SAND2020-11379PE

Automated Chemical Kinetics

Judit Zádor
Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA

Department of Chemistry Seminar

October 14, 2020

West Virginia University (virtual)

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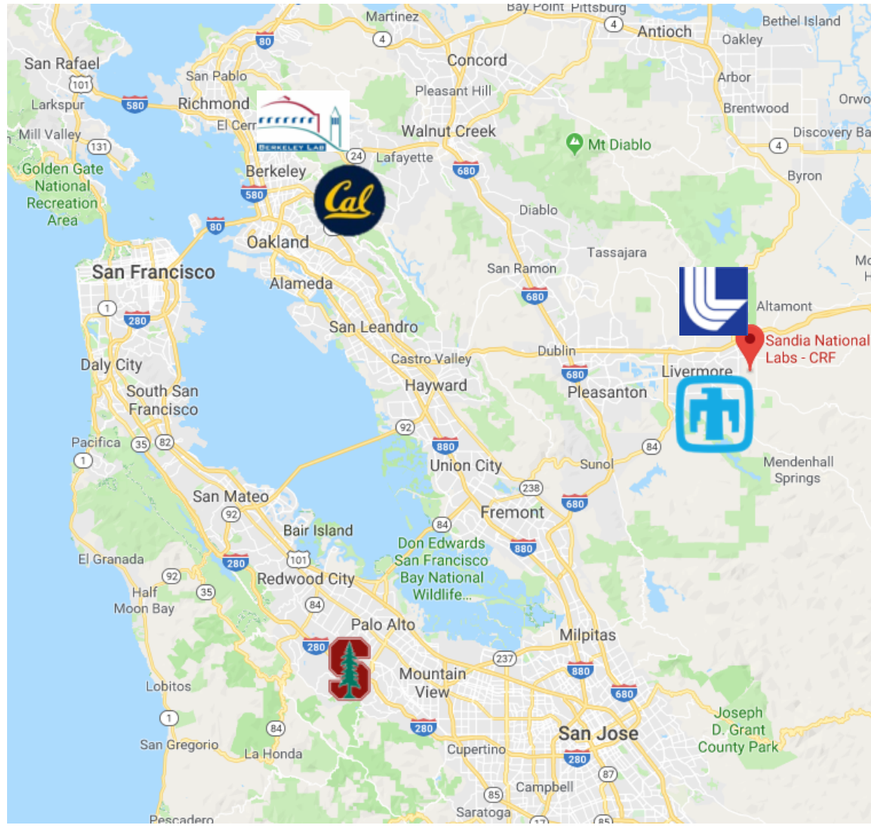
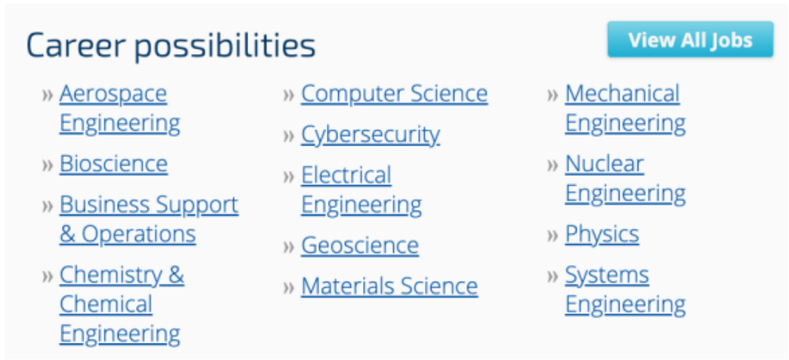
Sandia National Laboratories - Combustion Research Facility



https://www.sandia.gov/careers/ and various internship programs



Acknowledgement

Current and former postdocs contributing to this presentation


Ruben van de Vijver (now at U Ghen, Belgium)


Amanda L. Dewyer


Sangeeta Sur


Eric D. Hermes


Maciej Gierada

Collaborators for work in the presentation

Leonid Sheps (Sandia)
Habib N. Najm (Sandia)
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Richard H. West (Northeastern)
David Bross (Argonne)
Stephen J. Klippenstein (Argonne)
William H. Green (MIT)
Yury Suleimanov (Cyprus Institute)

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Exascale Catalytic Chemistry (ECC) project (ecc-project.sandia.gov)
Gas Phase Chemical Physics program of the US Department of Energy (DOE)

Outline

Brief introduction to combustion chemistry and gas-phase kinetics

Automated PES search with KinBot for gas-phase systems

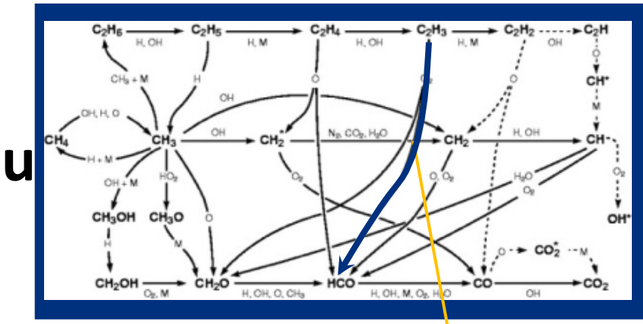
Recent applications of KinBot

Automated PES search for heterogeneous catalysis

Perspective: Complex workflows

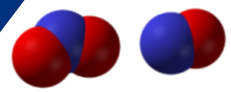
What is combustion chemistry?

Fu

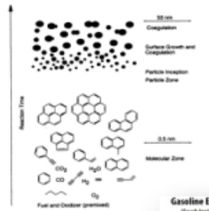


$_2O$ + energy

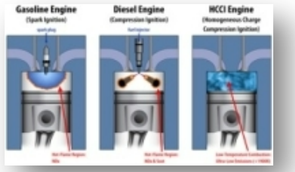
NO_x?



soot?

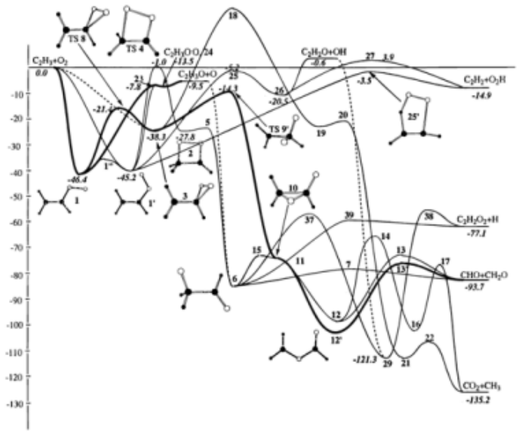


timing?



P and *T* dependence?

300 – 3000 K, 10 – 10^6 Torr

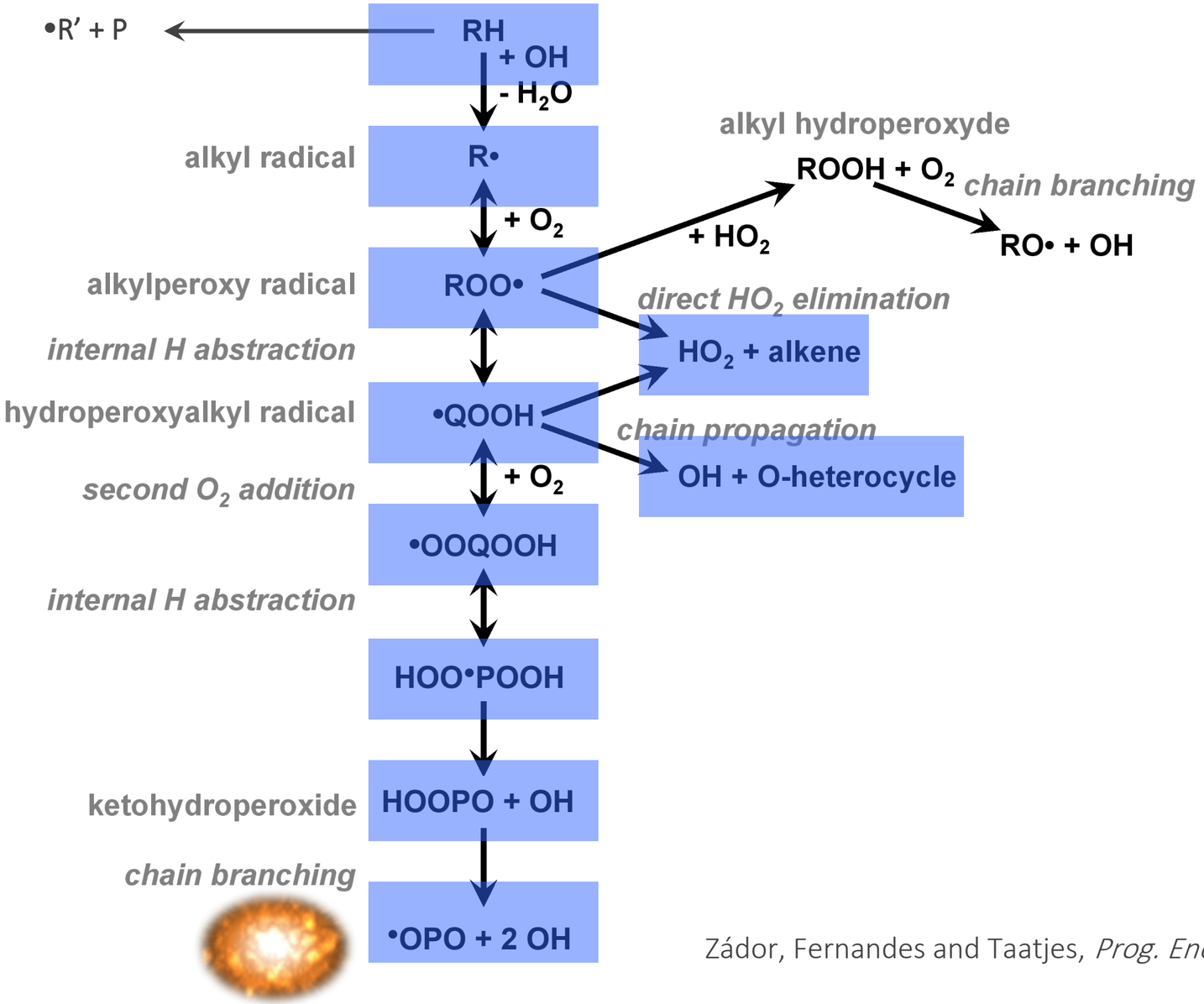


Mebel AM, Diau EWG, Lin MC, Morokuma K. *J Am Chem Soc* **1996,** 118:9759

At least 8 papers on the reaction kinetics of vinyl + O_2!

Details of combustion chemistry are critical in several areas.

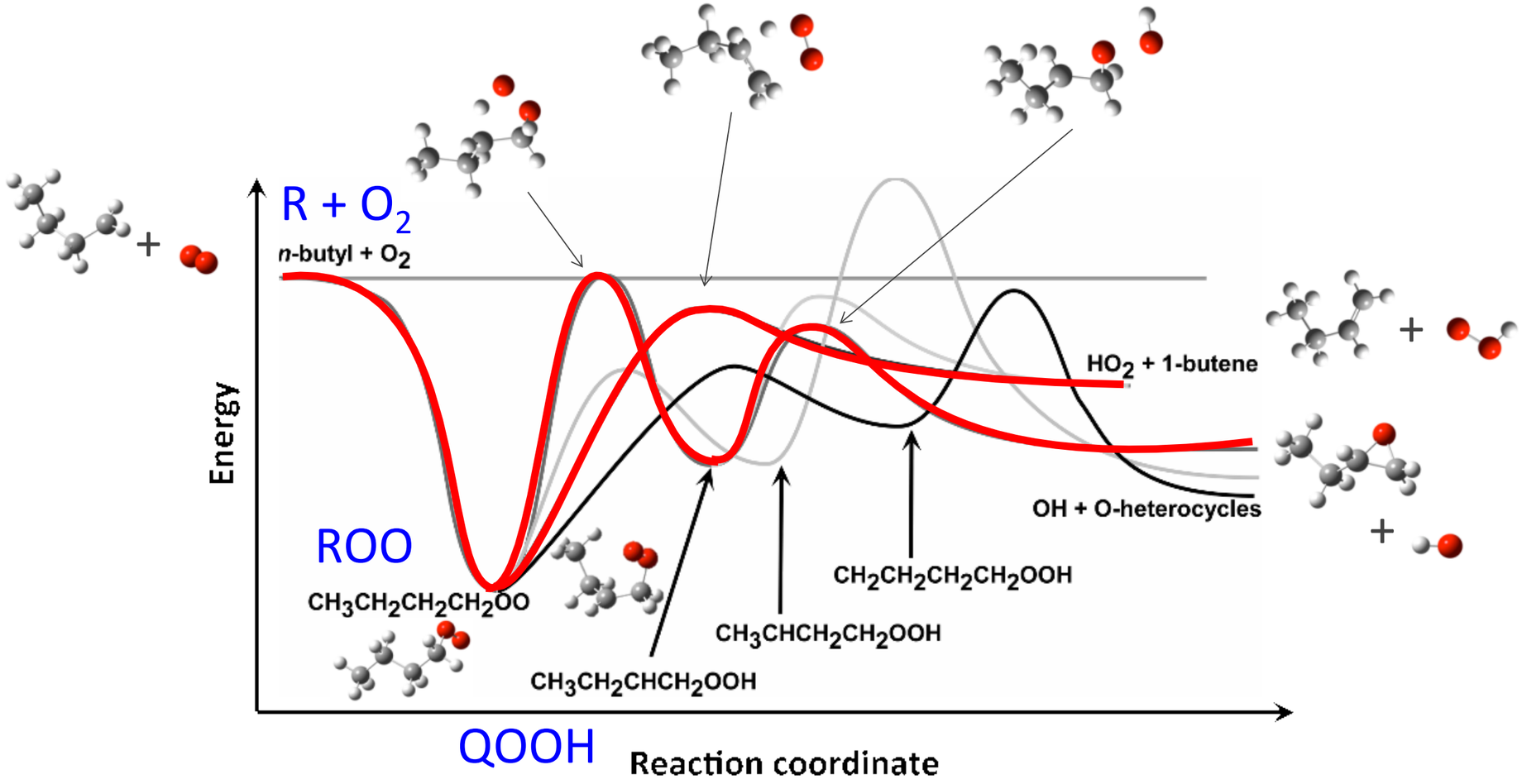
Reactions of alkyl radicals with O_2 control hydrocarbon autoignition at low T (< 900 K)



Zádor, Fernandes and Taatjes, *Prog. Energ. Comb. Sci.* 2011

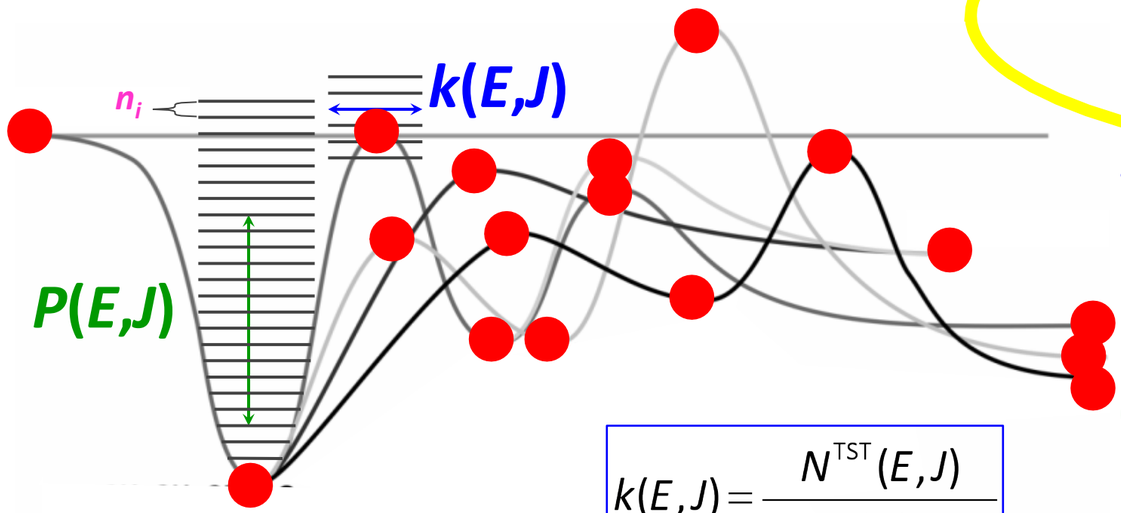
Note that the same set of reactions also plays an important role under atmospheric conditions.

