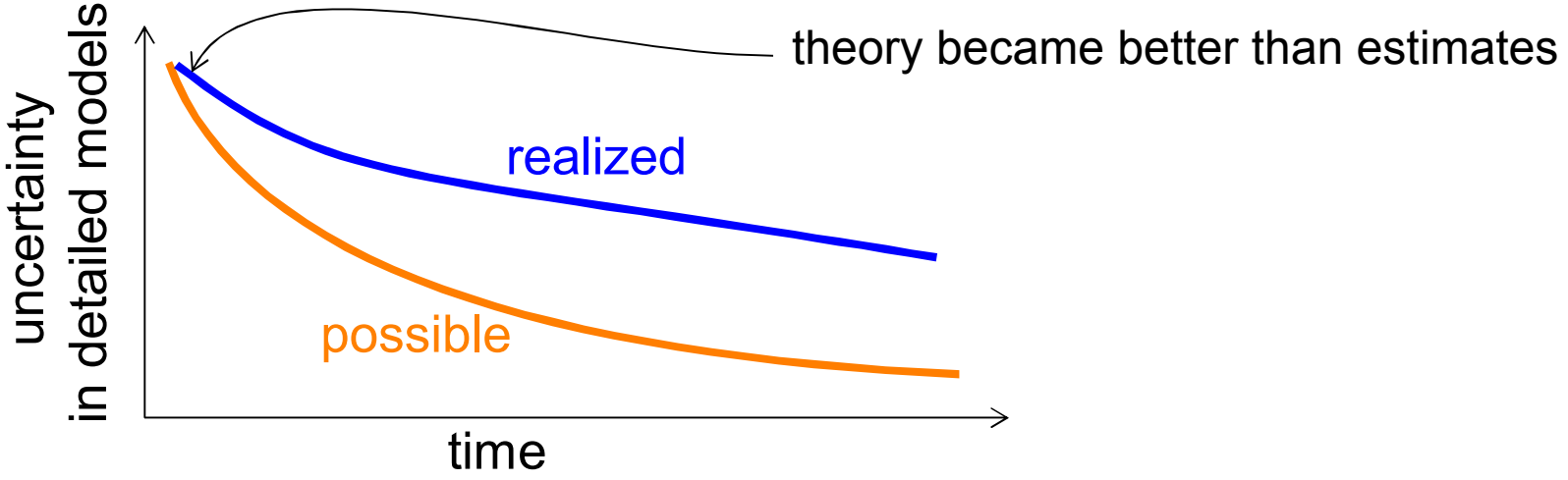
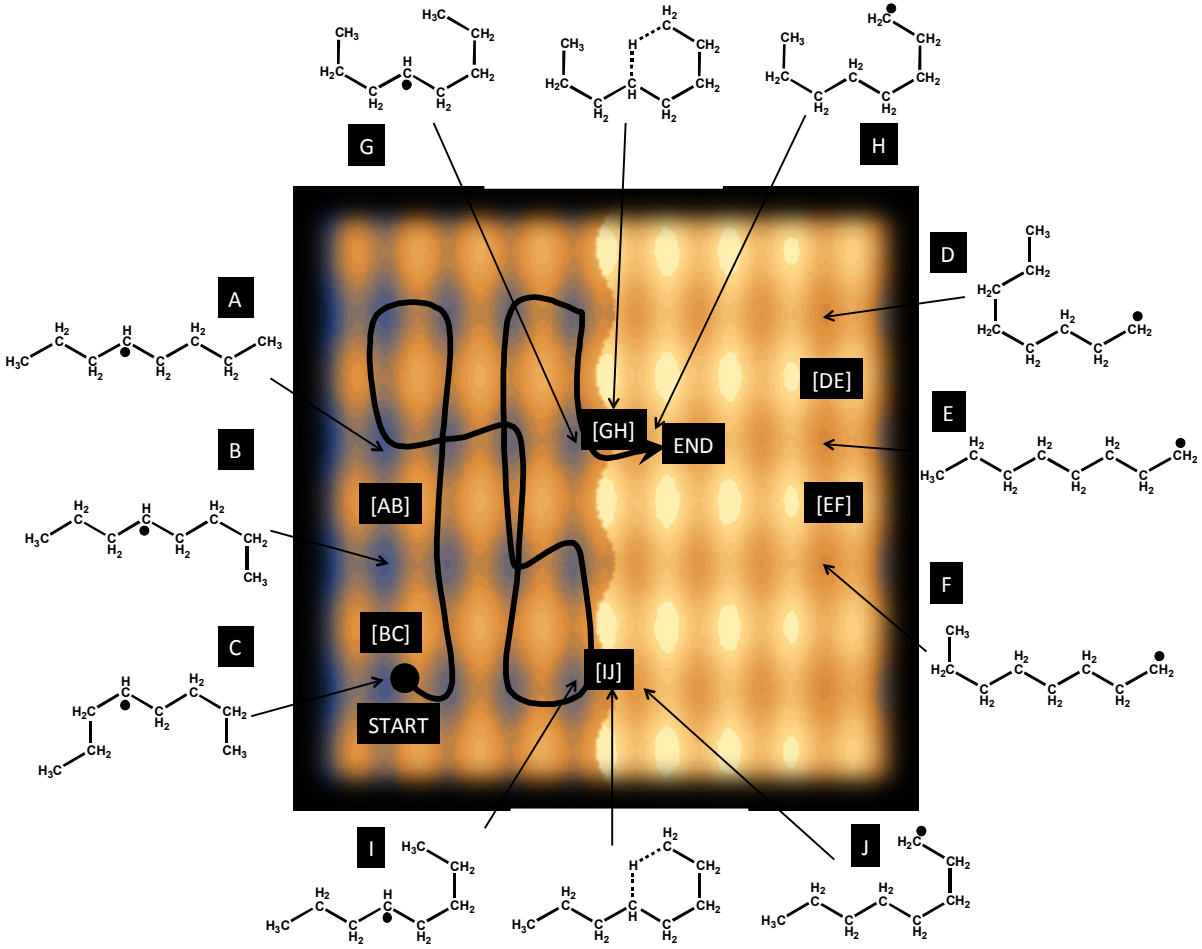
Reasons to Automate

