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"Deuxième Rencontre R"

Fast prediction of glycerol reactivity on metallic catalysts

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Content

1. Context of the project
2. Predicting simple alcohols reactivity on Rh
3. Predicting glycerol reactivity on Rh

I-Context of the project

Objective

Interest of biomass

"Biomass" designs "**materials** produced by the growth of microorganisms, **plants** or animals"[1]

- **Abundant,** especially **polyols**
- May be used as **building blocks** for **key chemicals** in industry

Importance of heterogeneous catalysis…

- **Catalytic** transformation of biomass with **transition metals**
- **Computational tools** to understand **reactivity** and to design **efficient catalysts**

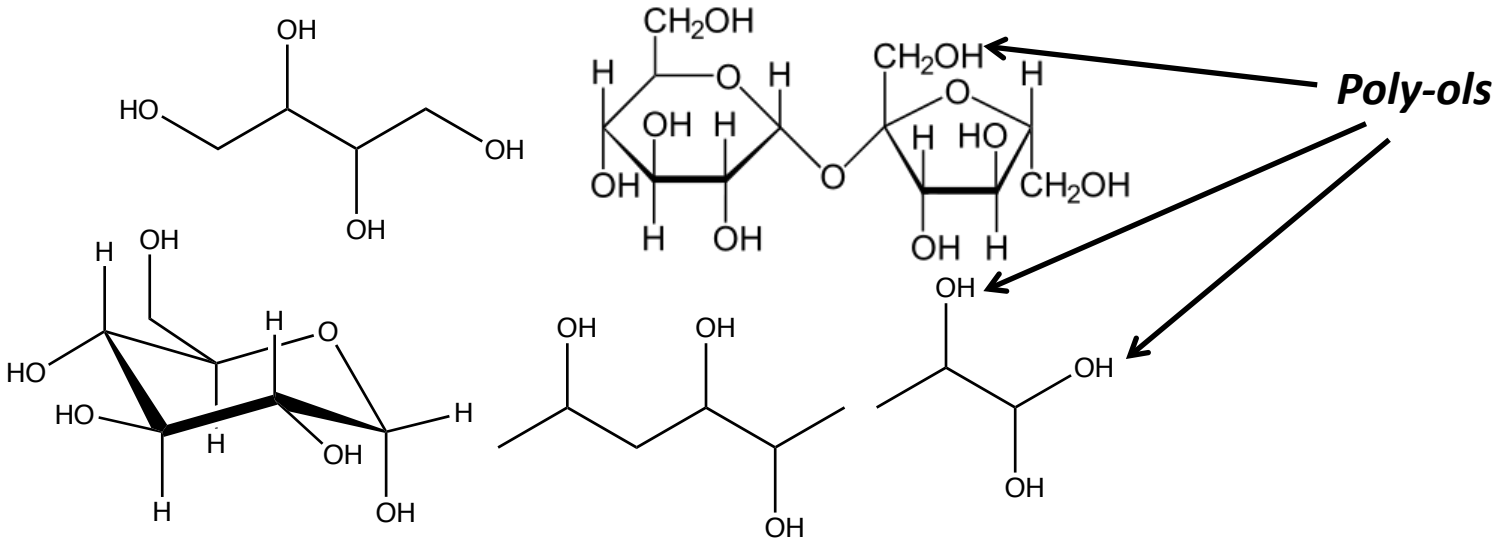
<u>*Objective*</u>

- **Fast screening** method of **polyols** reactivity on **metallic catalysts**

1-*IUPAC Recommendations*, Pure and Applied Chemistry, 1992, **64**, 143

Challenge

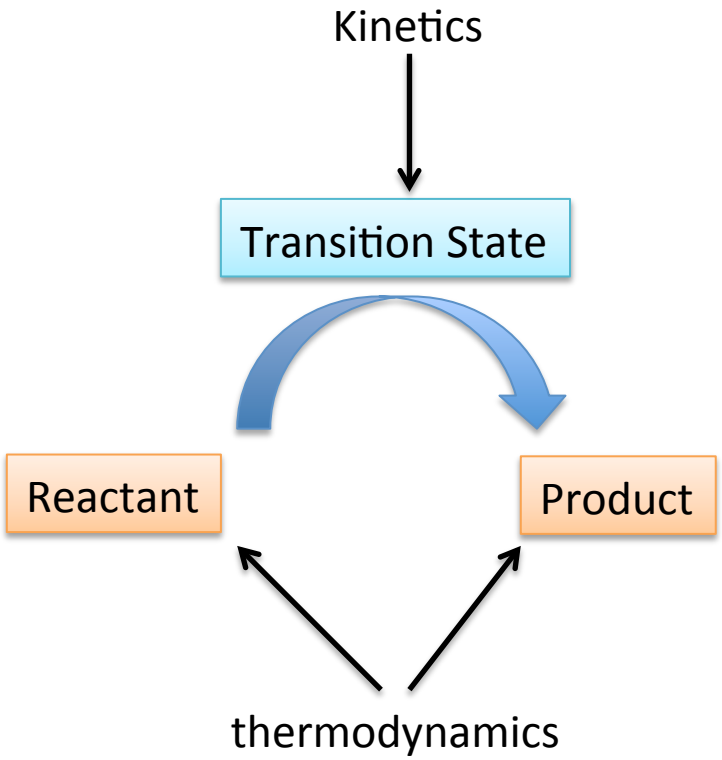
- Complexity of biomass molecules: **size & high functionalization**



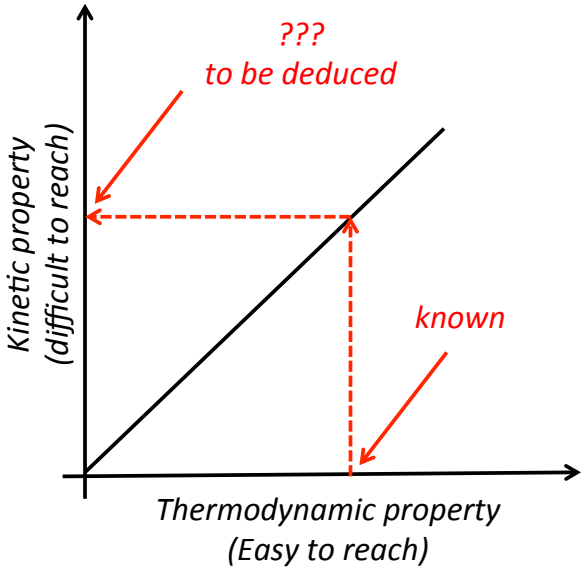
- Considerable **computational cost** to compute **reactivity** (several days/weeks with quantum chemistry codes)

Strategy: combination of 2 methods

1- DFT[a] (quantum chemistry)



2- Brønsted-Evans-Polanyi (BEP) type relationships[b]