A typical alkyl + O_2 potential energy surface (PES)



- Complicated competition between pathways.
- PESs get more complicated with increasing chain length.
- Functional groups influence the height of the barriers, sometimes dramatically.

The machinery of calculating rate coefficients from a PES: Master Equation



$$k(E,J) = \frac{N^{\mathrm{TST}}(E,J)}{h\rho^{\mathrm{reactant}}(E,J)}$$

Energy and other properties of stationary points (minima and saddle points) are calculated from quantum chemistry.

- electronic barrier
- ZPE
- harmonic frequencies
- anharmonic modes
  - hindered rotors
  - umbrella motions
  - etc.
- variational barrier
- rotational symmetry number
- tunneling
  - width of barrier
  - etc.

Transition-state theory is used to compute energy and angular-momentum specific rate constants, $k(E,J)$.

Collisional energy transfer redistributes population among energy “levels”.

Multiple-well master equation solution gives time-dependent populations for all species.

$$\frac{\mathrm{d}n_i(E,J)}{\mathrm{d}t} = Z_i \sum_{J'} \int_{E_{0_i}}^{\infty} P_i(E,J;E',J')\, n_i(E',J')\, \mathrm{d}E' - Z_i n_i(E,J) -$$

$$\sum_{j\neq i}^{M} k_{ji}(E,J)\, n_i(E,J) + \sum_{j\neq i}^{M} k_{ij}(E,J)\, n_j(E,J) - k_{\mathrm{d}_i}(E,J)\, n_i(E,J) +$$

$$k_{\mathrm{a}_i}(E,J)\, n_{\mathrm{R}} n_{\mathrm{m}} \rho_{\mathrm{Rm}}(E,J) \mathrm{e}^{-\beta E} / Q_{\mathrm{Rm}} - \sum_{p=1}^{N_p} k_{p_i}(E,J)\, n_i(E,J)$$

$$i = I, \ldots, M$$

$$\frac{\mathrm{d}\left|w(t)\right\rangle}{\mathrm{d}t} = \mathbf{G}\left|w(t)\right\rangle$$

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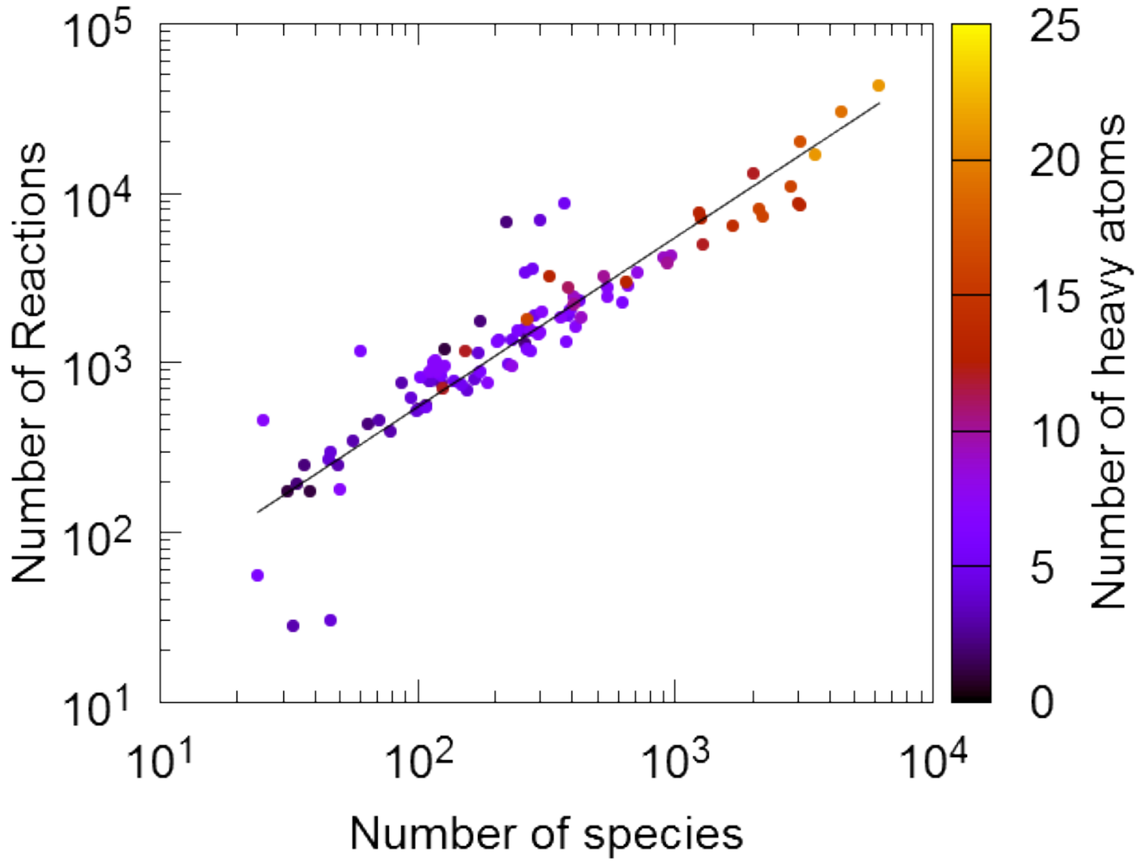
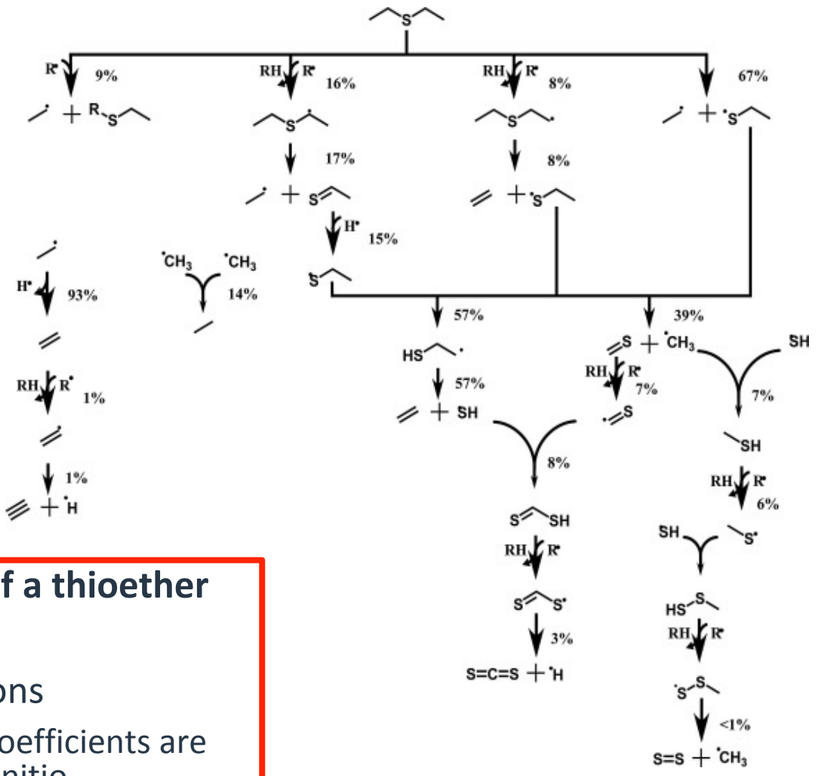
Detailed combustion mechanisms are data hungry



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



Pyrolysis of a thioether

66 species

444 reactions

- **23** rate coefficients are from ab initio calculations
- **421** rate coefficients are estimates

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

- Modern mechanisms are generated by computer codes (e.g., RMG, Genesys, etc.), but the underlying databases are largely empty, and thus the machinery relies on estimates.
- Atmospheric, interstellar, and catalytic chemistry models are plagued by the same problem.

We need to automate kinetics to get reliable results in a meaningful timeframe!

Automated PES search for chemical reactivity should…

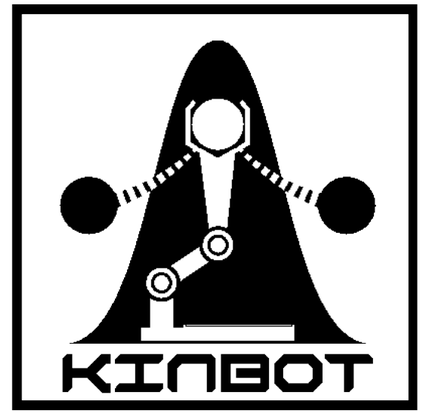
- Find all kinetically relevant reaction pathways
- Directly allow the calculation of rate coefficients as a function of pressure, temperature, or internal energy
- Require no user intervention
- Favorably scale for supercomputers
- Visualize results
- Be agnostic about quantum chemistry code and level of theory

KinBot 2.0: Translating chemistry into computer codes

Integrated tool for chemical kinetics

or

Kinetics functions for complex workflows



github.com/zadorlab/KinBot

Van de Vijver and Zádor, Computer Physics Communications 248 (2020) 106947

Python code coupled to…

Third party quantum chemistry software

- Gaussian
- Molpro
- NWChem (under development)

Atomic Simulation Environment (ASE)

Chemo-informatics tools

- OpenBabel
- RDKit

Master equation solvers

- MESS (Argonne)
- MESMER (Leeds)

Workload managers

- SLURM
- PBS

Postprocess

- PESViewer
- github.com/rubenvdvijver/PESViewer

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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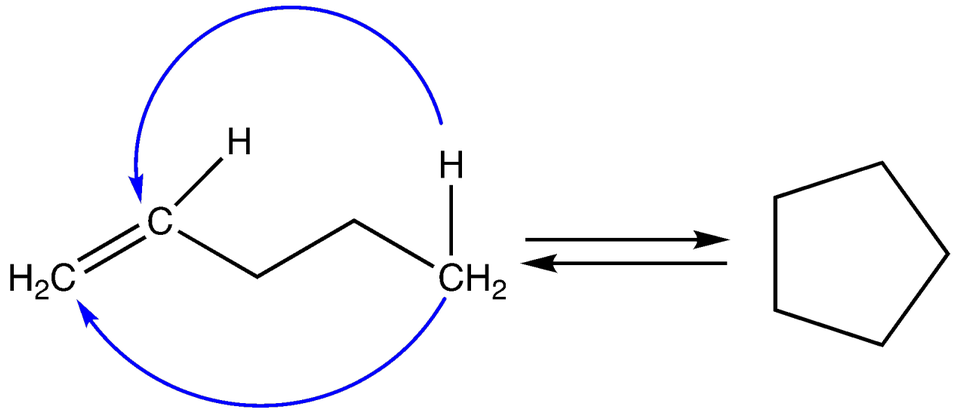
Structure comprehension + motif search (computerized arrow pushing)



Endocyclic closed-shell cyclization

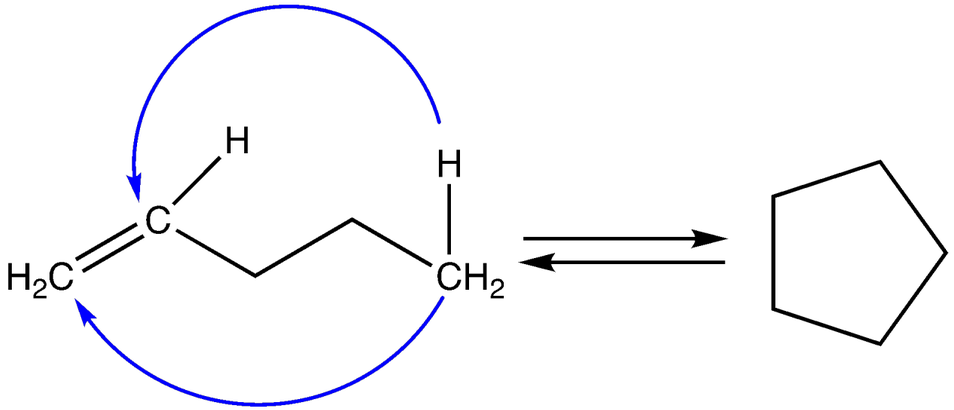
~20 reaction types

Core KinBot functionality: Find reactive saddle points

How is it done?

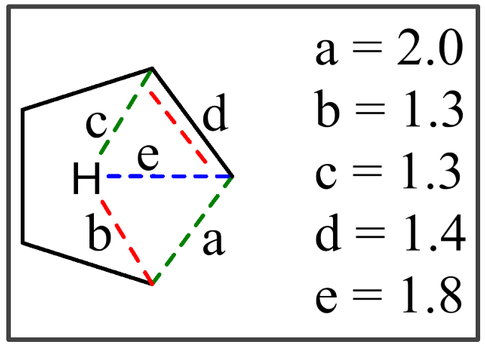
1. Identify the possibility of a reaction
2. Generate very good guess for a conformer of the saddle point
3. Optimize to nearest first-order saddle point

Use template + modify dihedrals, angles and bond lengths



Endocyclic closed-shell cyclization

~20 reaction types



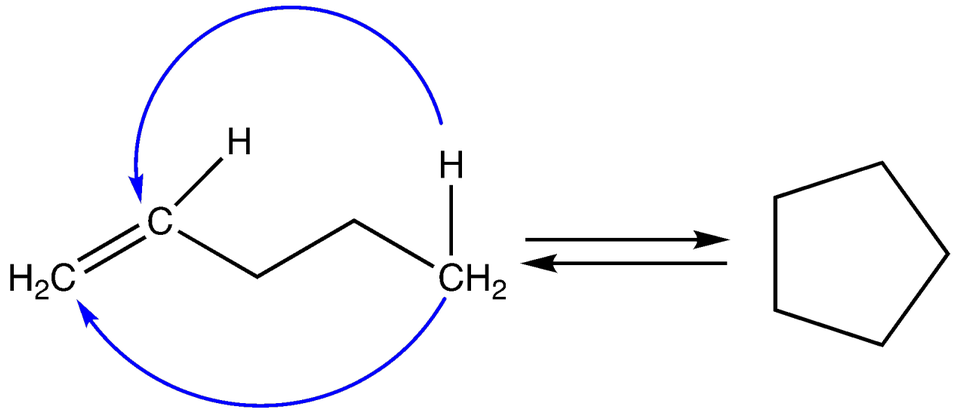
Series of constrained optimizations at a low level of theory (e.g., AM1)

