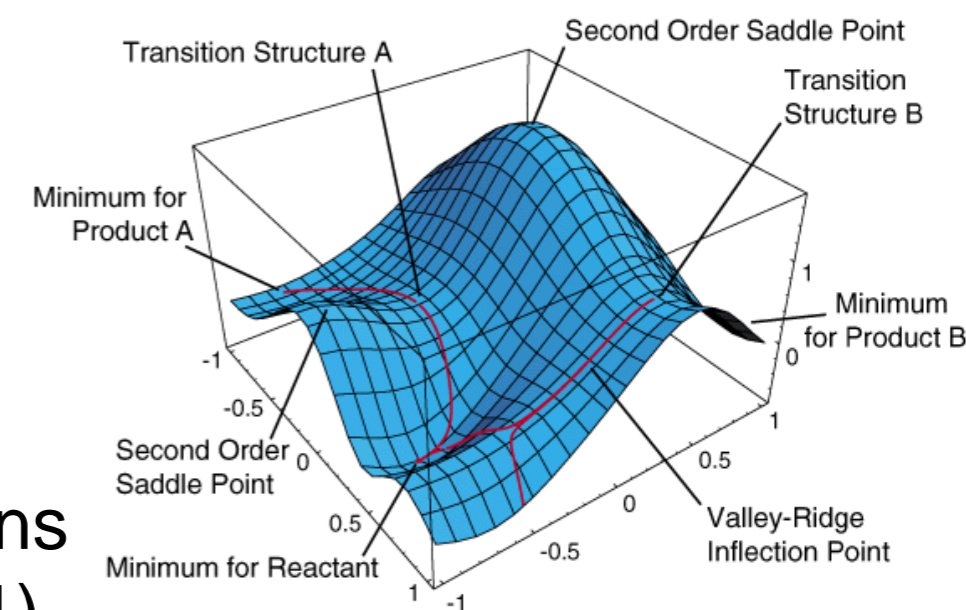


Endocyclic closed-shell cyclization



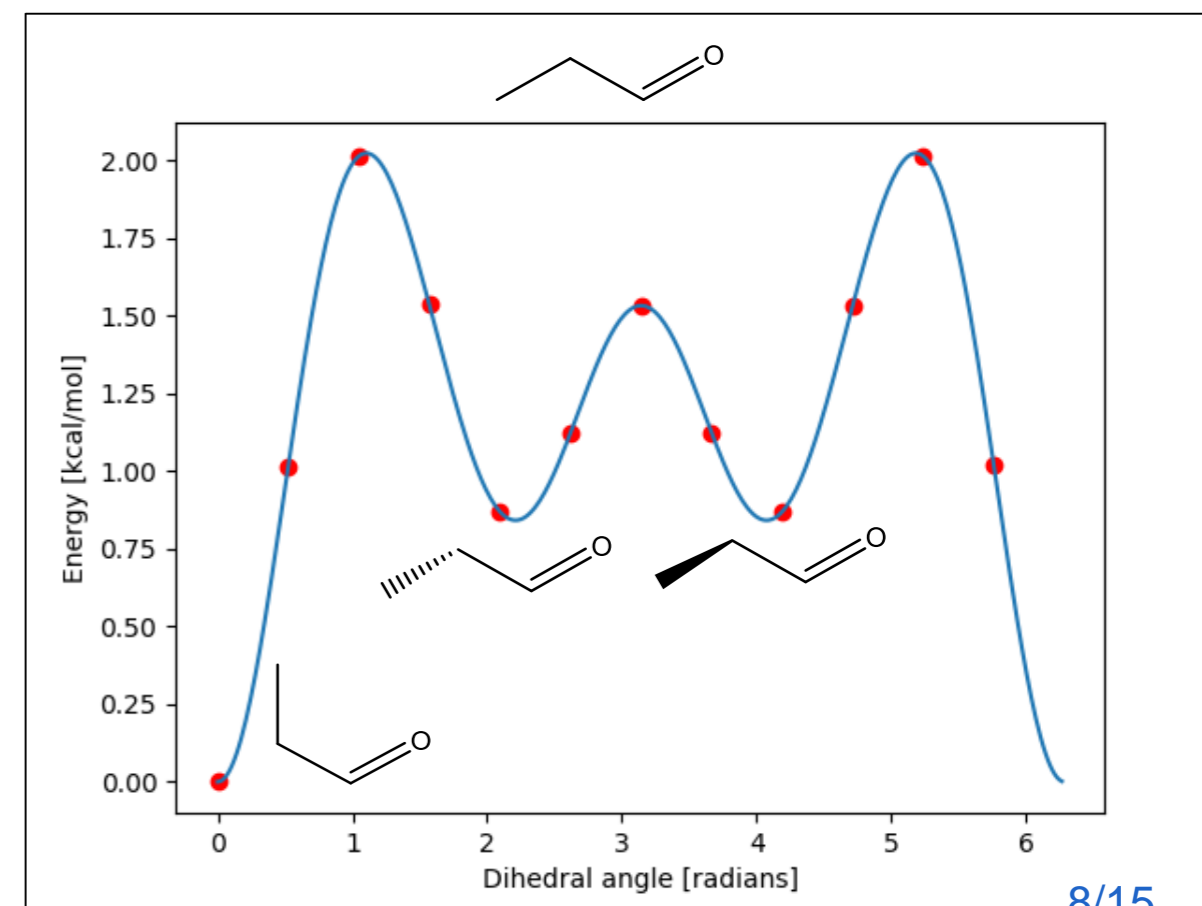
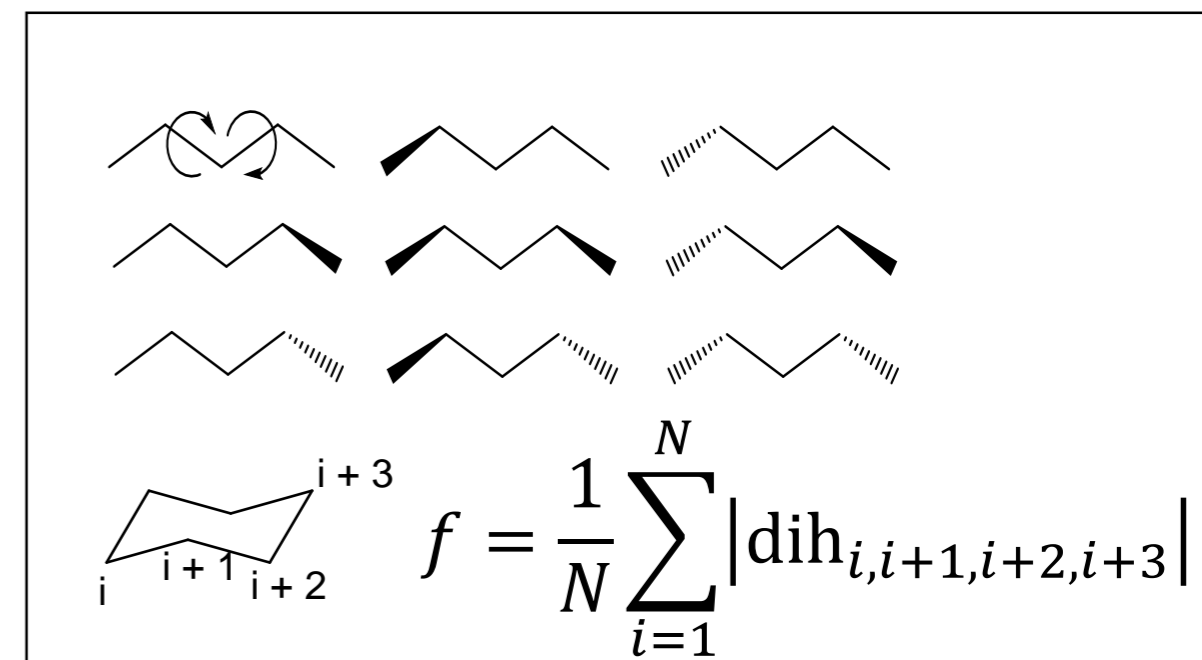