SAND2016-10675PE

1. There are almost trivial things to automate – why do by hand if we don't have to?
2. Saving the world is hard – we should focus on the important/hard/exciting problems, and let the computer figure out the repetitive parts.
3. Reveals emergent properties – data mining. Engineering/science bridge?
4. Unused resources – gas-phase chemistry is not effectively taking advantage of large (exascale?) computers.
5. Currently very slow deployment of theoretical advances.



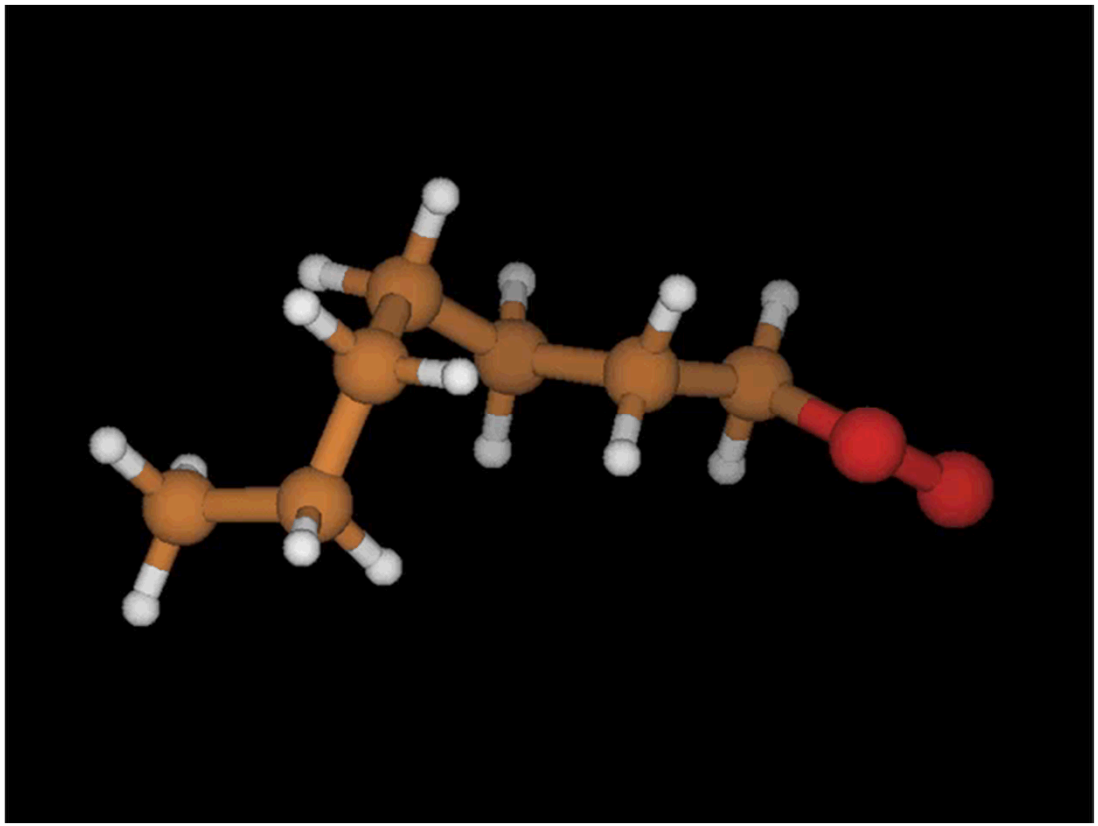
Reactive saddle points are only accessible from certain conformers