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

Optimize to exact first-order saddle point



Endocyclic closed-shell cyclization

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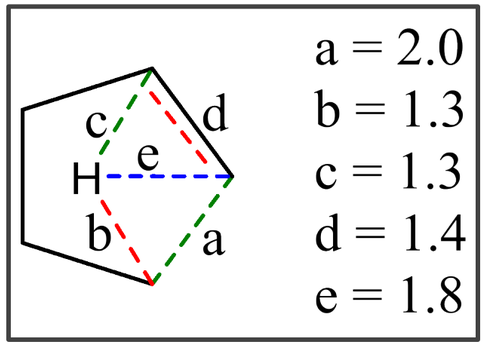
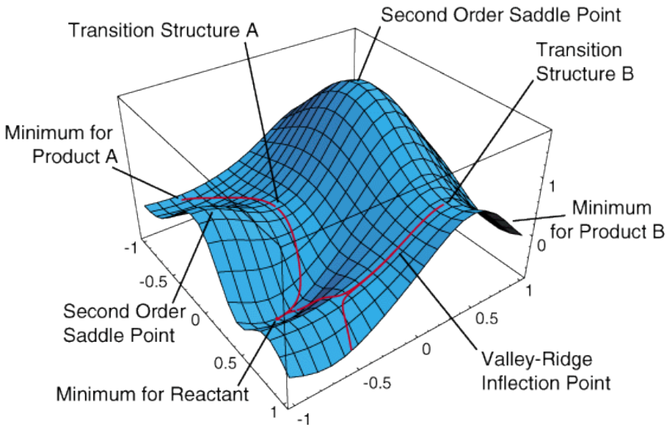
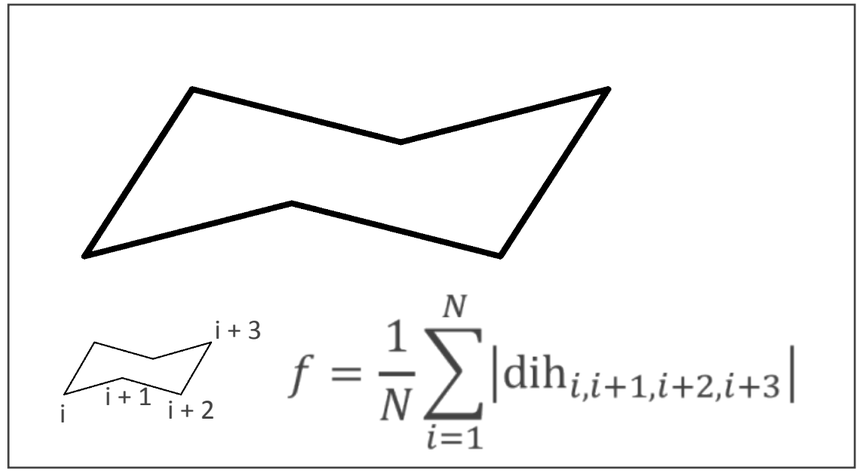


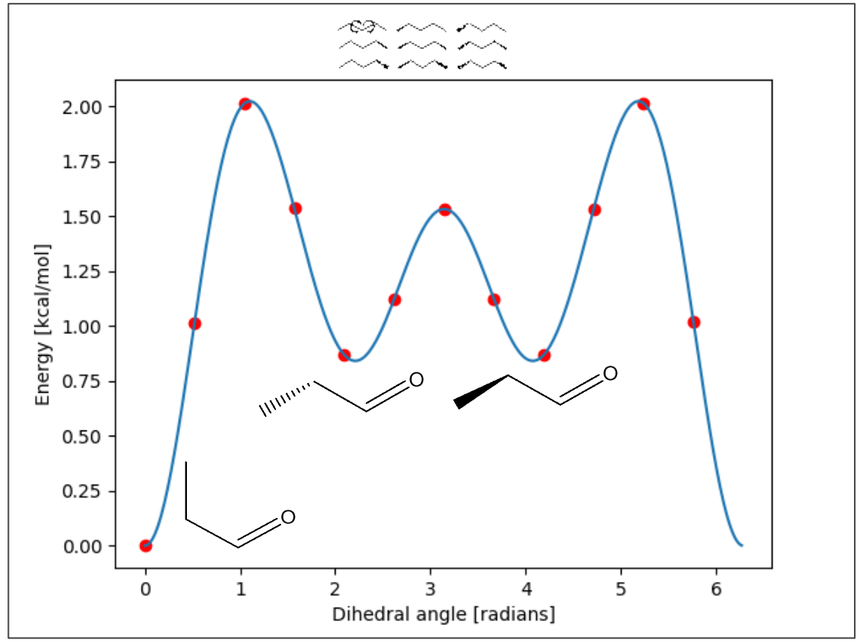
Series of constrained optimizations at a low level of theory (e.g., AM1)



Additional tools in KinBot: Steps towards accurate rate coefficients

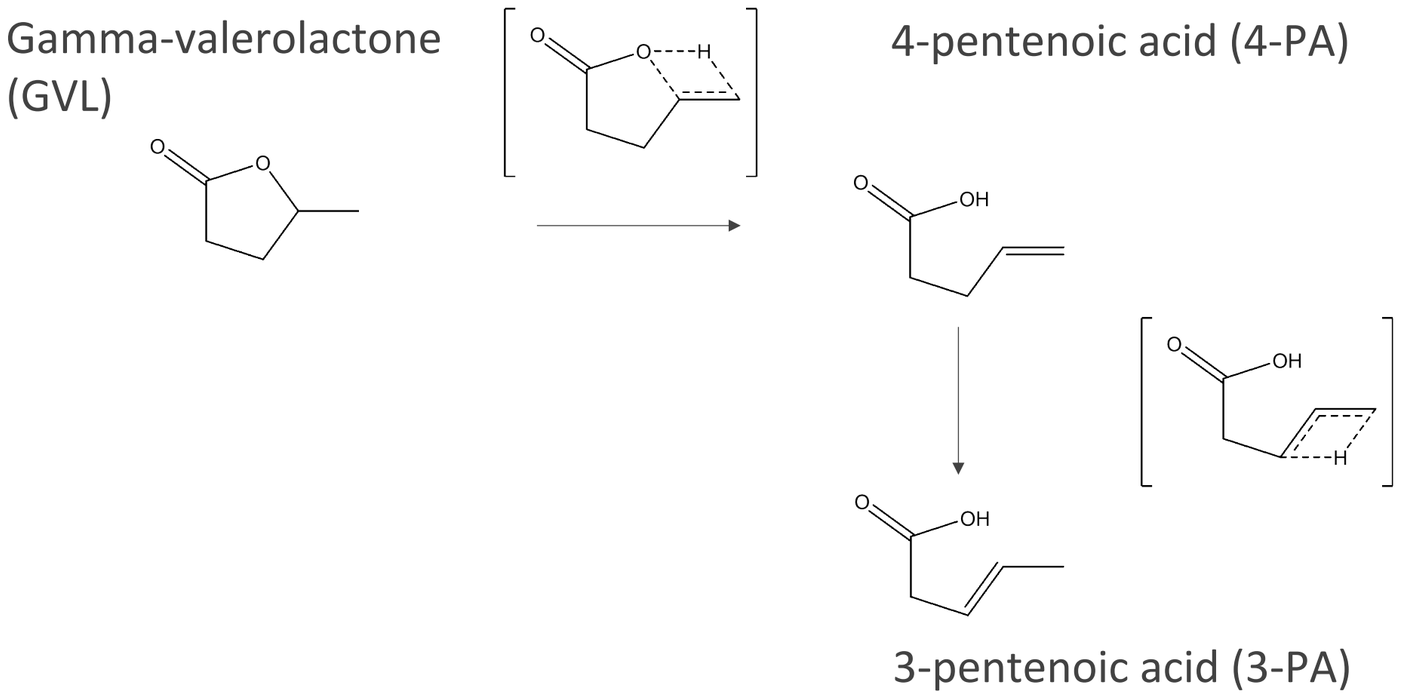
- OFF ON Conformational search
- OFF ON Higher-level optimization
- OFF ON Hindered rotor calculation
- OFF ON Coupled-cluster-like energies
- Symmetry calculation
  - Internal
  - External
    - Bond-centered
    - Atom-centered
    - Ring-centered
- OFF ON Run chemical master equation
- OFF ON Uncertainty quantification





Gamma-valerolactone thermal decomposition: Search for all channels starting from a given well

- 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)



1. De Bruycker, R. et al.; Proc. Combust. Inst. 2015, 35 (1), 515-523.
2. Ye, L. et al. ; RSC Adv. 2018, 8 (23), 12975-12983.

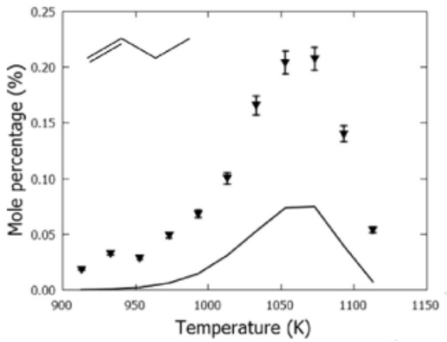
Van de Vijver and Zádor, Computer Physics Communications 248 (2020) 106947

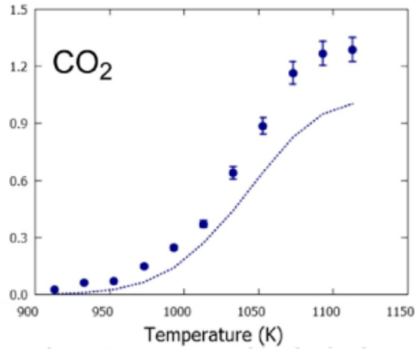
Gamma-valerolactone

Previously reported reaction (also found by KinBot)

New reaction by KinBot

New reaction with high barrier





lowest homolytic dissociation channel

88.8 kcal/mol

62.5 kcal/mol
[CC-F12: 63.33]

73.6 kcal/mol
[CC-F12: 78.53]

70.0 kcal/mol

70.2 kcal/mol

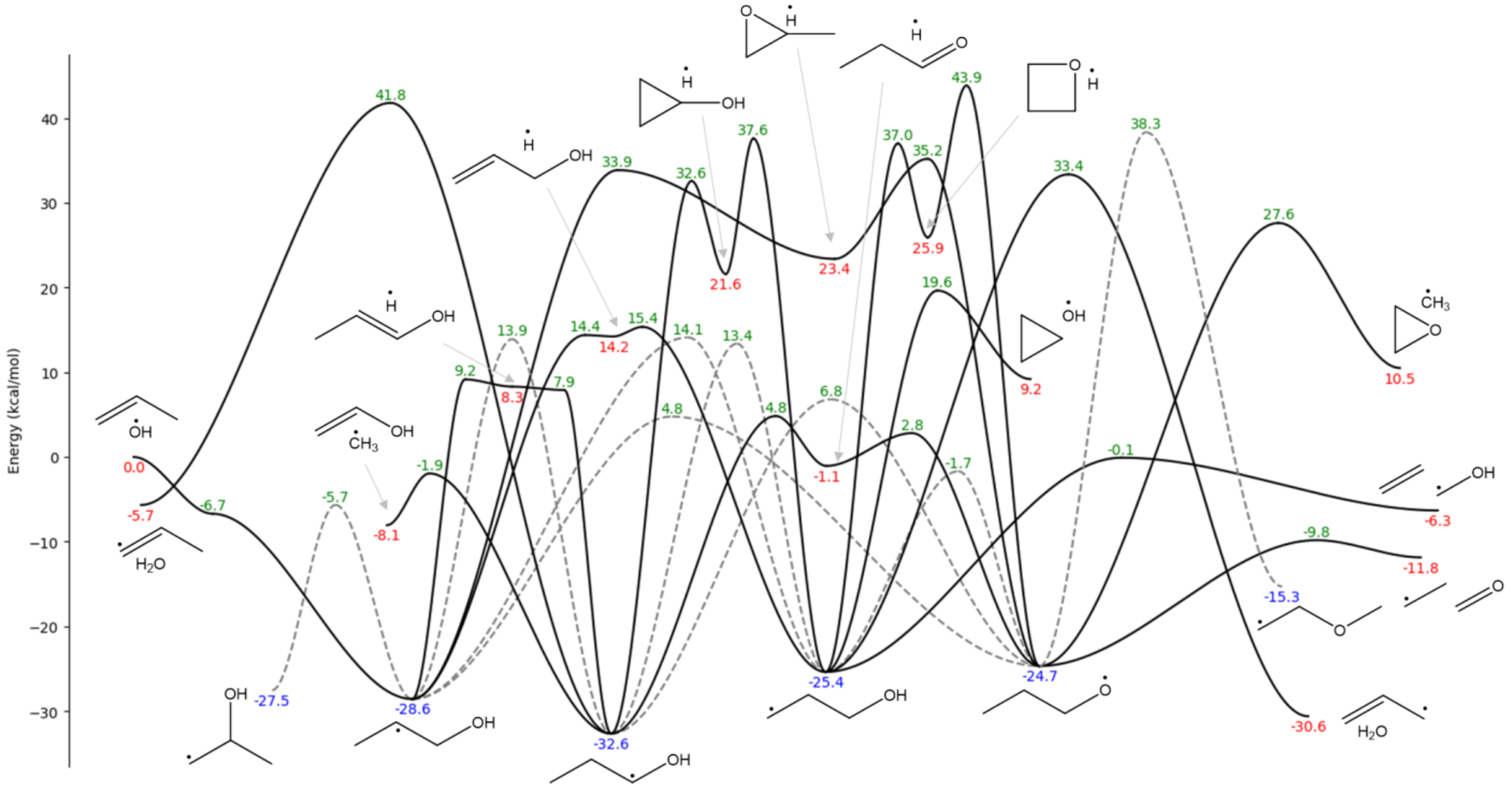
Energy (kcal/mol)

De Bruycker, R. et al.; Combust. Flame. 2016, 164, 183-200.