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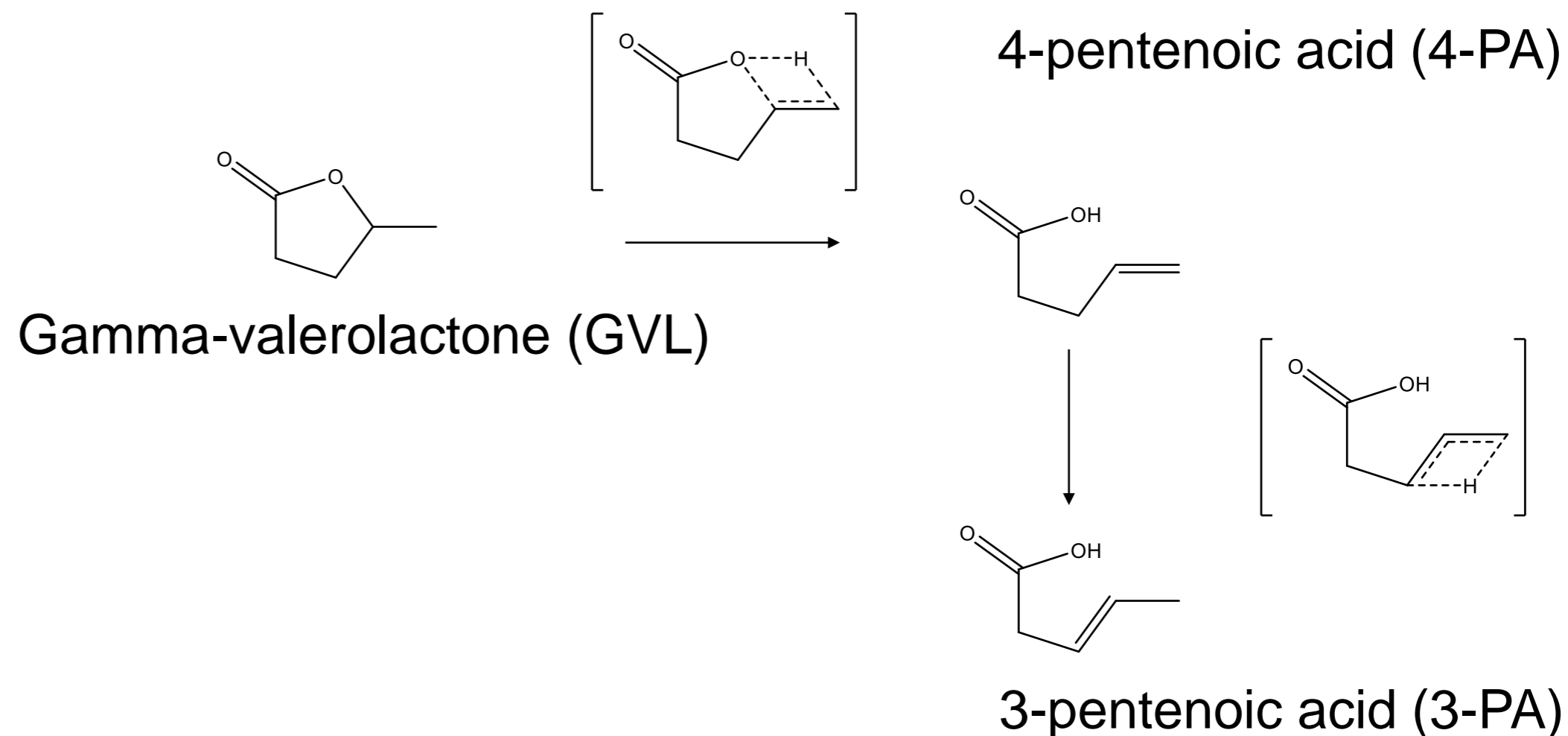
Additional tools in KinBot: Steps towards rate coefficients