KinBot gets very close to the saddle points for floppy molecules by a combination of heuristics and stepwise optimizations.

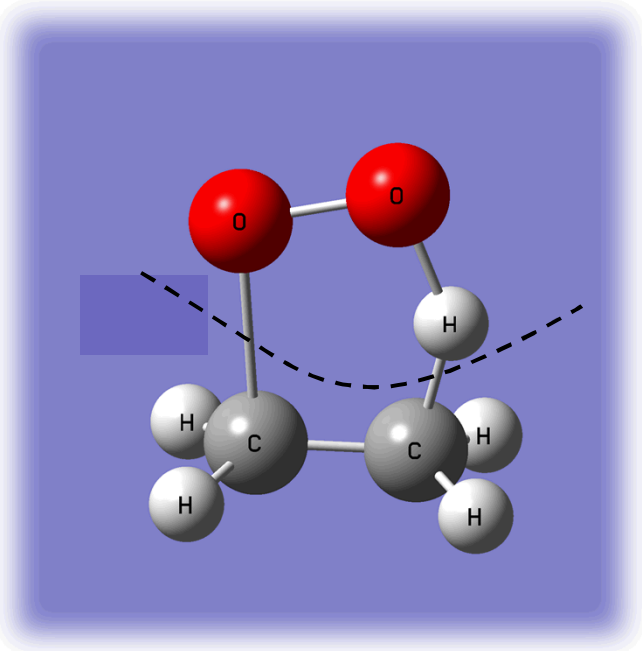
Reactive saddle points are only accessible from certain conformers

‘snake puzzle’

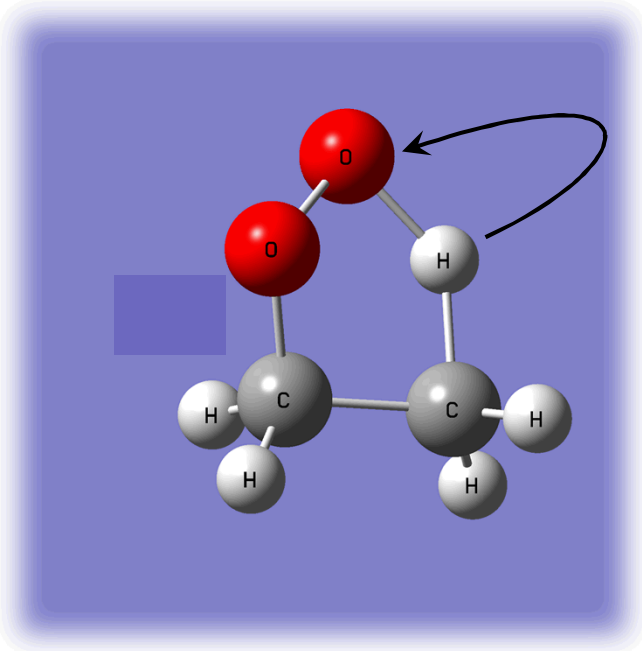


KinBot locates reactive saddle points on the global PES in stepwise geometry manipulations (B3LYP/6-31+G*) using trigonometric considerations and partial optimizations.
Modified force fields are tested as an alternative approach.
Currently on-line coupled to Gaussian and off-line to Molpro (high-level energies).