Van de Vijver and Zádor, Computer Physics Communications 248 (2020) 106947

C_3H_6+OH: A “complete” PES search

- Important reaction in combustion
- Studied in the past[1,2]
- Reaction searches: B3LYP/6-31G
- High-level calculations: B3LYP/6-311++G(d,p)
- KinBot agrees with previous PES for relevant energies
- Found several new high-energy channels (e.g., water elimination)



Bimolecular product formation reactions

Isomerization reactions

1. Zádor, J. et al.; PCCP 2009, 11 (46), 11040-11053.
2. Kappler, C. et al.; Z. Phys. Chem., 2011, 225, 1271.

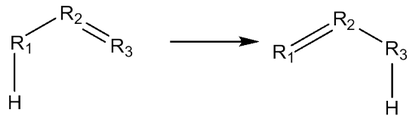
Van de Vijver and Zádor, Computer Physics Communications 248 (2020) 106947

Sigmatropic [1,3] hydrogen shift: Capturing trends

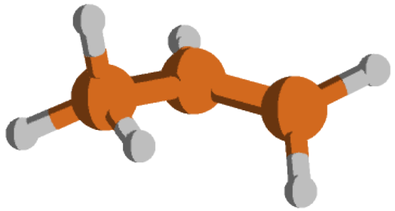
- A pericyclic reaction. Net result: one σ-bond is changed to another σ-bond in an uncatalyzed intramolecular process
- Woodward-Hoffmann
- Möbius-Hückel

→ Antrafacial is thermally allowed

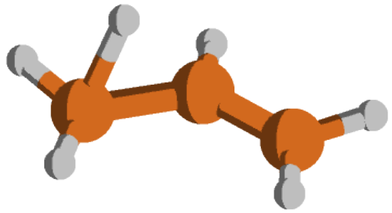
→ Suprafacial is thermally forbidden



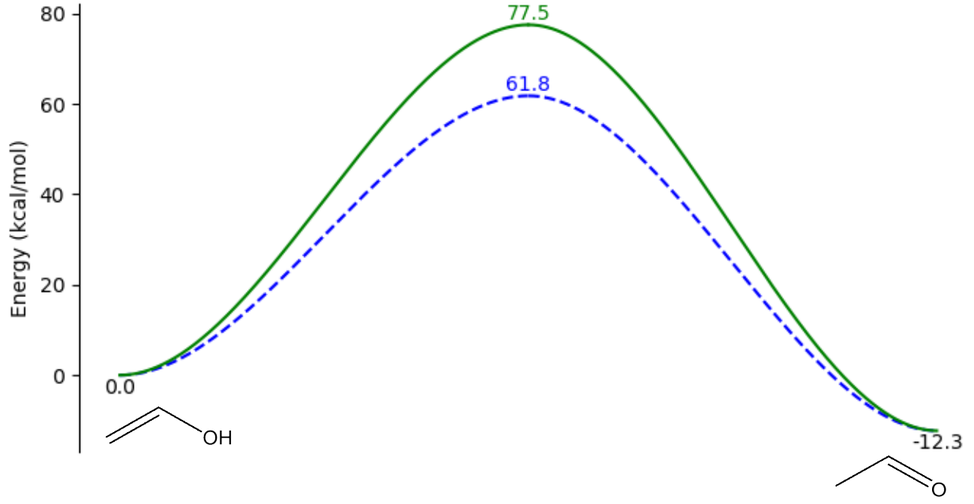
antrafacial

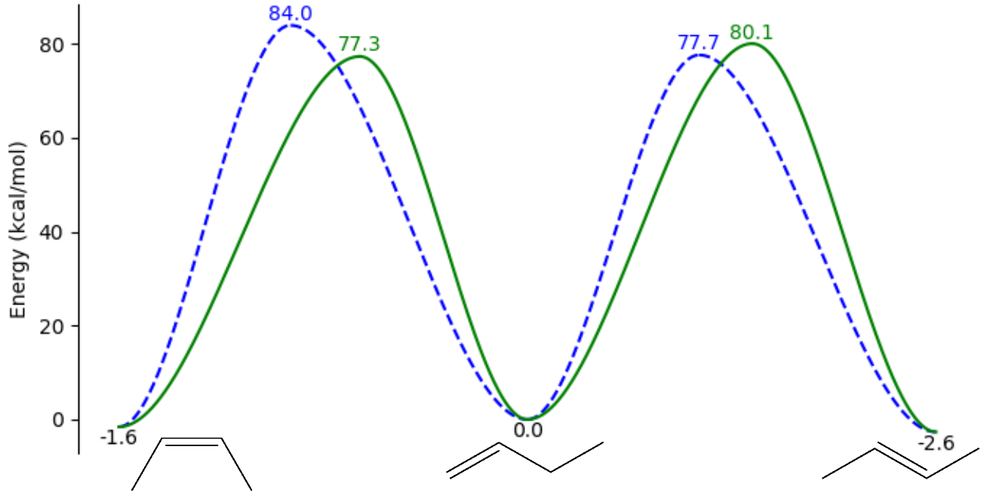


suprafacial



Reactant	Antra	Supra	Product
Vinyl alcohol	**61.8**	77.5	Actealdehyde
Propene	**81.2**	83.5	Propene
Formic acid	**38.5**		Formic acid
2-methyl-1-butene	**75.7**	78.9	2-methyl-2-butene
Propanal	**72.7**	83.9	Trans-1-propenol
Propanal	77.1	82.3	Cis-1-propenol
1-butene	84.0	**77.3**	Cis-2-butene
1-butene	77.7	80.1	Trans-2-butene
3-methyl-1-butene	81.9	**74.9**	3-methyl-2-butene
4-pentenoic acid	87.6	**78.7**	Cis-3-pentenoic acid
4-pentenoic acid	81.8	82.3	Trans-3-pentenoic acid





Some reactions violate the rules!

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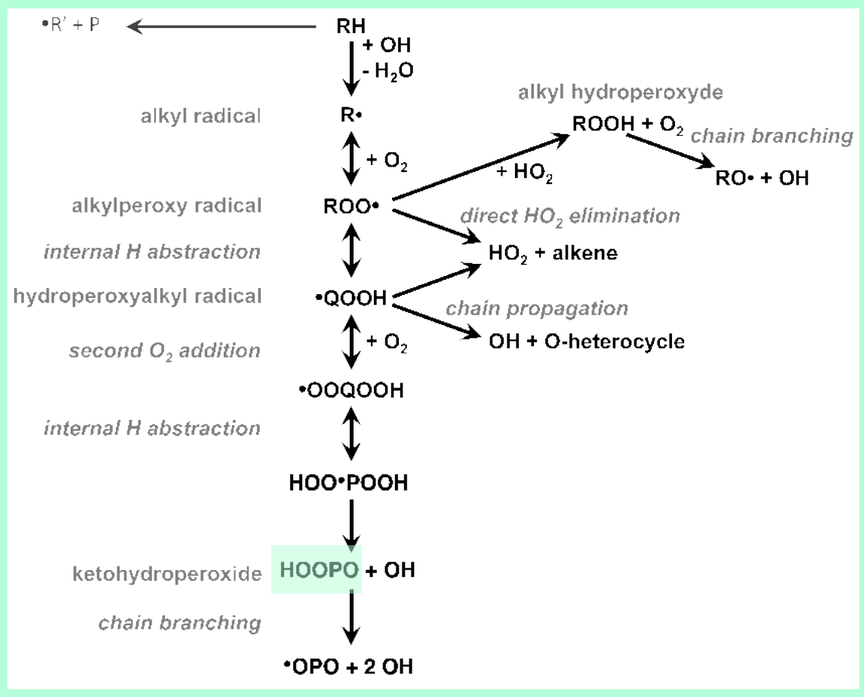
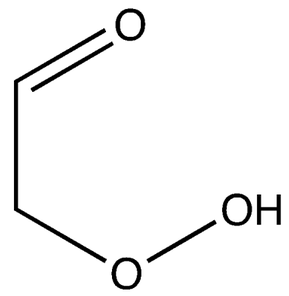
Autoignition and ketohydroperoxides (KHPs)

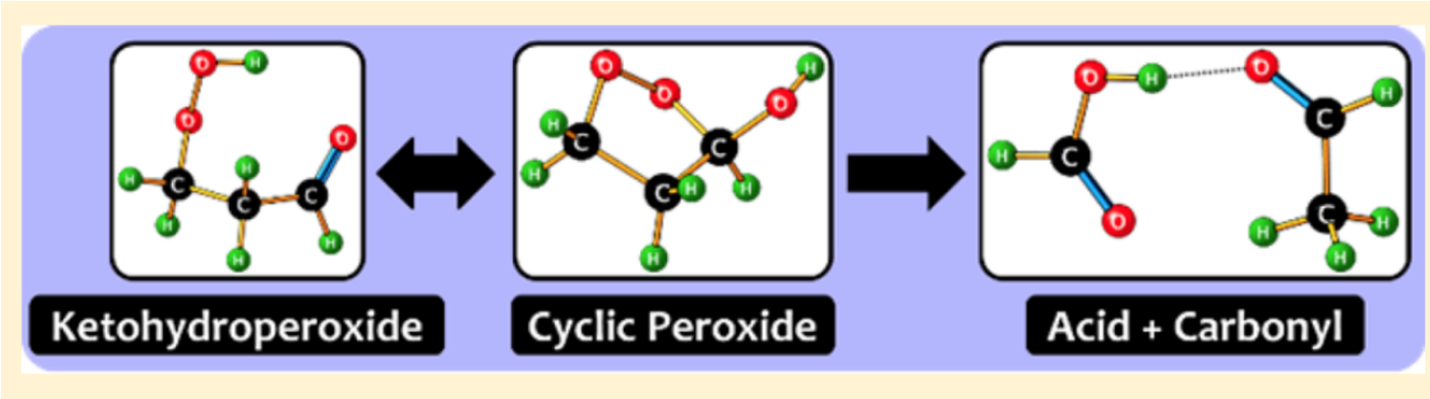




KHPs are

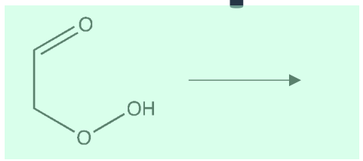
- The lowest *E* products in the first stages of low-temperature oxidation of hydrocarbons
- Closed shell molecules

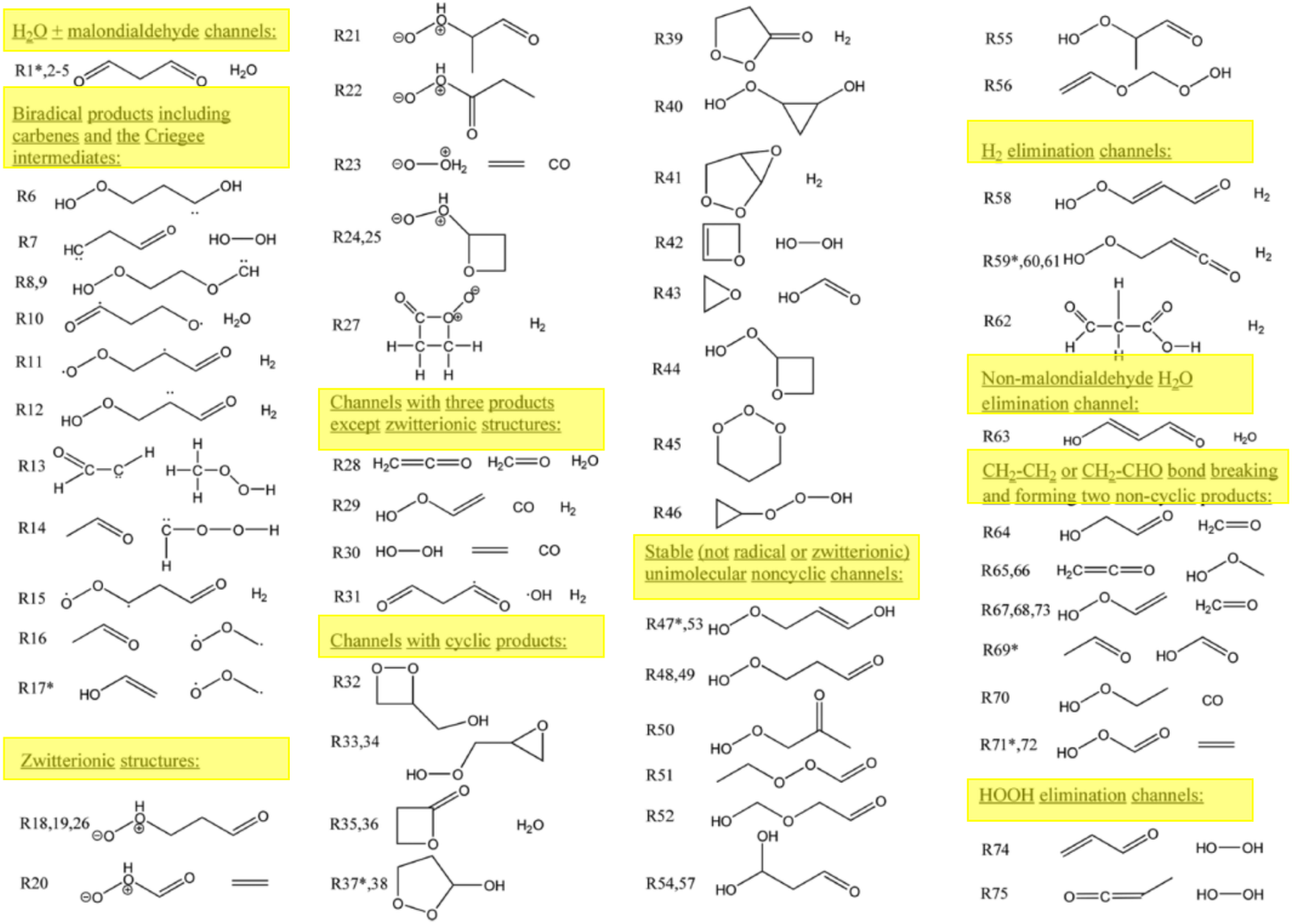
Jalan et al., 2013, JACS, “Korcek decomposition”



Are there other important pathways besides the cyclic peroxide formation?
Can we find them with automated tools?

Comparative ketohydroperoxide study





Grambow, Jamal, Li, Green, Zádor, Suleimanov, *J. Am. Chem. Soc.* **2017**

- First benchmark / comparative study of PES search methods
- We discovered **75 reaction pathways** for this simple molecule with the combination of four methods:
  - Single-Component Artificial Force Induced Reaction (SC-AFIR) Method **7**
  - Freezing String Method (FSM) **39**
  - Single-Ended Growing String Method (SSM) **50**
  - Growing String Method (GSM) **46**
  - KinBot 1.0 (old version) **48**

New combinatorial approach: **71**

Van de Vijver, Zádor, Marin, Van Geem,
ACS abstract, 2019 San Diego

Response paper

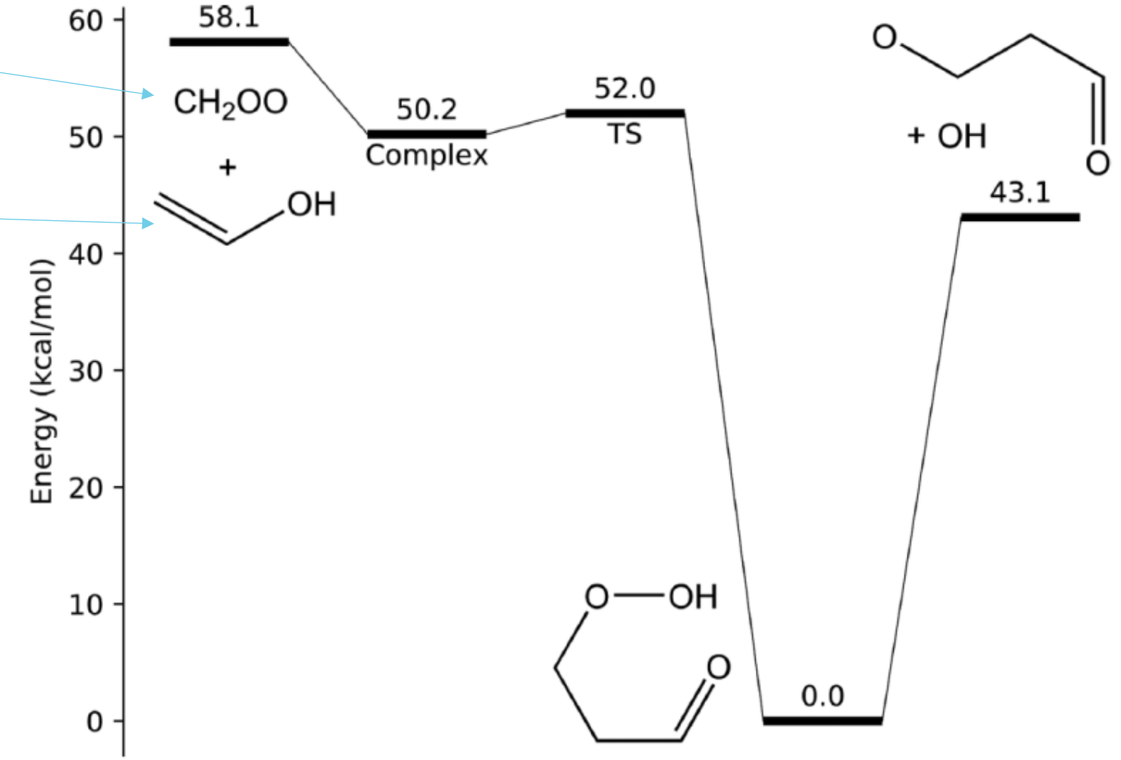
Maeda, S.; Harabuchi, Y.,
J. Chem. Theory Comput. 2019, 15, 2111-2115.