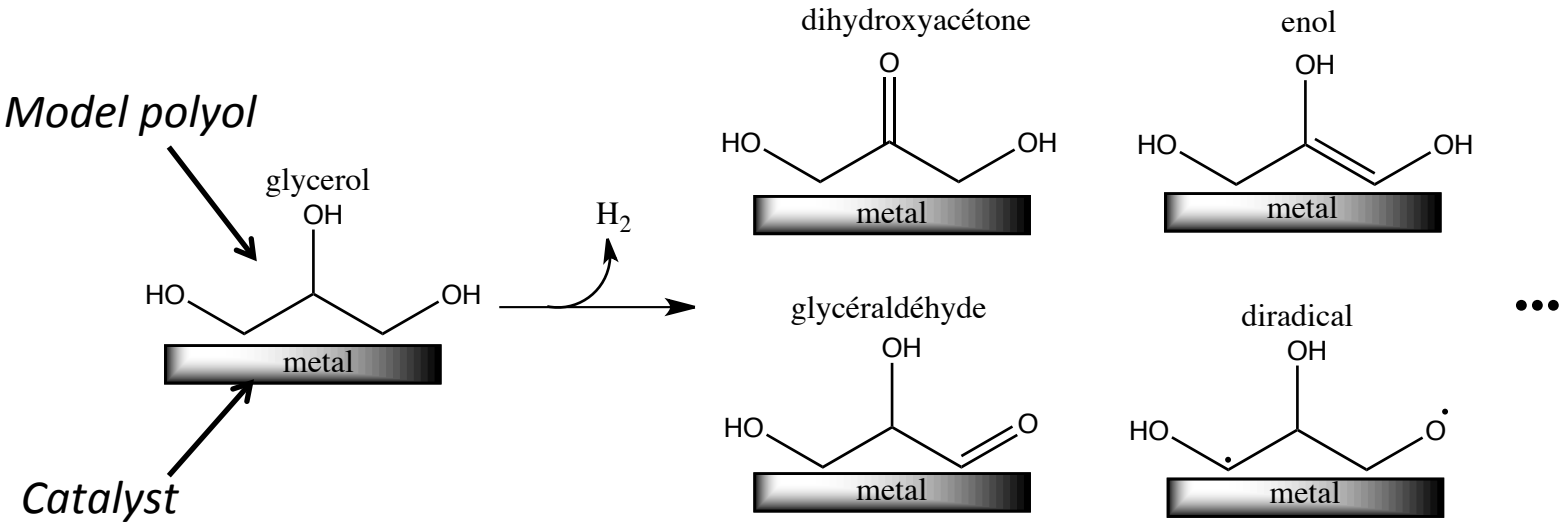


a-Calculated with VASP 4.36

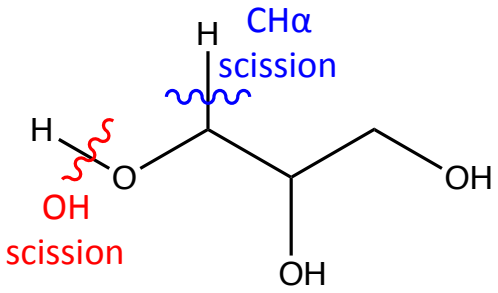
b-Established with R software

Strategy: model system

- **Glycerol dehydrogenation on Rh (111)**



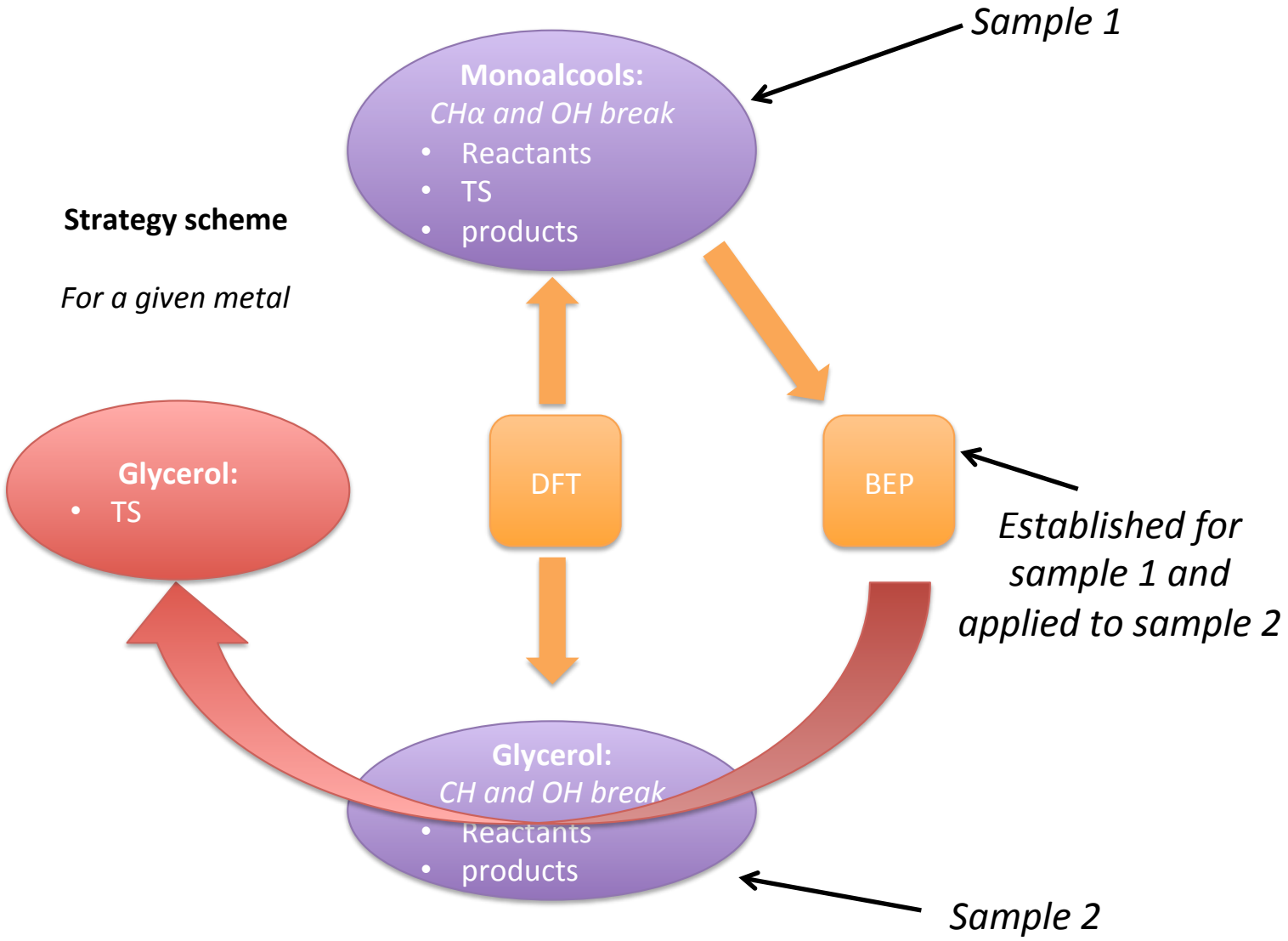