KinBot is a sophisticated guess-generator



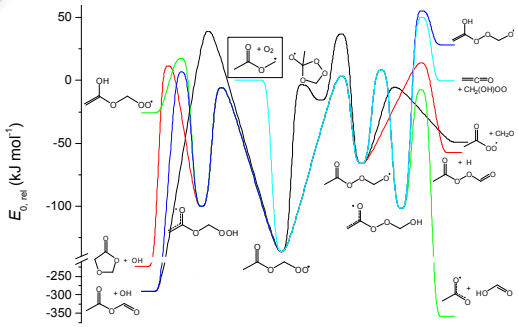
Alkyl peroxy eliminating HO_2 (decelerates ignition)

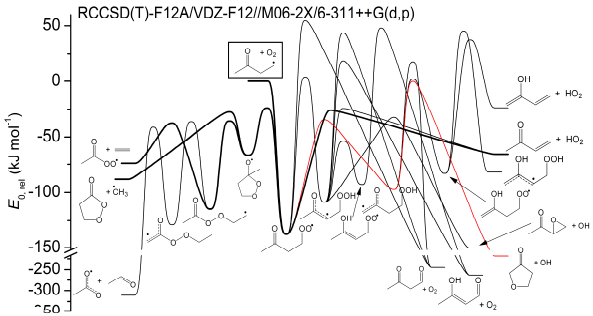


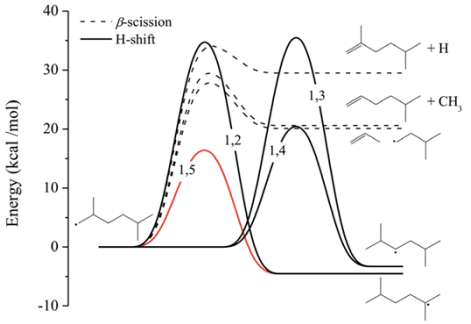
Alkyl peroxy isomerization (accelerates ignition)

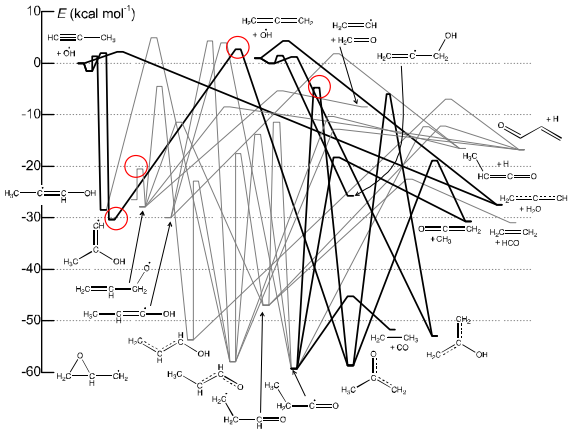
Some important saddle points are very close to each other in coordinate space. Heuristics are necessary and useful.