Comparative ketohydroperoxide study

RCCSD(T)-F12a/cc-pVTZ-F12//UM06-2X/aug-cc-pVTZ

Criegee intermetiate
(formaldehyde oxide)

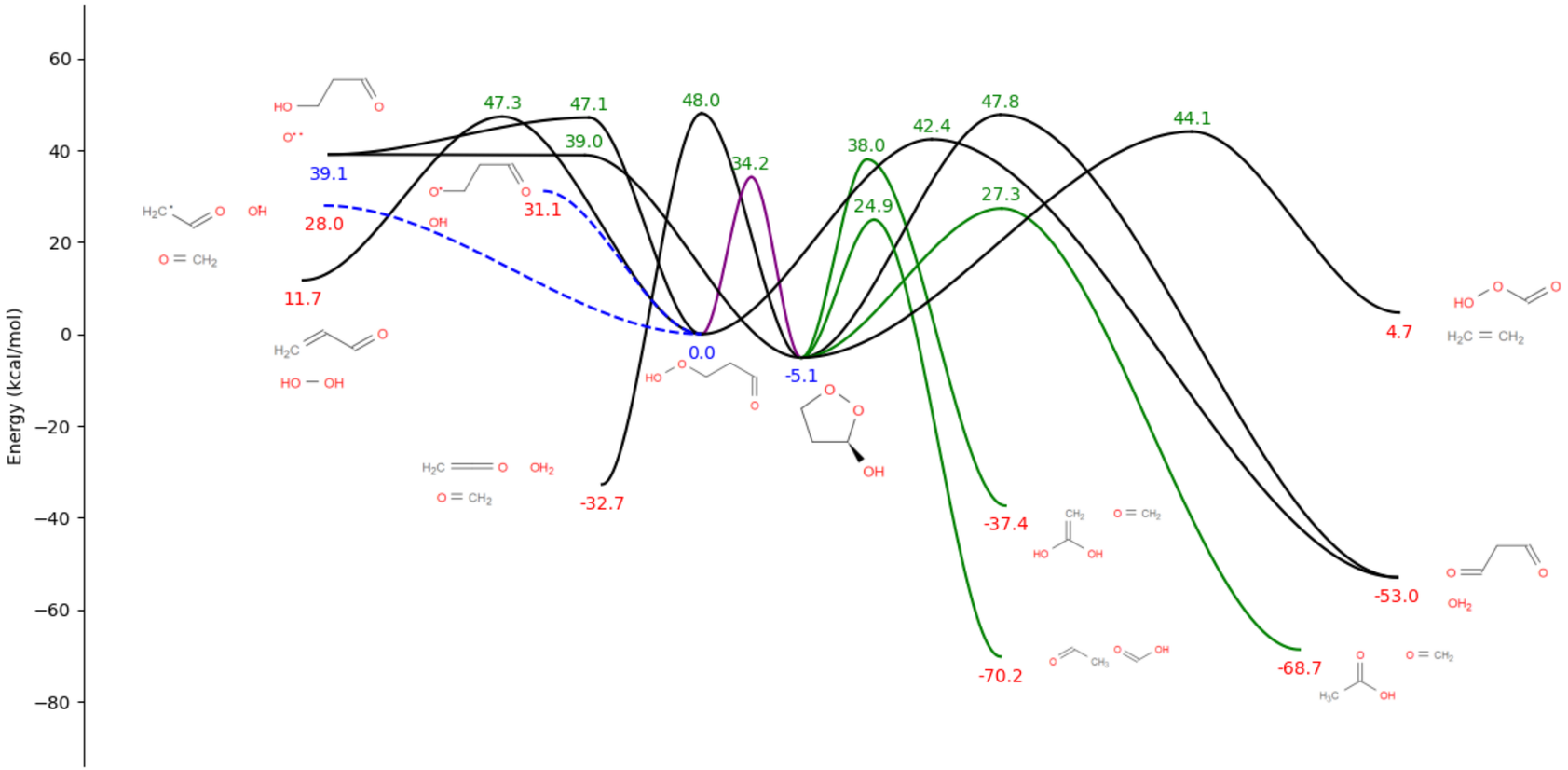
Ethenol



One of the most interesting reactions we found could play a role in atmospheric systems generating OH.

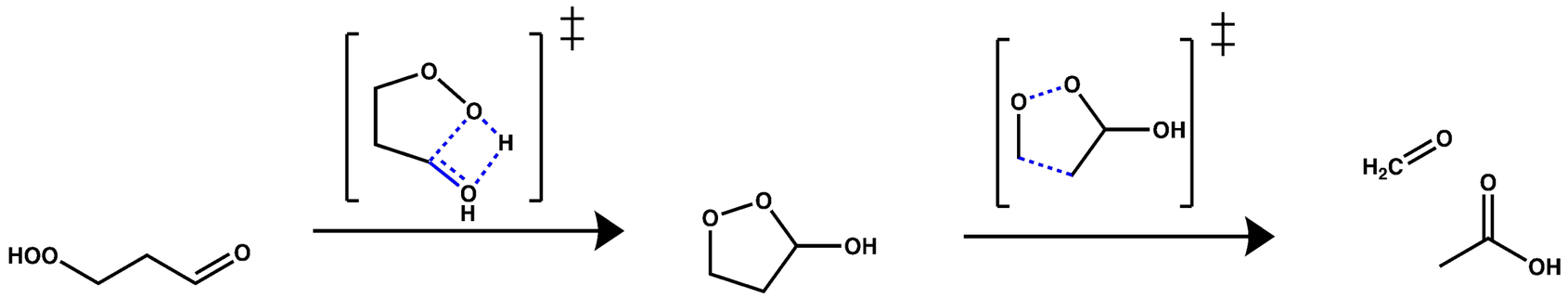
Grambow, Jamal, Li, Green, Zádor, Suleimanov, *J. Am. Chem. Soc.* **2017**

Kinetics calculations for small KHP



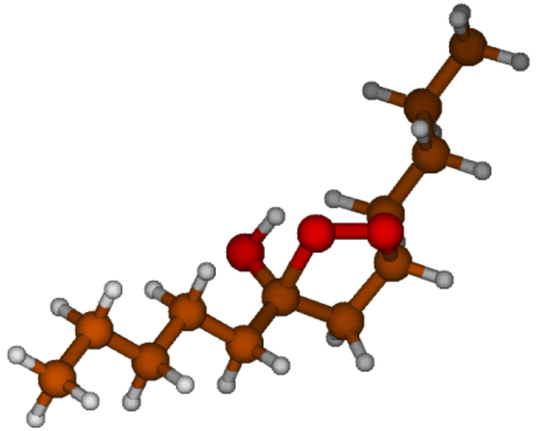
- Our homolytic reaction search shows that there isn't just one, but two important homolytic scissions.
- Barrierless reactions require treatment with Variable Reaction Coordinate TST (VRC-TST) with multi-reference electronic structure methods.
- These are currently not automated.

Simplified calculations for ~60 KHPs in n-dodecane and i-octane combustion mechanisms

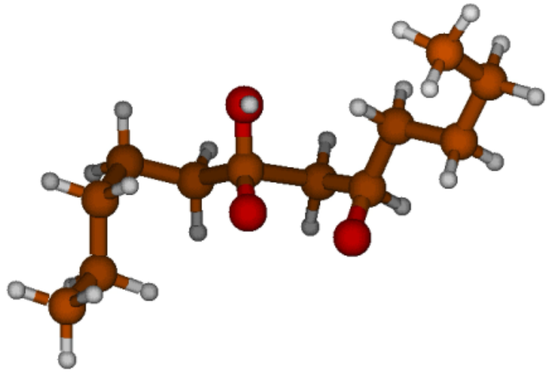


Cyclic Peroxide Formation

Korcek Decomposition



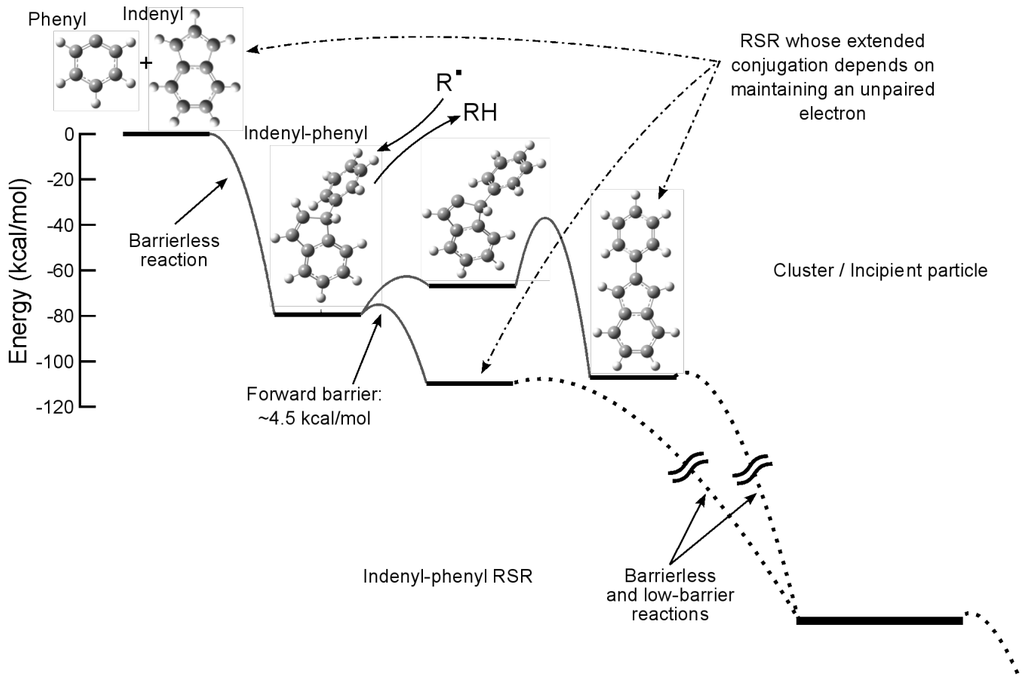
Cyclic Peroxide Formation TS



Korcek Reaction TS

These large molecules require simplifications in the methodology

KinBot and machine learning: Towards understanding soot formation



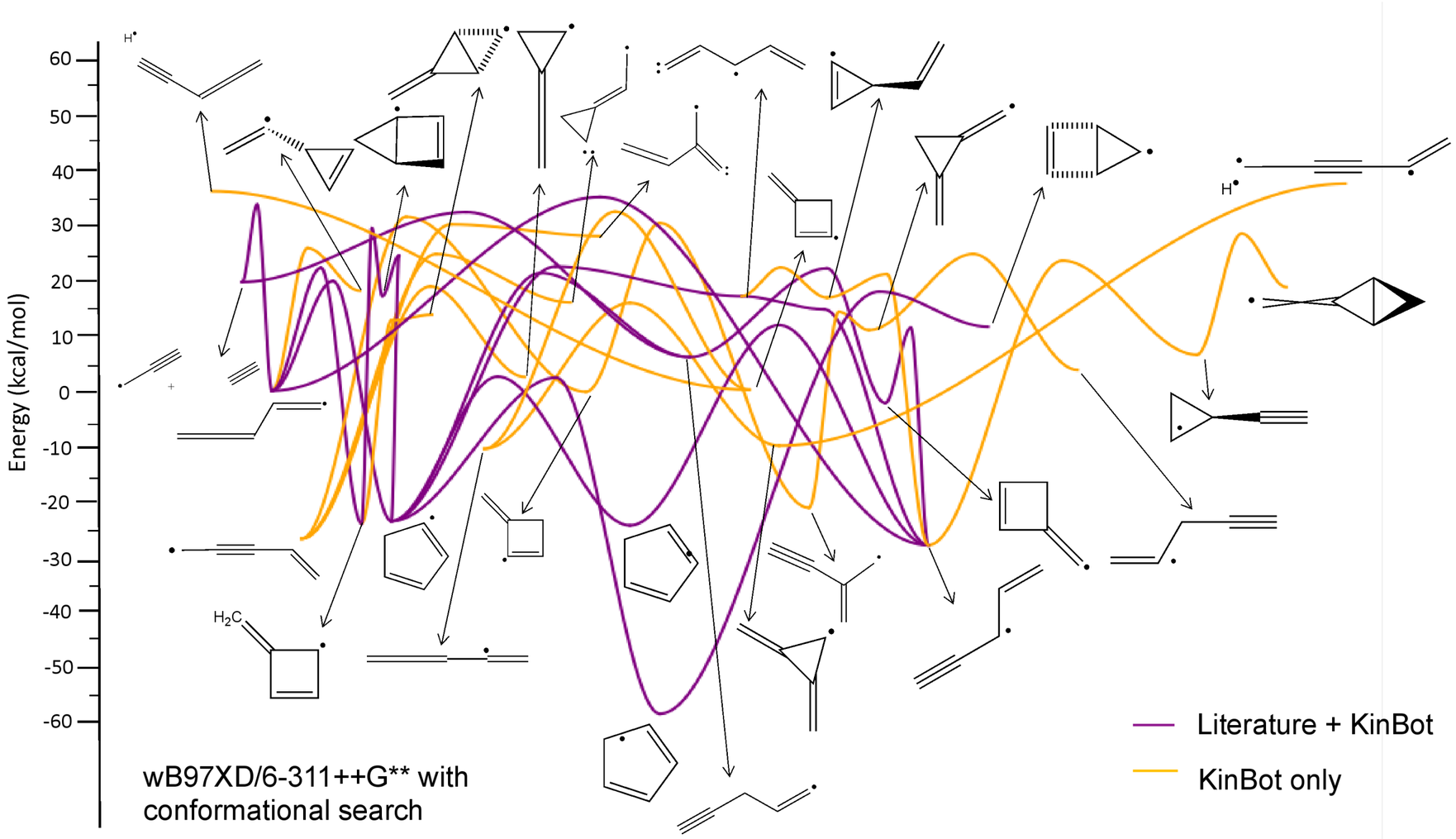
Potential energy diagram showing formation of an adduct of a resonantly stabilized radical (RSR) (indenyl) and another radical species (phenyl). Subsequent H abstraction stabilizes the bond and regenerates an RSR whose extended conjugation requires an unpaired electron. Repeated similar reactions lead to hydrocarbon clustering and incipient soot formation.