- **2 kinds** of reaction



Strategy: summary

Strategy scheme

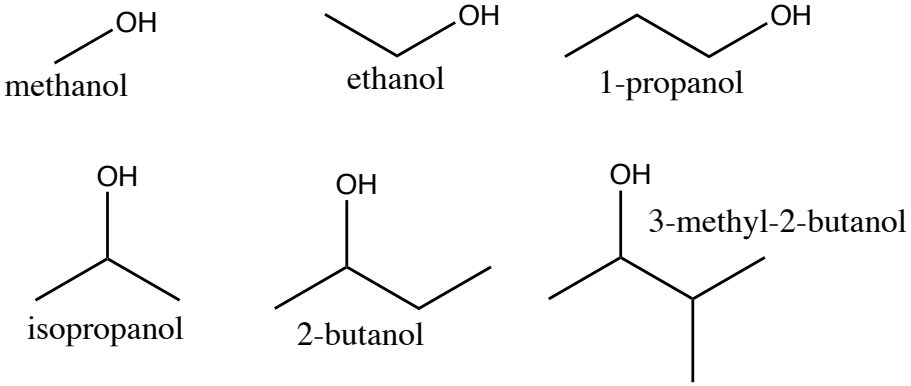
For a given metal



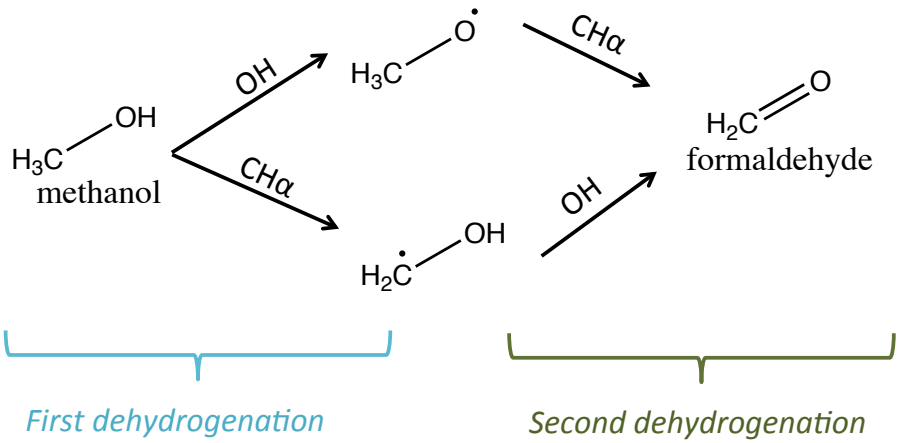
II- Simple alcohols dehydrogenation on Rh (111)