- OFF ON – Conformational search
- OFF ON – Higher-level optimization
- OFF ON – Hindered rotor calculation
- OFF ON – Coupled-cluster-like energies
- Symmetry calculation
- Internal
- External
- OFF ON – Run chemical master equation



Gamma-valerolactone thermal decomposition

- Potential biofuel
- Studied in the past^{1,2}
- Reactions of GVL, 4-PA and 3-PA
- Reaction searches:
B3LYP/6-31G
- High-level calculations:
B3LYP/6-311++G(d,p)

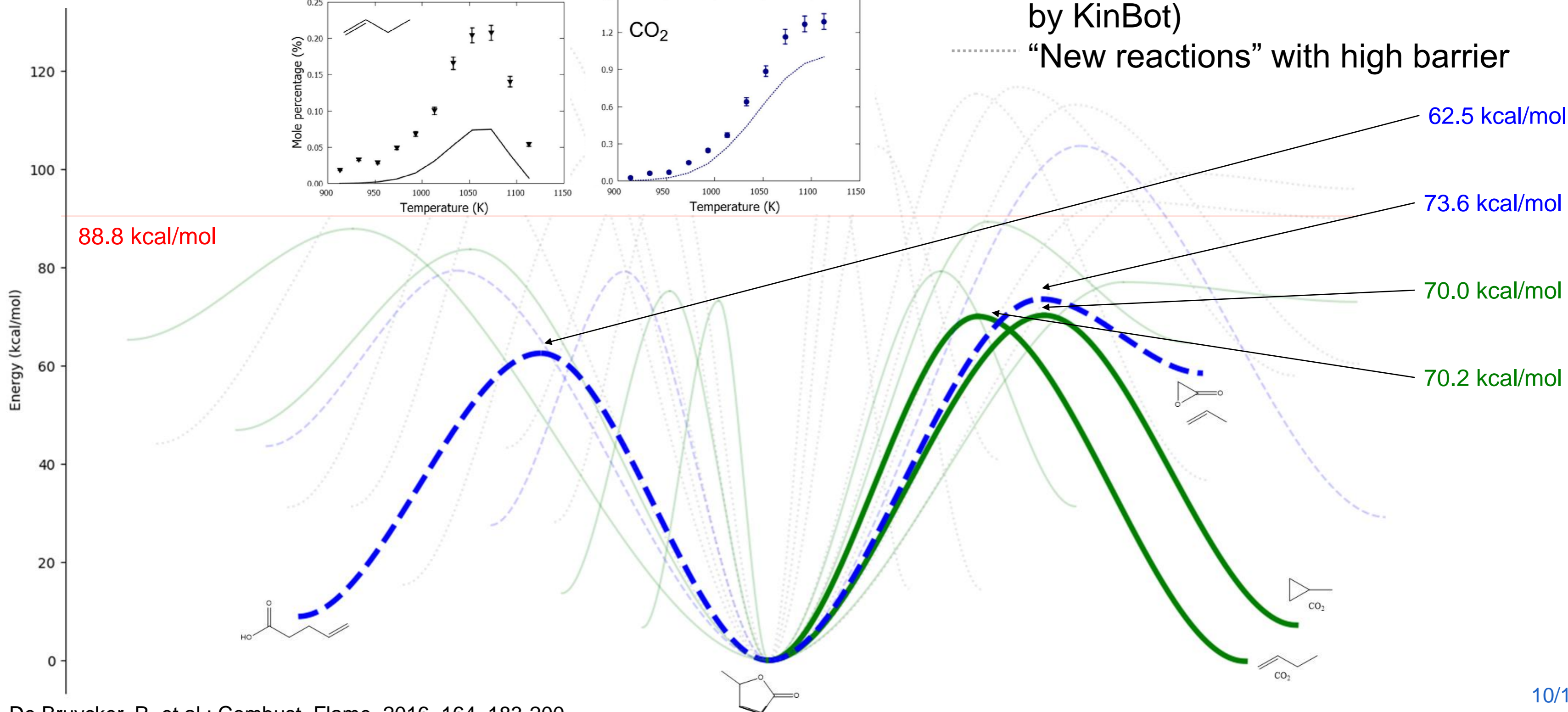
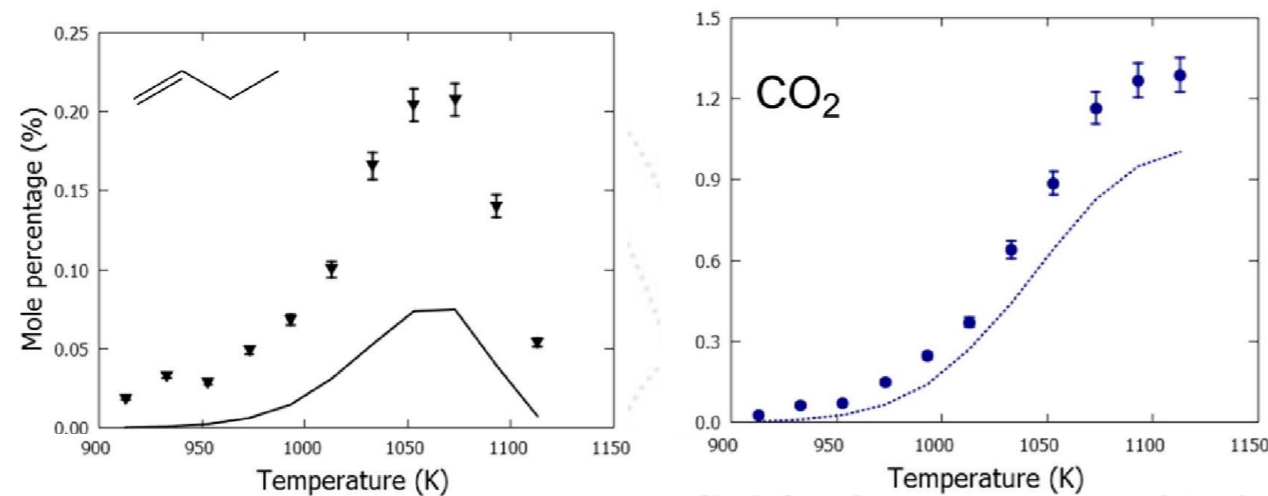