K. O. Johansson, M. P. Head-Gordon, P. E. Schrader, K. R. Wilson, H. A. Michelsen, Science 361, 997–1000 (2018)

Starting with smaller systems to study the growth of resonantly stabilized radicals, e.g. C_5H_5

- Explore & identify all relevant transition states and structures using KinBot
- Generate many PES samples, and use to train neural network potential energy surface (NNPES) models
- Leverage these using multifidelity methods to explore and build NN-PES models for successively larger systems

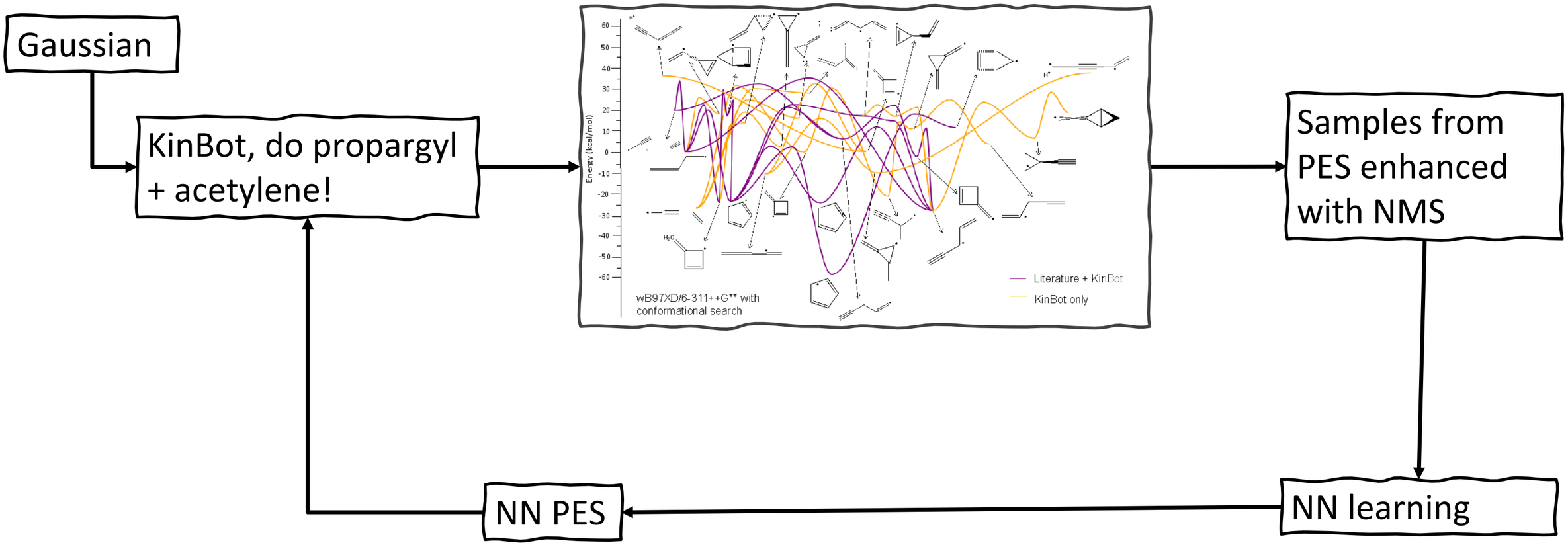
Propargyl + acetylene, a classic reaction



KinBot has unveiled new pathways even for a simple reaction

For machine learning applications, structures are sampled and perturbed to represent the chemically relevant configurations for a given class of processes

Can machine-learned PESs be used for kinetics?



Can we recreate the original PES and rate coefficients with the NN PES?

- Is the NN PES and its gradient smooth enough?

This exercise never has been done before.

Outline

Brief introduction to combustion chemistry and gas-phase kinetics

Automated PES search with KinBot for gas-phase systems

Recent applications of KinBot

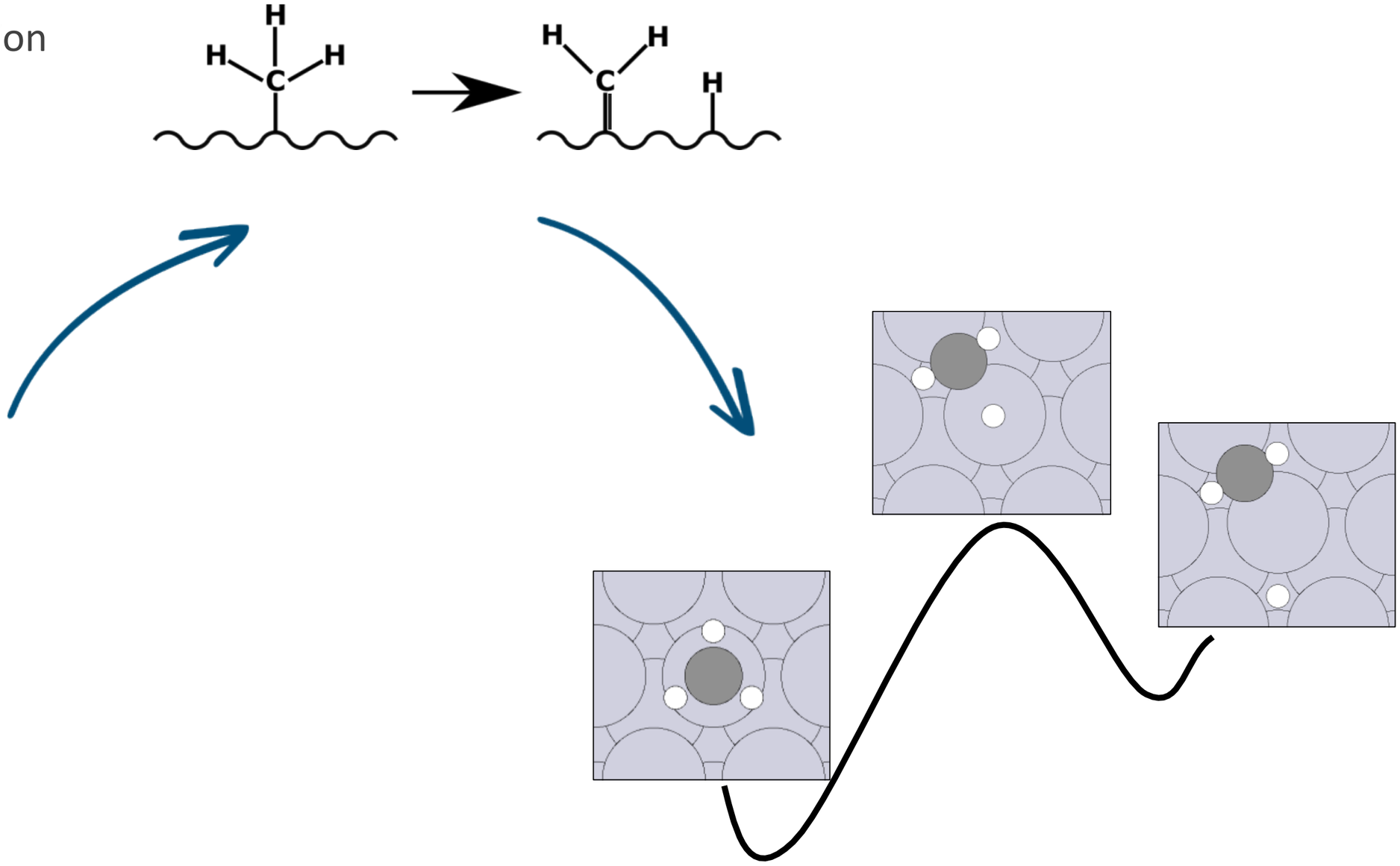
Automated PES search for heterogeneous catalysis

Perspective: Complex workflows

From formal catalytic reactions to *ab initio* kinetics

RMG reaction representation

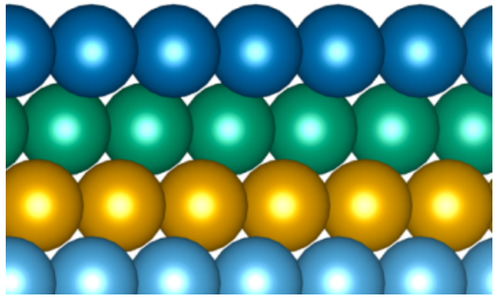
```
- index: 0
  reaction: CH3X + X <=> CH2X + HX
  reaction_family: Surface_Abstraction
  reactant: |

    1 *1 C u0 p0 c0 {2,S} {3,S} {4,S} {5,S}
    2 *2 H u0 p0 c0 {1,S}
    3    H u0 p0 c0 {1,S}
    4    H u0 p0 c0 {1,S}
    5    X u0 p0 c0 {1,S}
    6 *3 X u0 p0 c0
  product: |

    1 *1 C u0 p0 c0 {3,S} {4,S} {5,D}
    2 *2 H u0 p0 c0 {6,S}
    3    H u0 p0 c0 {1,S}
    4    H u0 p0 c0 {1,S}
    5    X u0 p0 c0 {1,D}
    6 *3 X u0 p0 c0 {2,S}
```



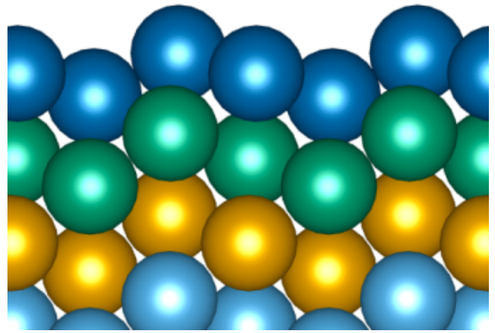
There are many potential binding sites even for simple surfaces

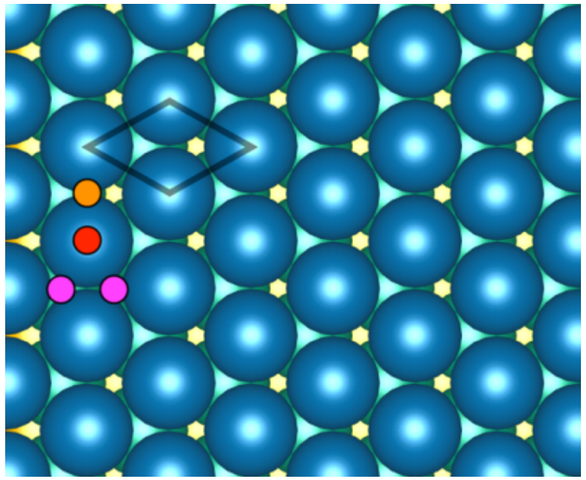
FCC(111)

FCC(211)

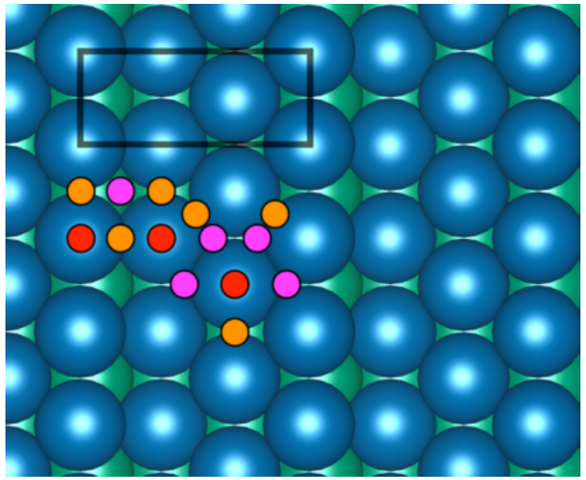


← Side view →





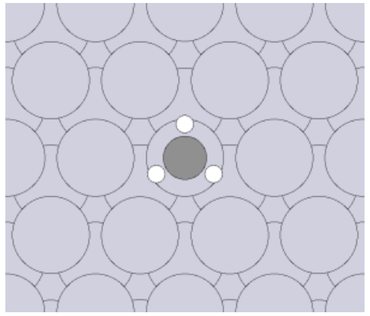
← Top view →

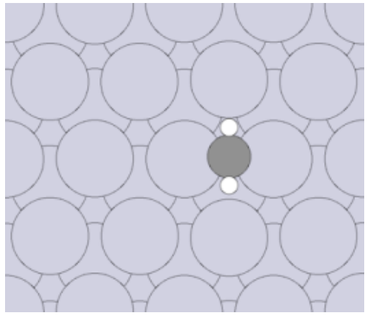


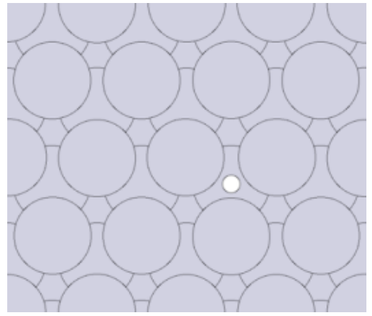
...and there are even more for high-index metal facets or nanoparticles.

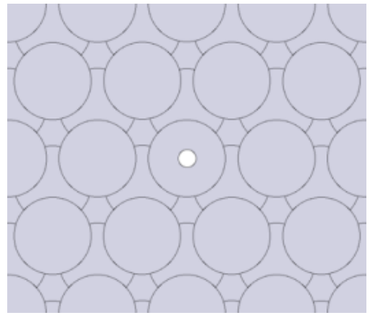
There are only few minima on Pt(111) for these species