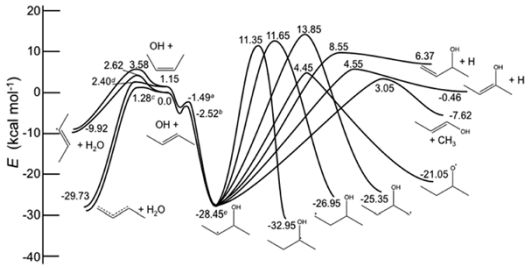
Example Gallery

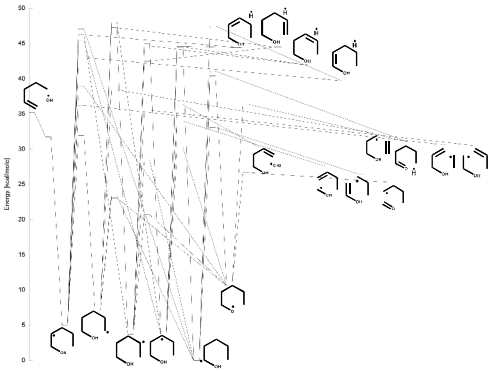


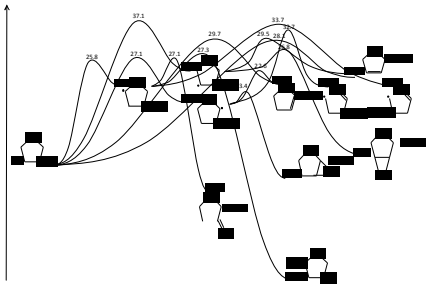


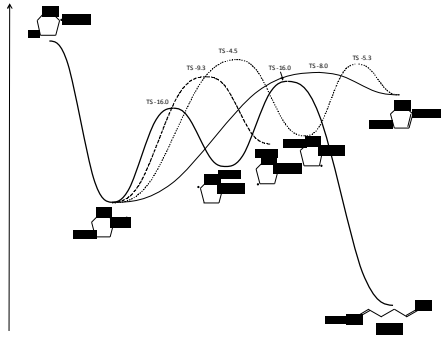


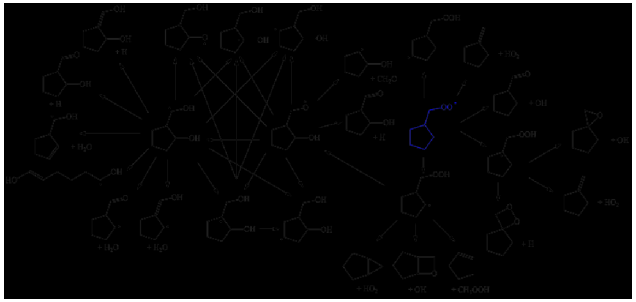




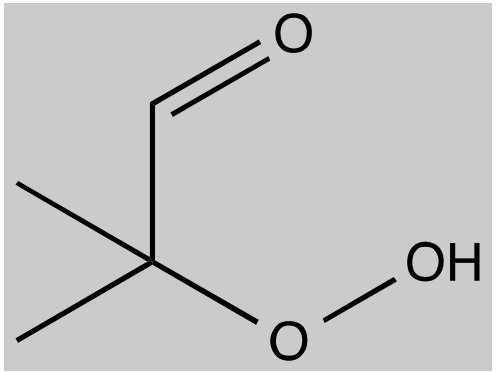








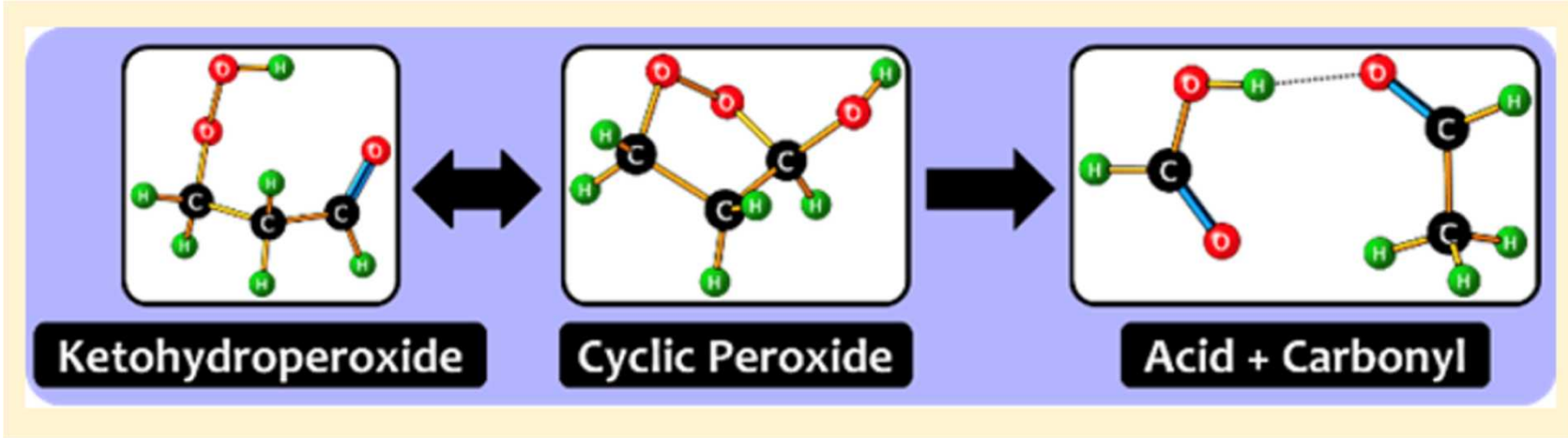
Autoignition and ketohydroperoxides (KHPs)