Reactions sample

- Set of simple alcohols



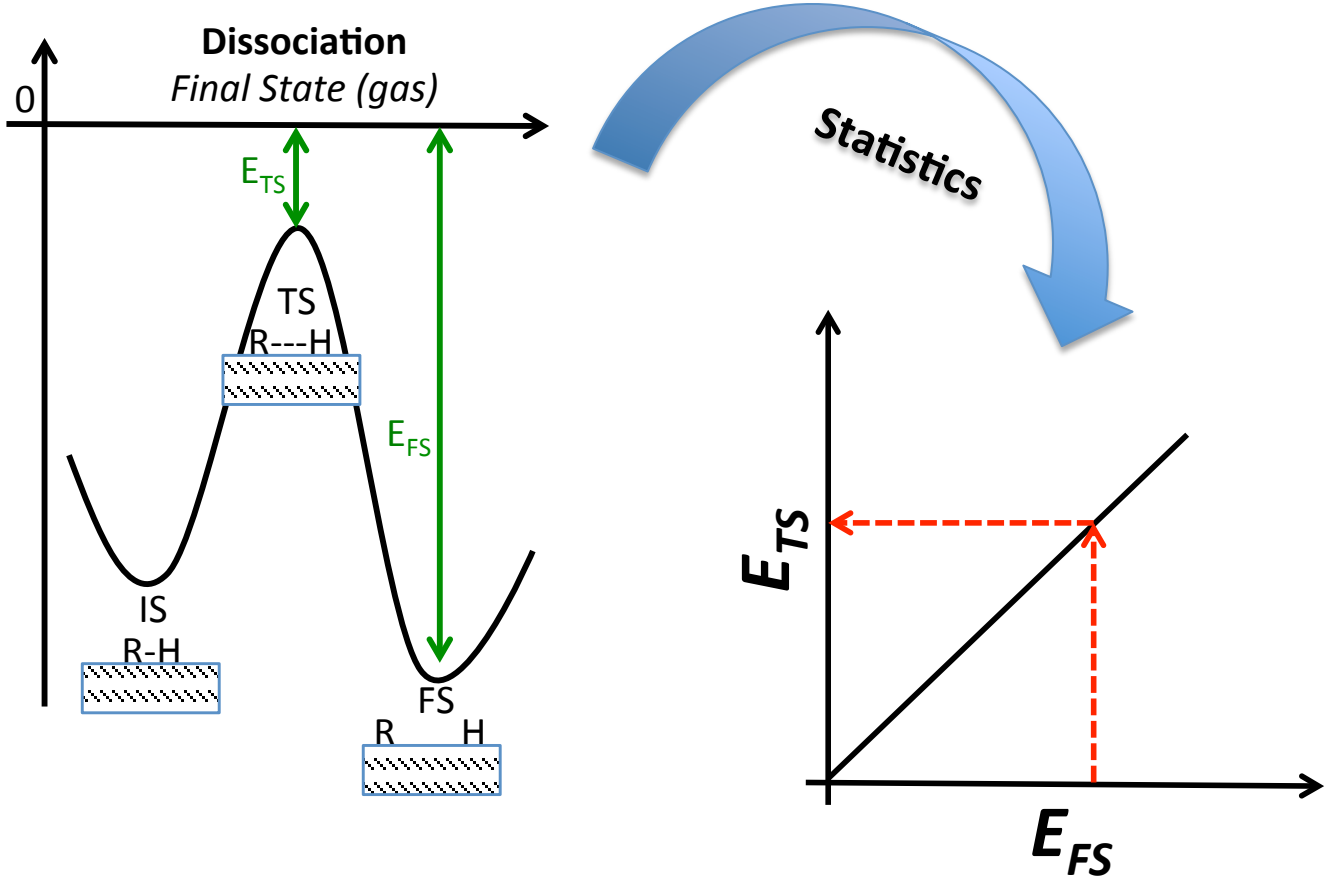
- Elementary reactions



- For each step: **reactant, TS and product** are DFT calculated

Focus on one BEP type relationship