Single well: Gamma-valerolactone

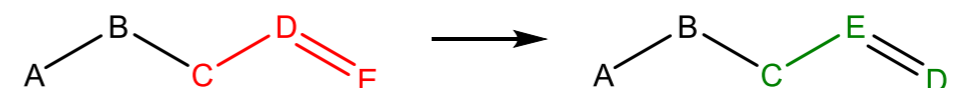
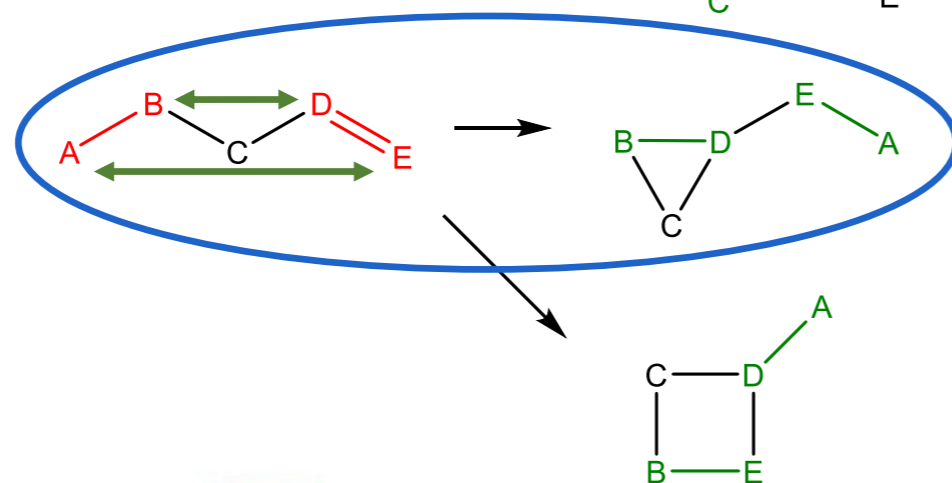
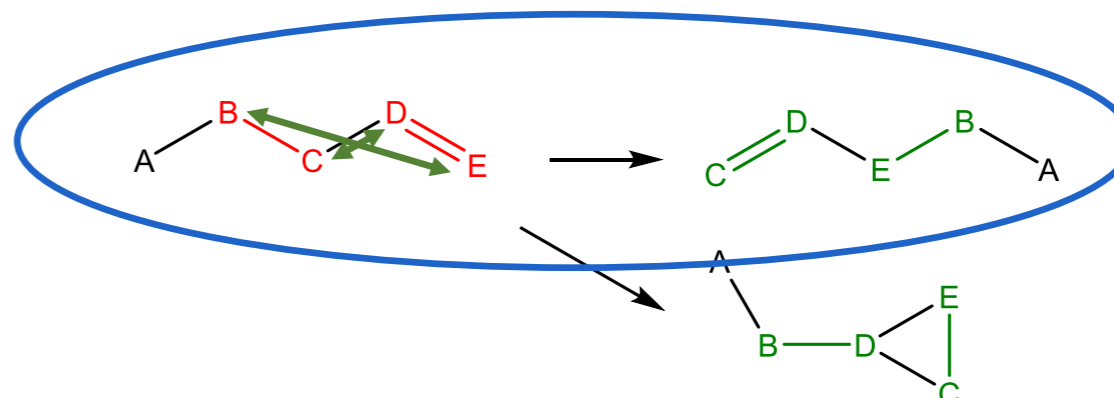
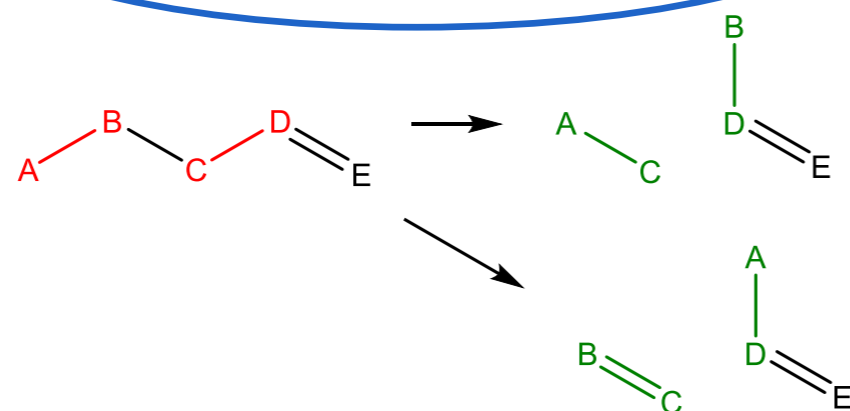
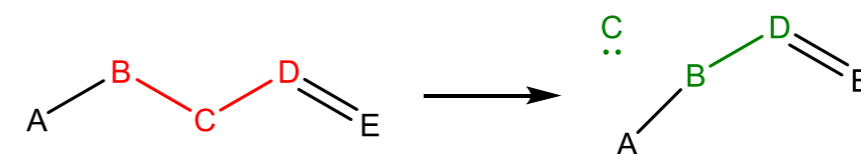
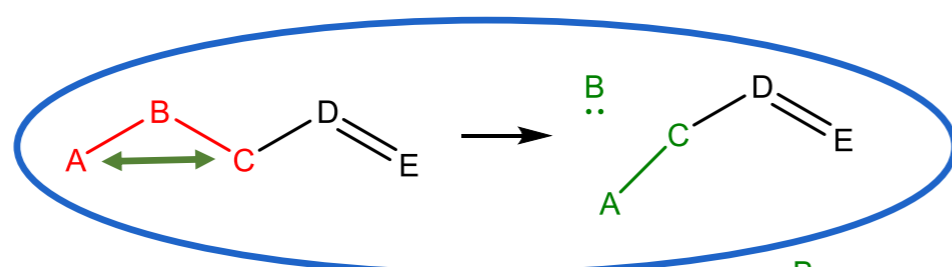
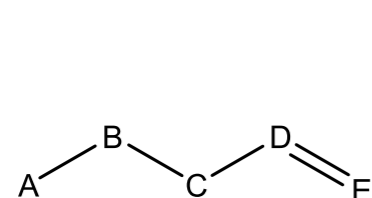
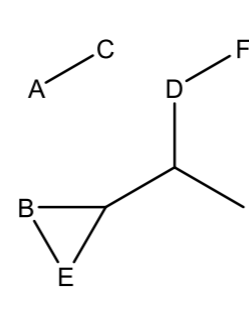
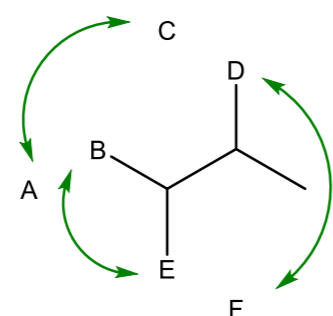
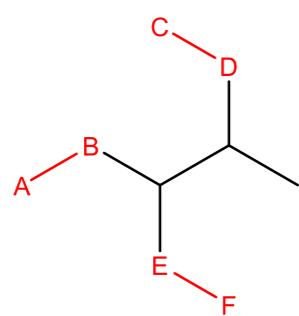
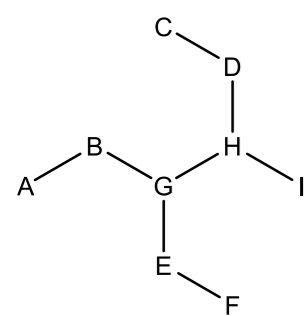
Below 1050K: Molecular chemistry