KHPs are

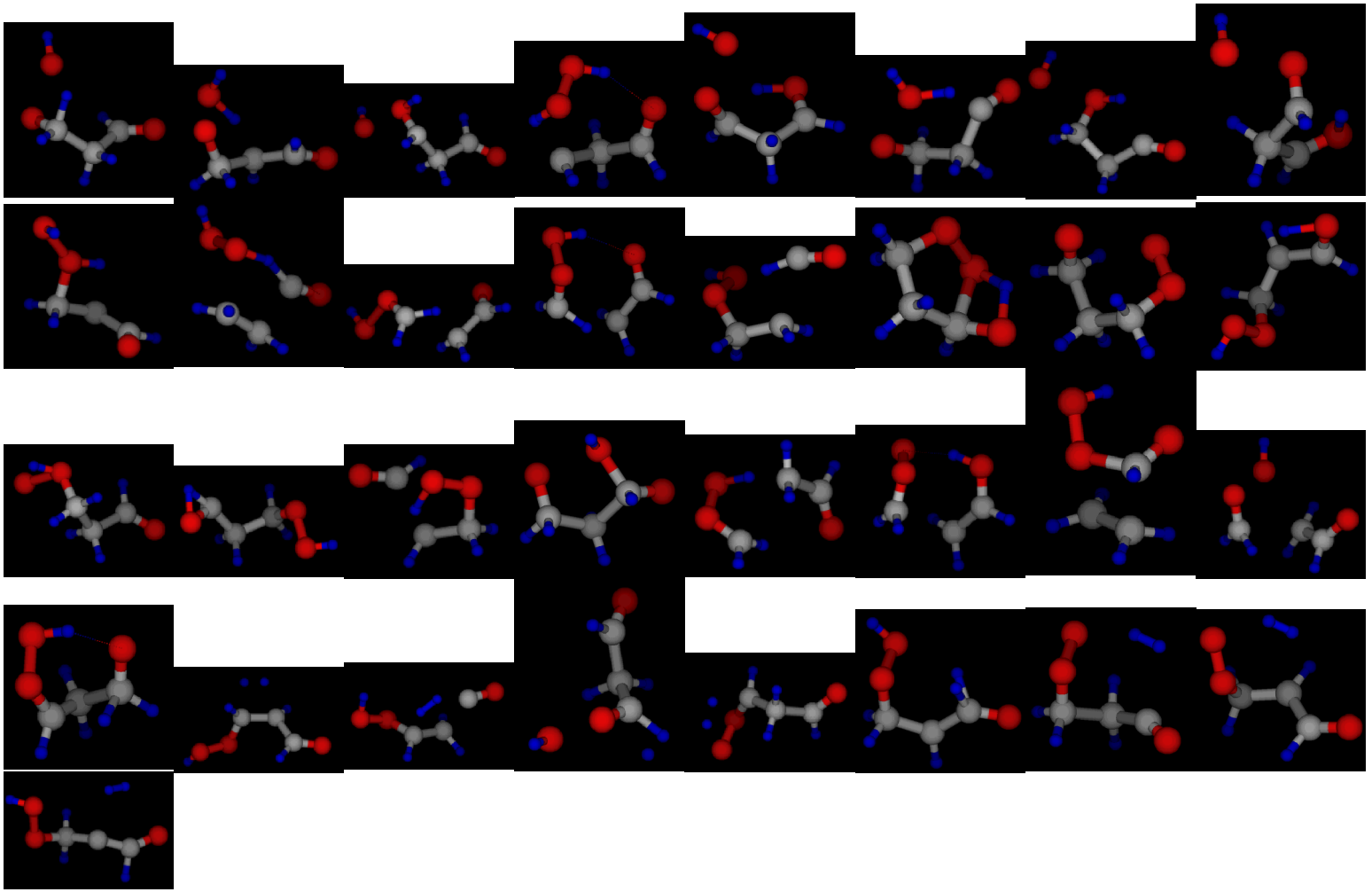
- The lowest *E* products in the first stages of low-temperature oxidation of hydrocarbons
- Closed shell molecules