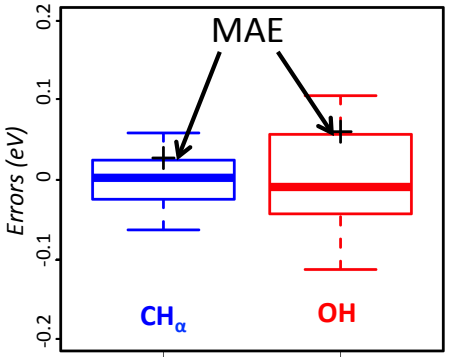
TSS.diss.FS/FS[1]

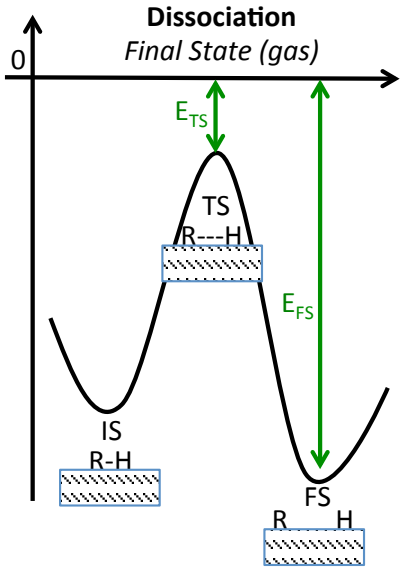


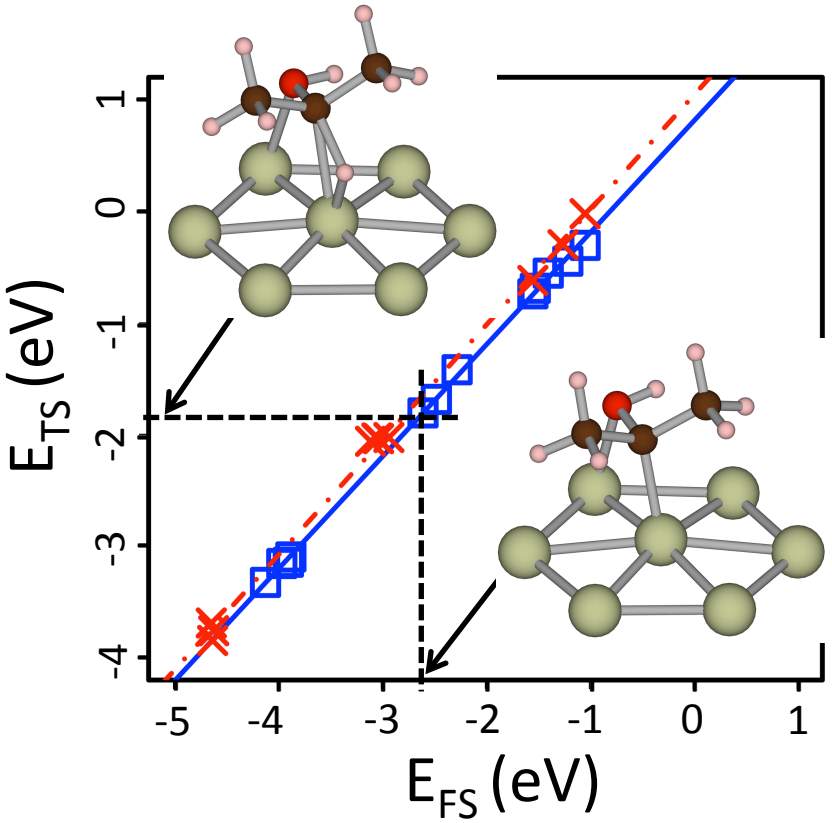
1-Loffreda, D.; Delbecq, F.; Vigné, F.; Sautet, P. Angew. Chem., Int. Ed. 2009, 48, 8978–8980