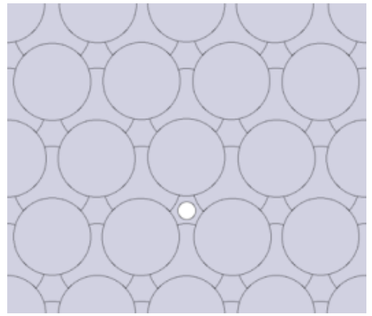
CH_3 → CH_2 + H



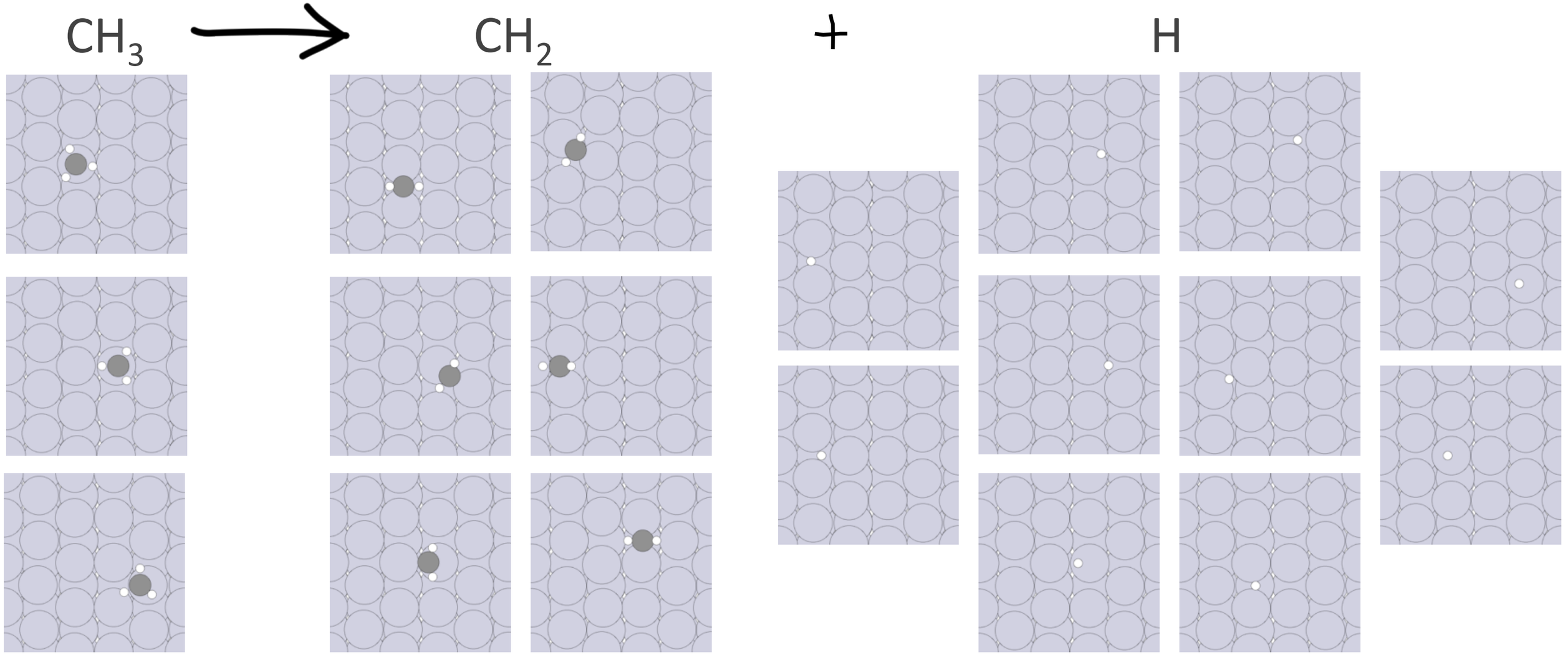




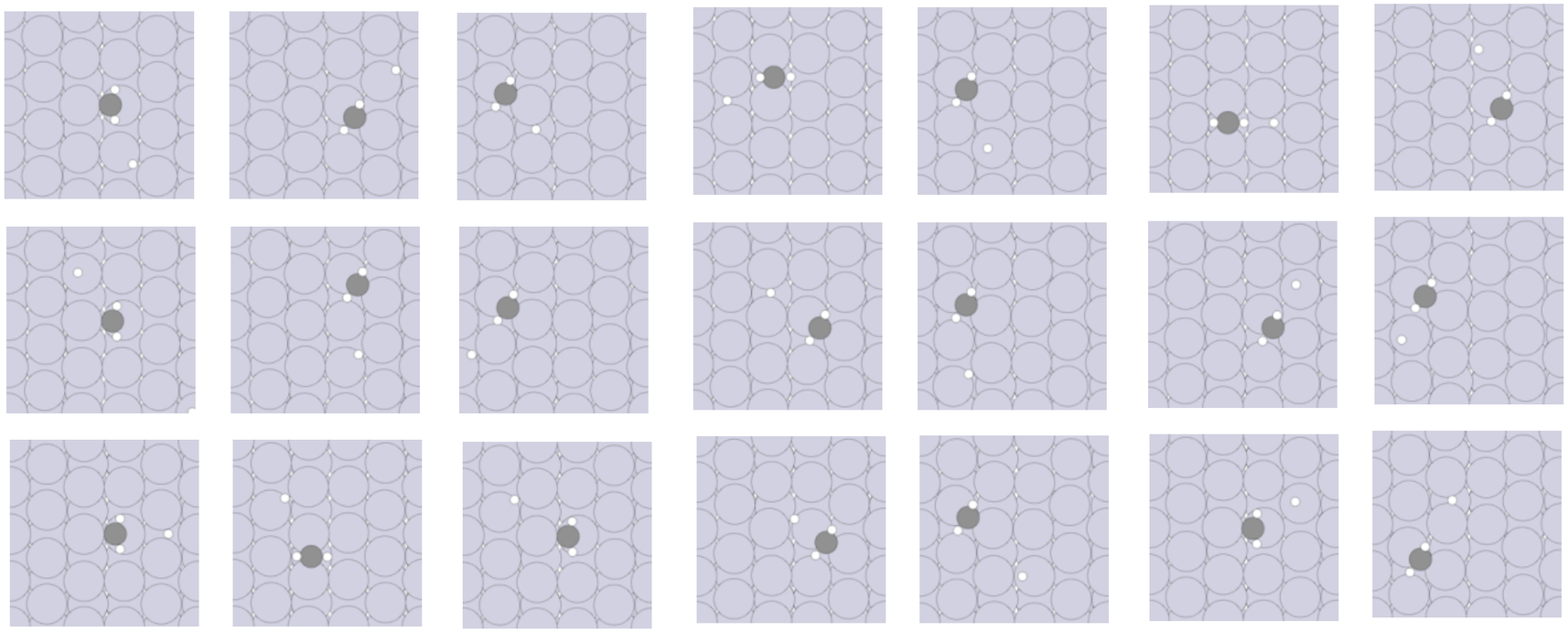




But there are a lot more already on Pt(211)



CH_2 + H co-adsorbed minima on Pt(211)



…There are **73** total minima!

It is difficult or impossible to know a priori which minima are directly connected to the reaction of interest, and which involve diffusion of adsorbates in addition to reaction.

From structures to saddle points

Pt(111):

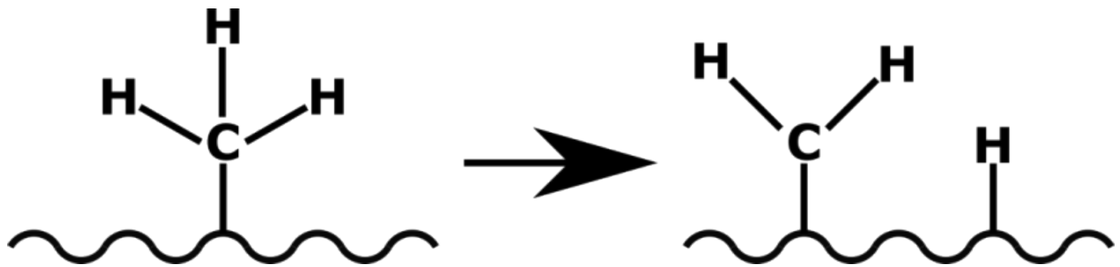
$\Delta_r E$: 0.267 +/- 0.053 eV

Pt(211):

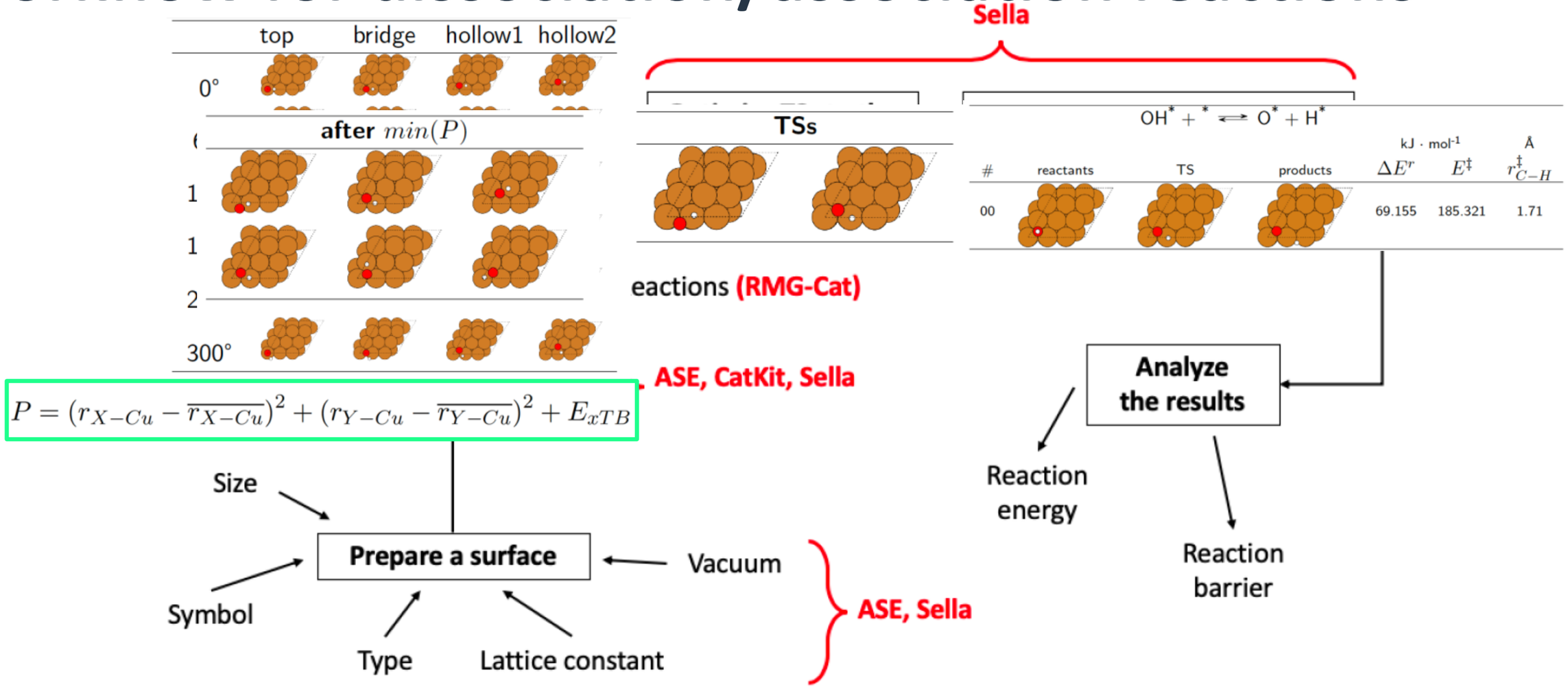
$\Delta_r E$: 0.064 +/- 0.415 eV

- There are a few hundred possible proposed pathways just for $CH_3 \longrightarrow CH_2 + H$ on Pt(211)
- GP-NEB is still too expensive

Brute force combinatorial search is probably not the best approach.
Let's try a single-ended approach from the monodentate species.



Workflow for dissociation/association reactions



The workflow is ASE based.
Symmetrically equivalent structures are filtered between steps.
Geometry optimization is done with Sella, our own optimizer.

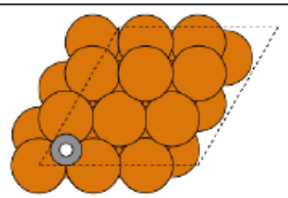
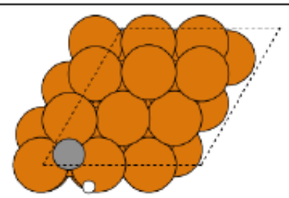
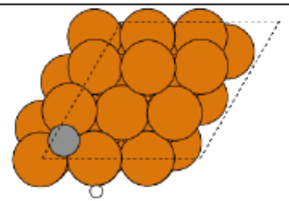
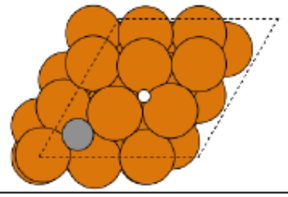
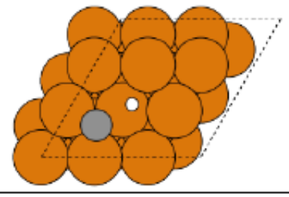
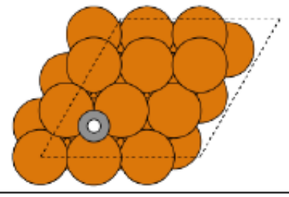
https://github.com/grimme-lab/xtb
https://gitlab.com/ase/ase
https://github.com/SUNCAT-Center/CatKit
https://github.com/zadorlab/sella

Hermes, E. D.; Sargsyan, K.; Najm, H. N.; Zádor, J., *J. Chem. Theory Comp.* **2019,** *15* 6536-6549.

Does it work for other diatomics on an FCC(111) surface?

$$CH^* + * \longrightarrow H^* + C^* \text{ on Cu(111)}$$

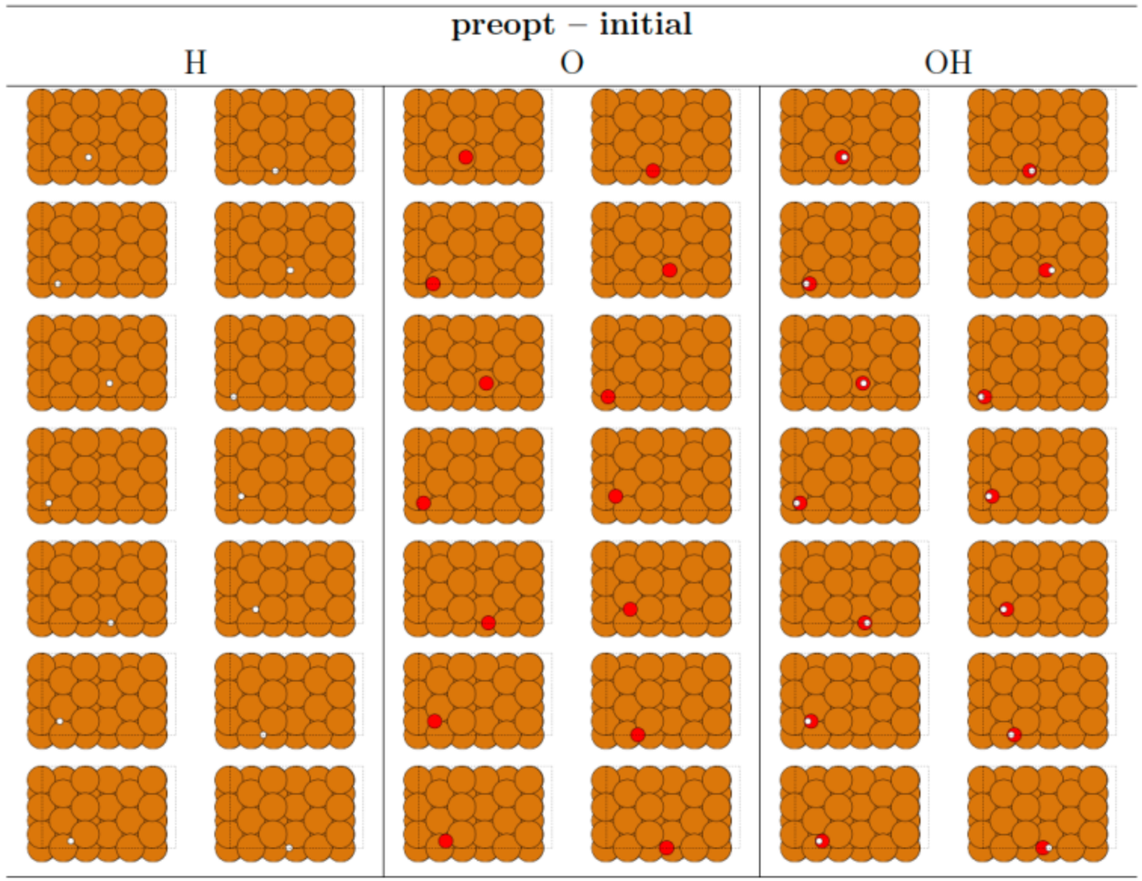
run optIRC

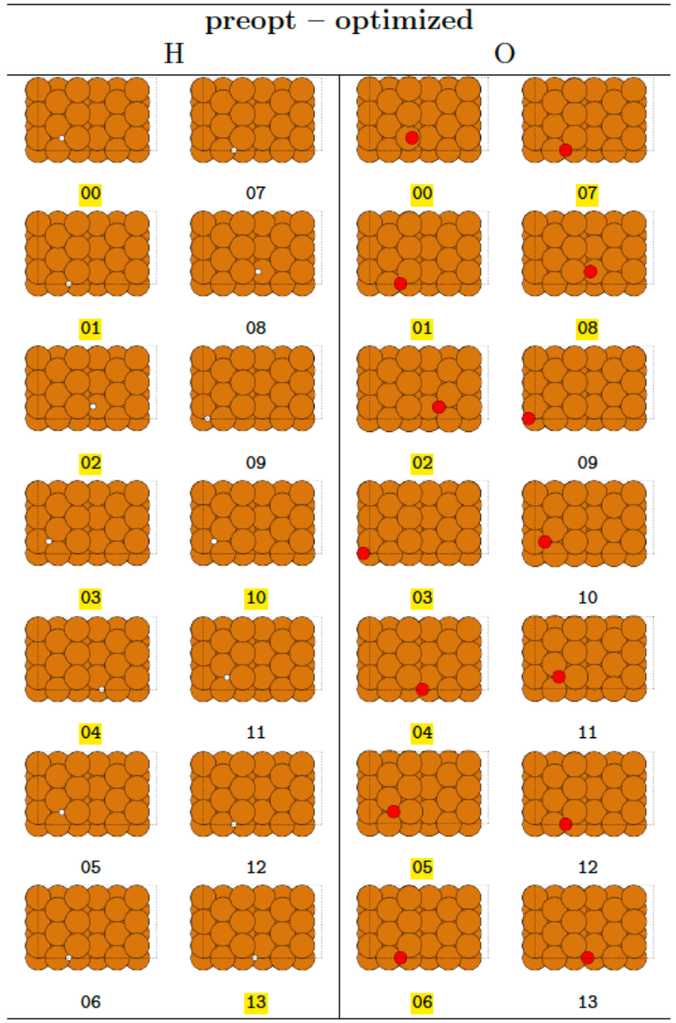
#	forward	TS	reverse	ΔE^r (kJ · mol^{-1})	$E^{\ddagger}$ (kJ · mol^{-1})	$r^{\ddagger}_{C-H}$ (Å)
00				132.836	183.297	1.82
01				117.379	197.932	2.00

It seems like.