Jalan et al., 2013, JACS, “Korcek decomposition”



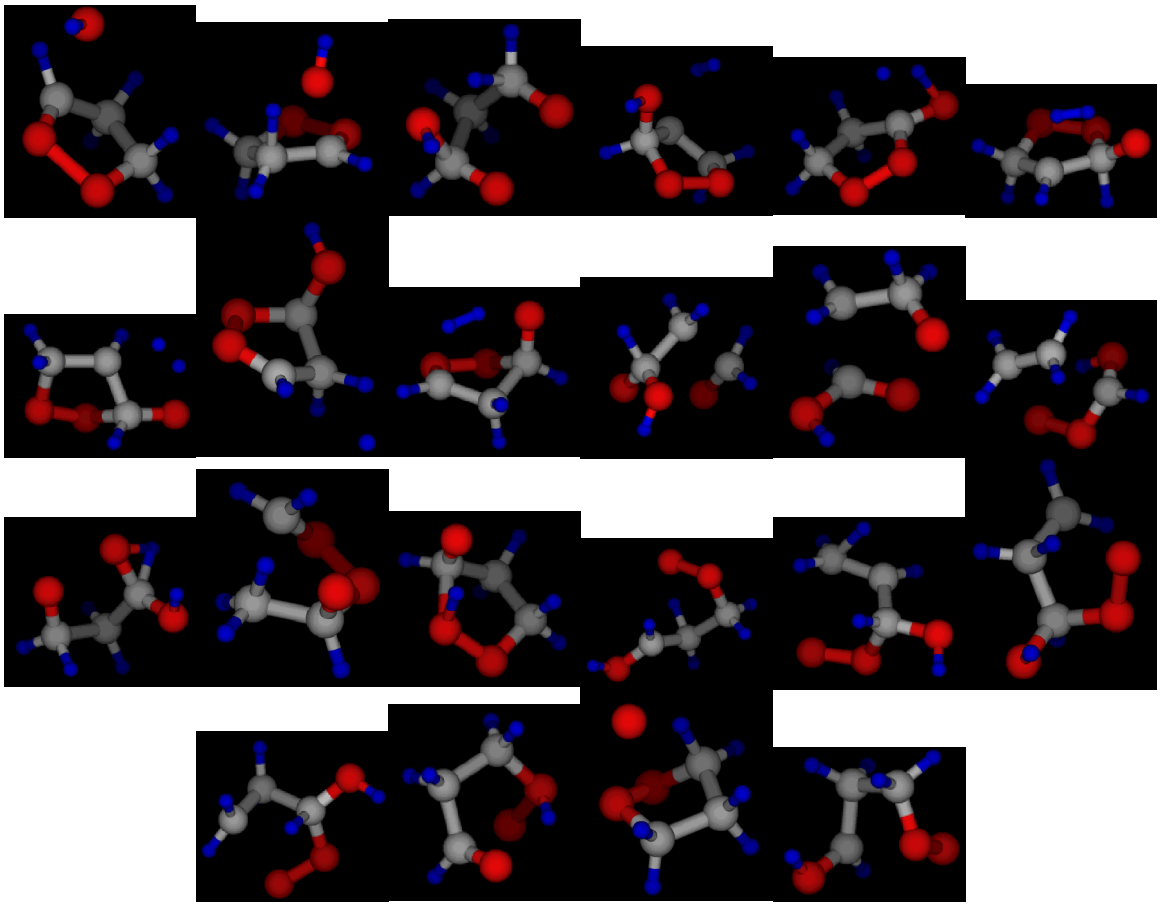
Are there other important pathways besides the cyclic peroxide formation?