Above 1050K: Radical chemistry

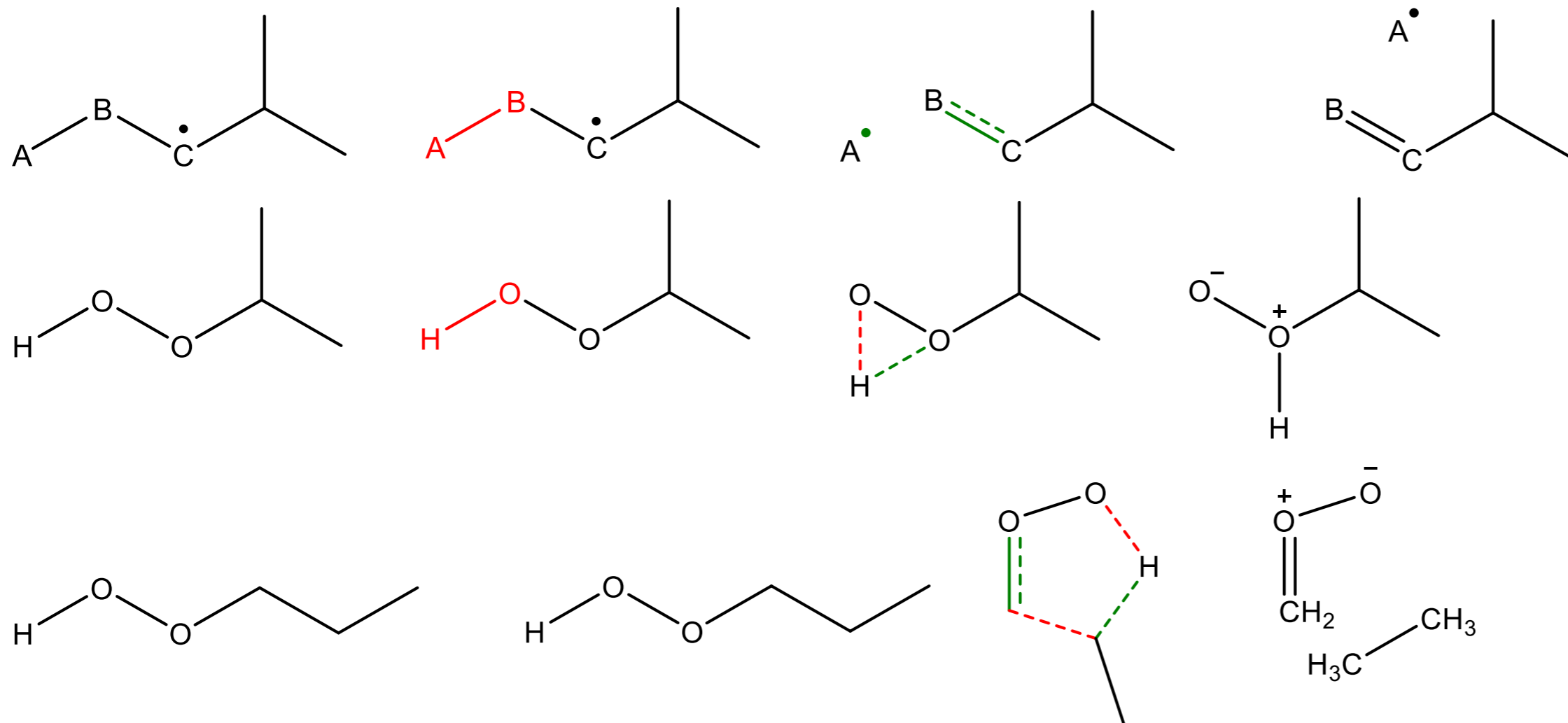
- “New reactions” by KinBot
- - - Previously reported reaction (also found by KinBot)
- ⋯ “New reactions” with high barrier