Does it work for diatomics on an FCC(211) surface?

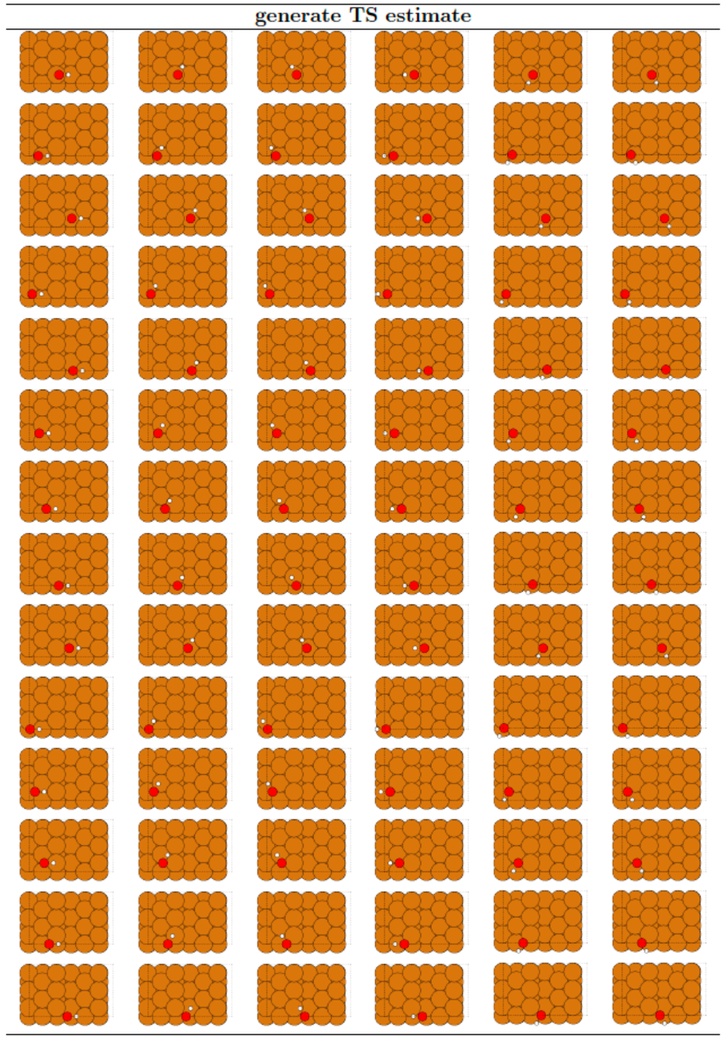
$$OH^* + * \longrightarrow H^* + O^* \text{ on Cu(111)}$$





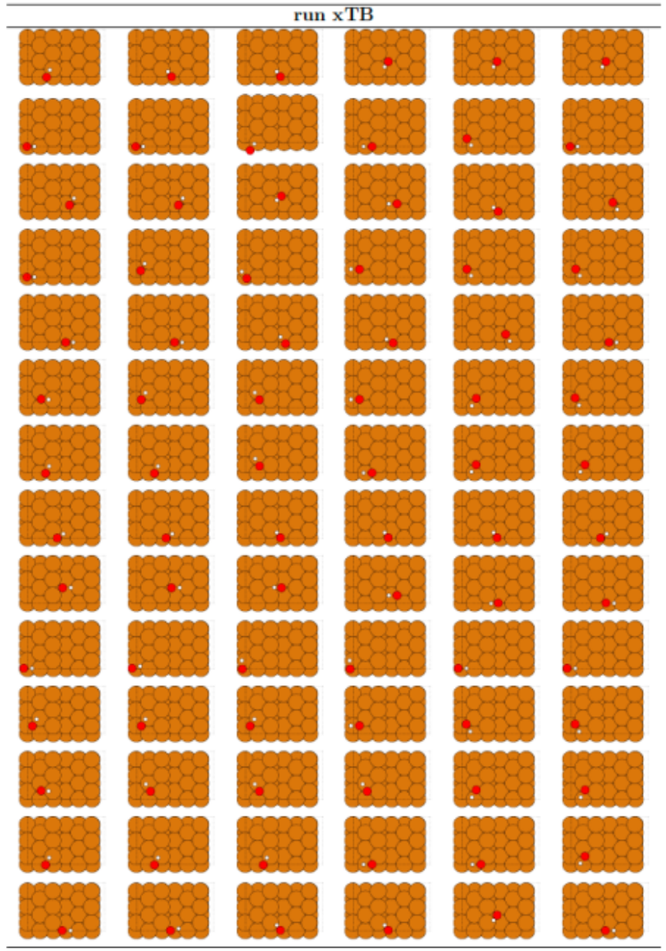
Does it work for diatomics on an FCC(211) surface?

OH* + * ⟶ H* + O* on Cu(111)



Does it work for diatomics on an FCC(211) surface?

$$OH^* + * \longrightarrow H^* + O^* \text{ on Cu(111)}$$

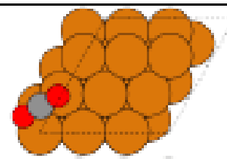
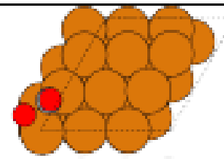
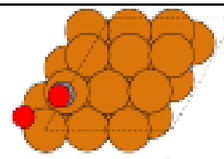
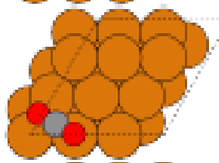
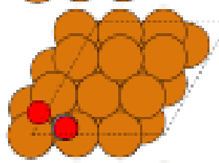
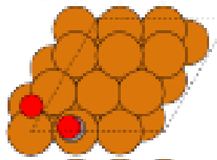
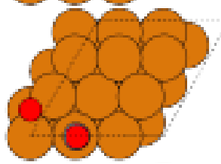
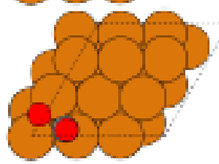
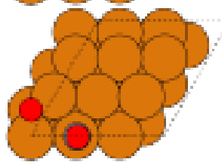
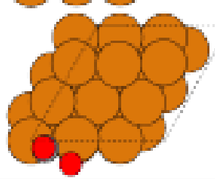
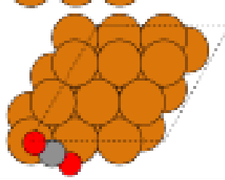


- 20 of these are unique (84 original structures).

Does it work for triatomics on an FCC(111) surface?

CO_2* + * ⟶ O* + CO* on Cu(111)

run optIRC

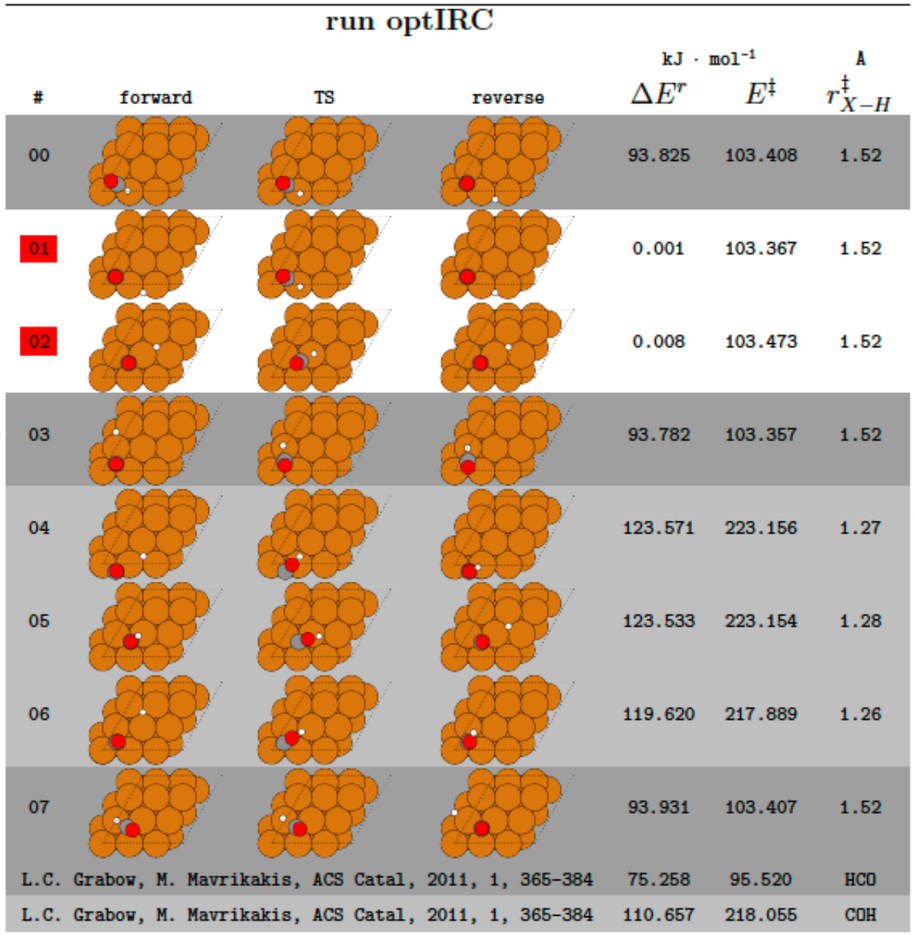
#	forward	TS	reverse	ΔE^r (kJ · mol^{-1})	$E^{\ddagger}$ (kJ · mol^{-1})	$r^{\ddagger}_{C-O}$ (Å)
00				-111.682	50.449	1.77
01				-118.958	46.756	1.82
02				0.000	45.747	1.82
03				-111.765	50.451	1.77
L.C. Grabow, M. Mavrikakis, ACS Catal, 2011, 1, 365-384				-108.063	62.715	

same

Here the methodology seems to work.

Does it work for triatomics on an FCC(111) surface?

HCO* + * ⟶ H* + CO* on Cu(111)



unsuccessful search

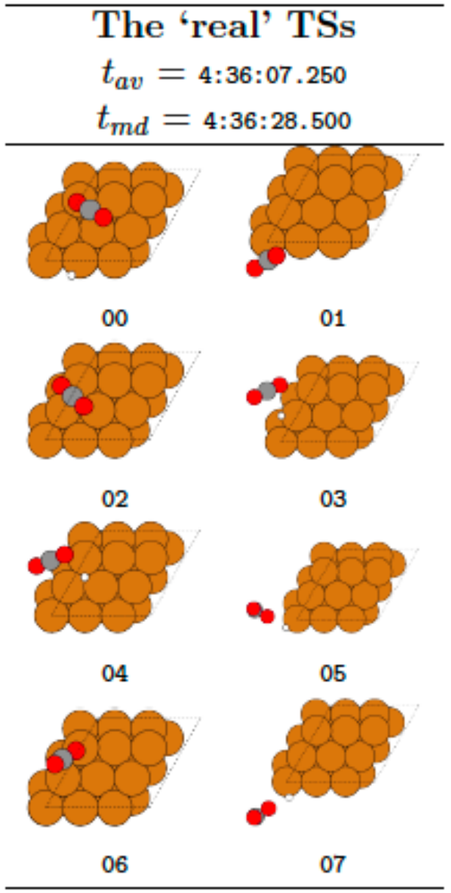
desired reaction

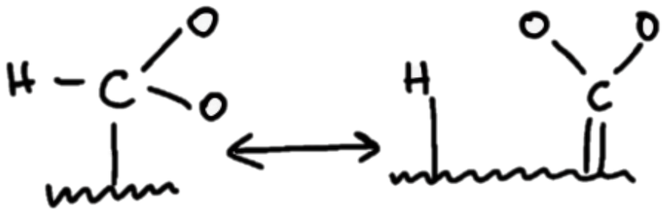
undesired reaction forming *COH

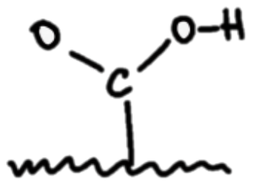
- These observations lead to using f_2, the scaling for the forming bond to the surface.
- We need to explore the sensitivity to the scaling factors.

Does it work for larger adsorbates on an FCC(111) surface?

$$HCOO^* + * \longrightarrow H^* + CO_2^* \text{ on Cu(111)}$$







- Preliminary results, IRCs to be done
- H might also join O instead of C

Outline

Brief introduction to combustion chemistry and gas-phase kinetics

Automated PES search with KinBot for gas-phase systems

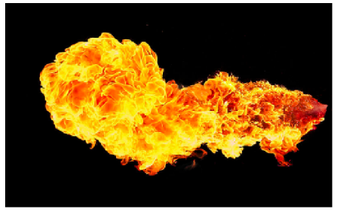
Recent applications of KinBot

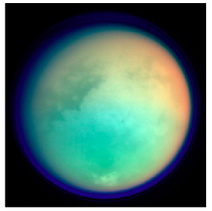
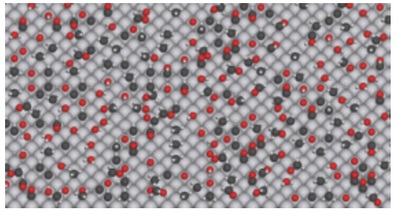
Automated PES search for heterogeneous catalysis

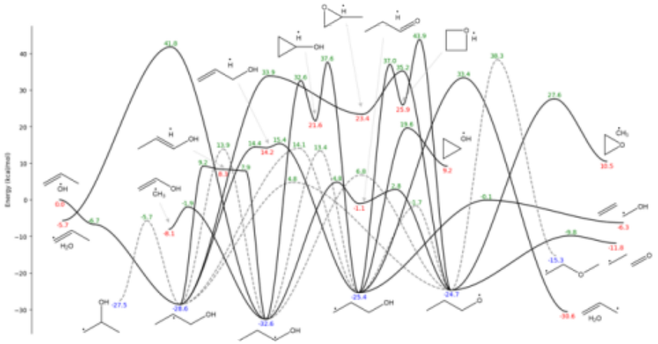
Perspective: Complex workflows

Perspective

To meet the challenges of fuel development, air pollution control, and catalysis, automation is inevitable for the discovery of molecular level process.





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

We are participating in two concerted, multi-institutional exascale projects to build **complex workflows**:

- Combustion: Predictive Automated Combustion Chemistry (PACC), PI: S. J. Klippenstein, Argonne
- Catalysis: Exascale Catalytic Chemistry (ECC, ecc-project.sandia.gov), PI: J. Zádor, Sandia