Recent Test for C3 KHP



33 channels for one KHP: H_2O, H_2O_2, H_2, CO, OH, acids, aldehydes, enols, peracids, Criegee, Korcek, etc.

Recent Test for a C3 Cyclic Peroxide

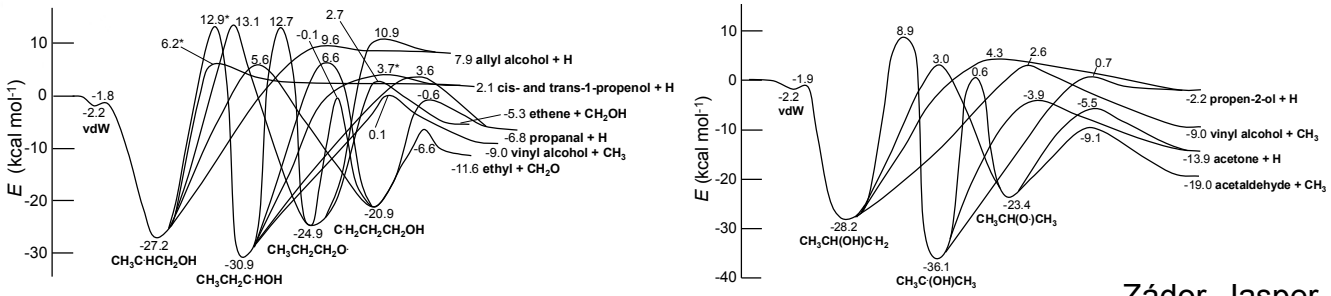


22 channels, eliminations, complicated isomerizations, etc.

Complexity of PES Dramatically Increases with Unsaturation

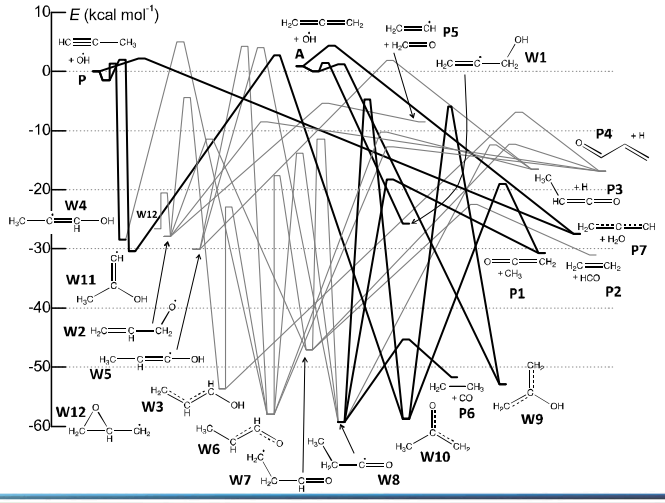
propane + OH: no wells (abstraction only)

propene + OH: 7 wells



Zádor, Jasper, Miller, PCCP 2009

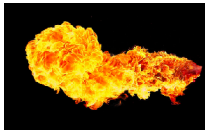
allene/propyne + OH: 20+ wells, 12 can be reached via < 5 kcal mol^{-1} barriers

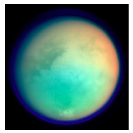


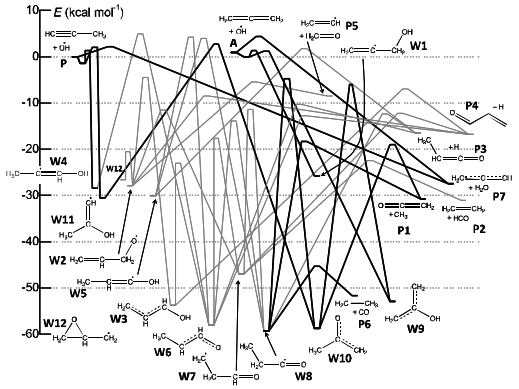
Zádor, Miller, PROCI 2015

Perspective

Automation is necessary.







Automation is possible in elementary kinetics calculations, mainly to speed up research, and generalize knowledge, and explore.

Fundamentally new pathways often involve difficult electronic structure problems, very hard to automate blindly.

Also, high unsaturation is complicated as well as roaming and barrierless pathways, and excited states.