Combinatorial reaction search



Combinatorial reaction search



How many bonds to break and form?

1, 2 or 3

Formation of lone electron pairs

Yes: carbene formation

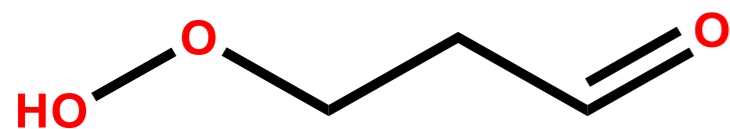
Formation of zwitterions

Yes

Formation of biradicals

Yes: criegee intermediates

Combinatorial search for ketohydroperoxide



Grambow et al.¹: 55 product species via 75 unique pathways

Maeda and Harabuchi²: 85 product species

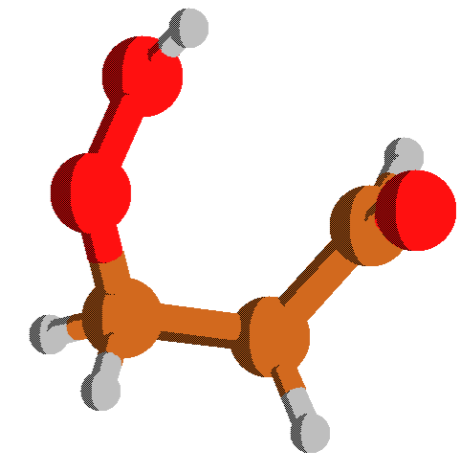
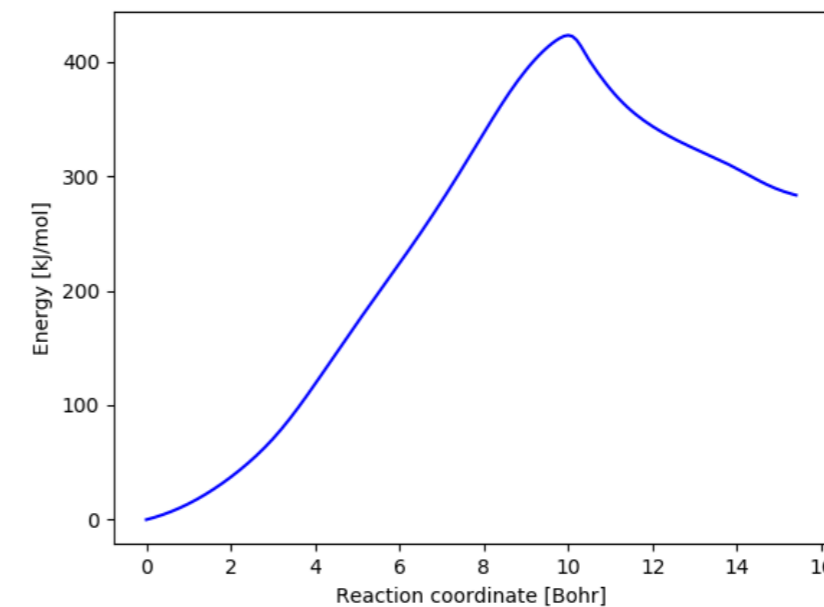
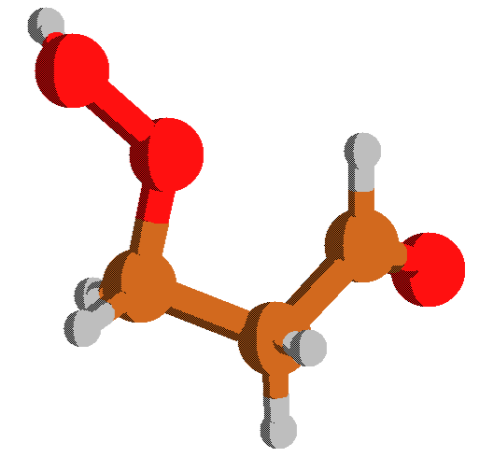
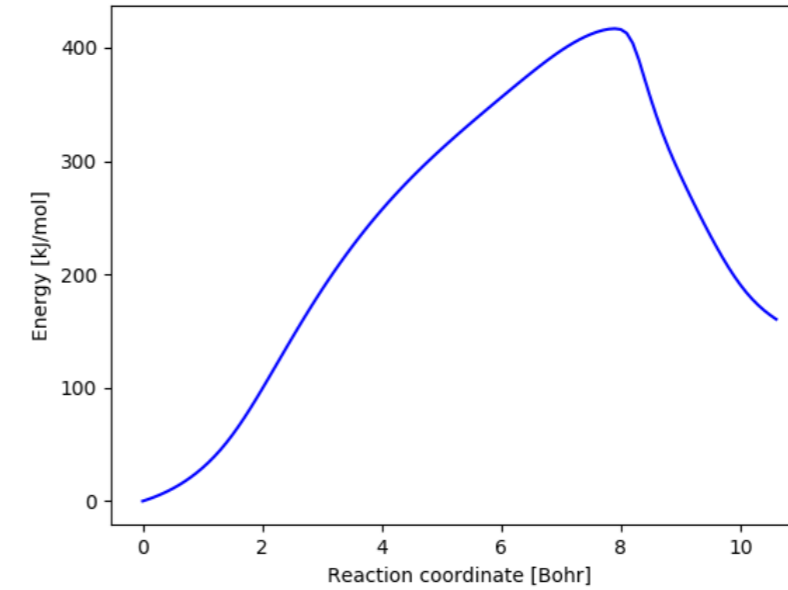
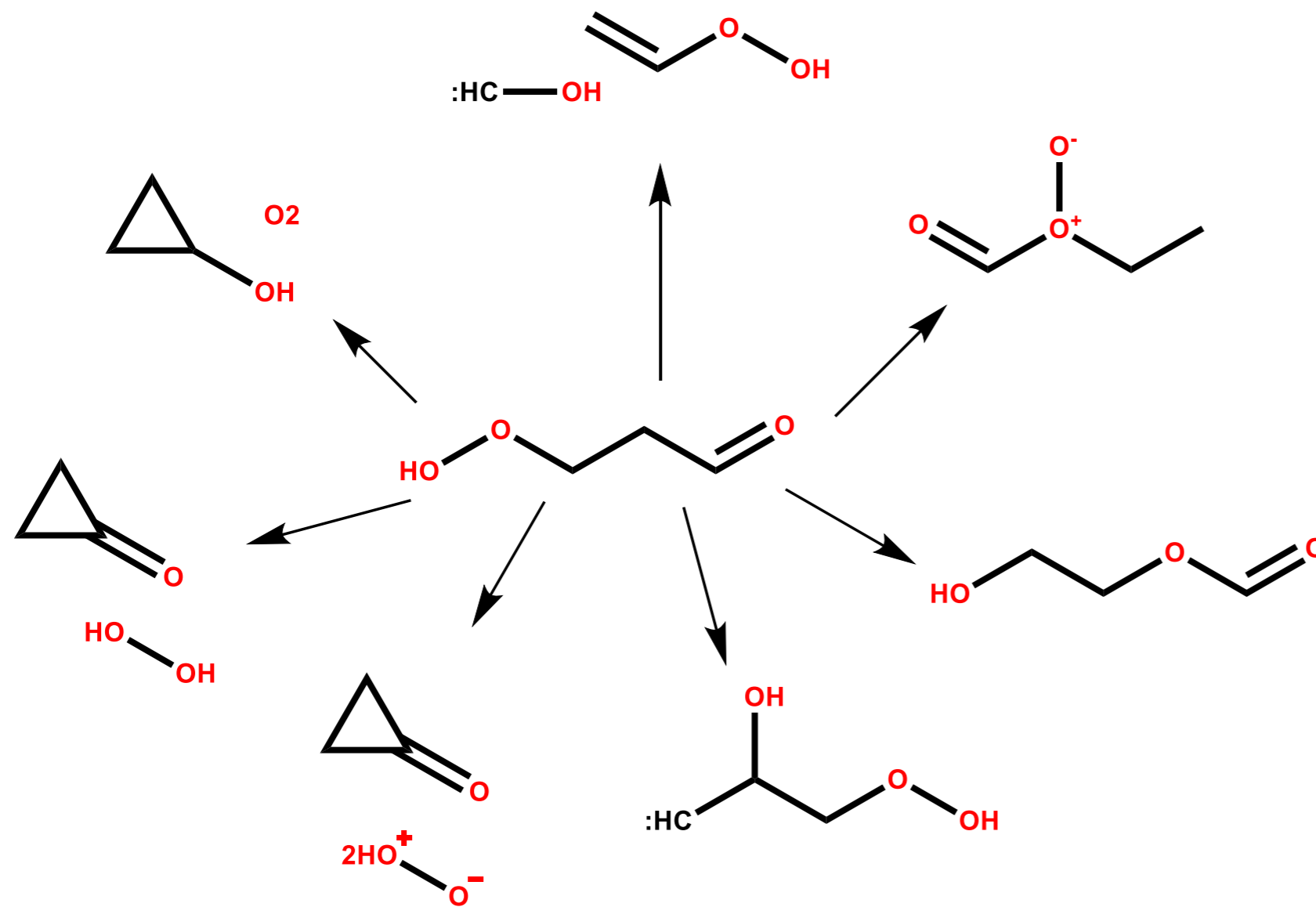
KinBot:

2320 reaction searches

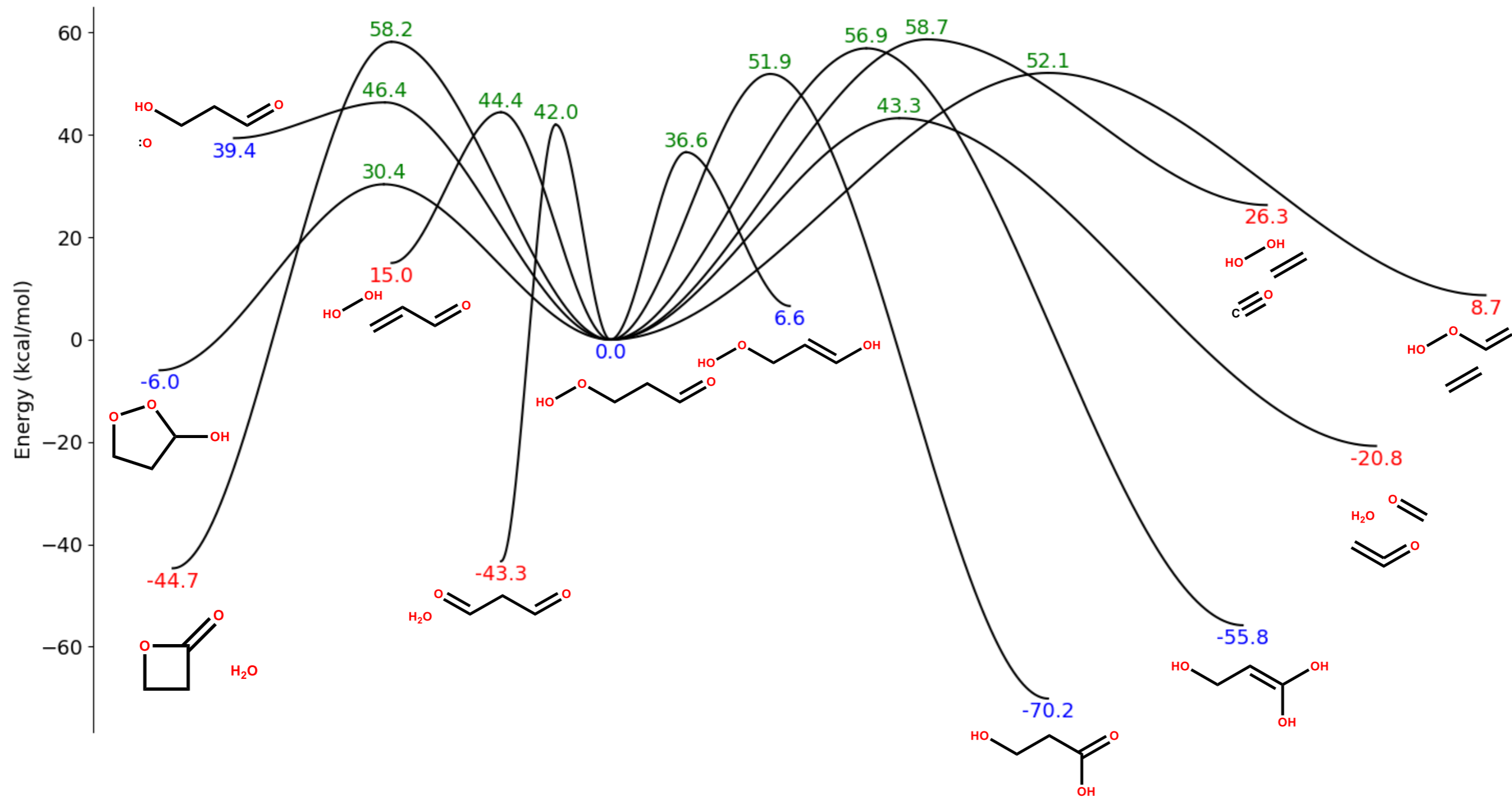
805 successful searches, 71 unique ones

1. First order saddle point located
2. One IRC leads to the reactant
3. Other IRC leads to another species

Combinatorial search for ketohydroperoxide



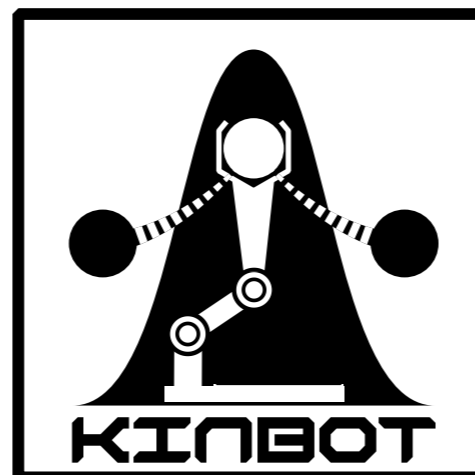
Combinatorial search for ketohydroperoxide



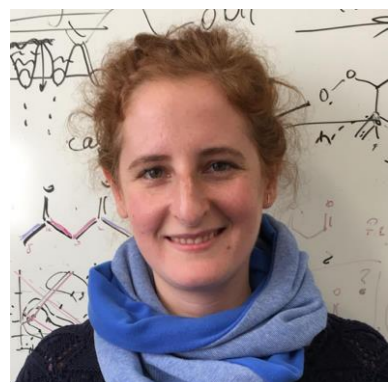
Conclusions

Kinbot can automatically explore PES's and find relevant reactions

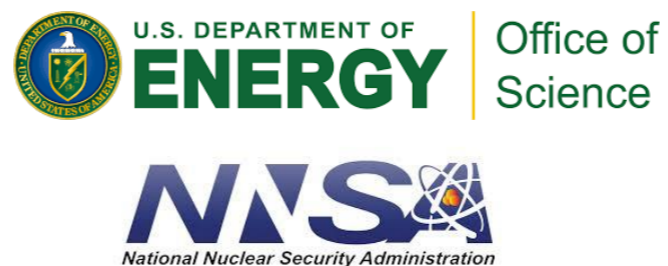
KinBot now includes a combinatorial search able to find many unexpected pathways



Acknowledgments



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