Prediction of simple alcohols dehydrogenation

TSS.diss.FS/FS







Statistics

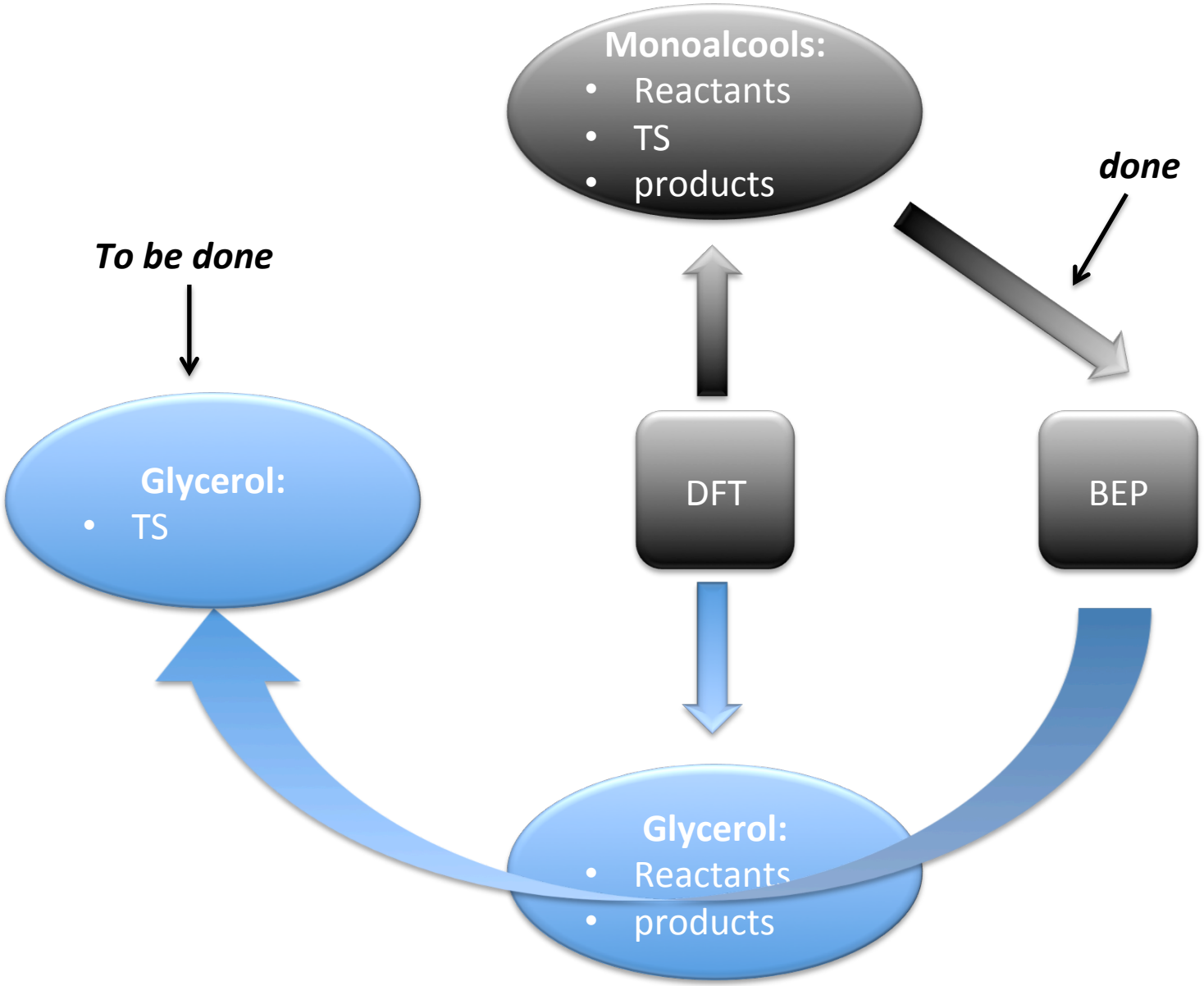
CHα Rh	slope	intercept	MAE	MAX
TSS.diss.FS/FS	1.00±0.02	0.81±0.06	0.03	0.06

→ **CHα:** $E_{TS} = \hat{E}_{TS} \pm 0.09$

OH Rh	slope	intercept	MAE	MAX
TSS.diss.FS/FS	1.03±0.04	1.04±0.14	0.06	0.11

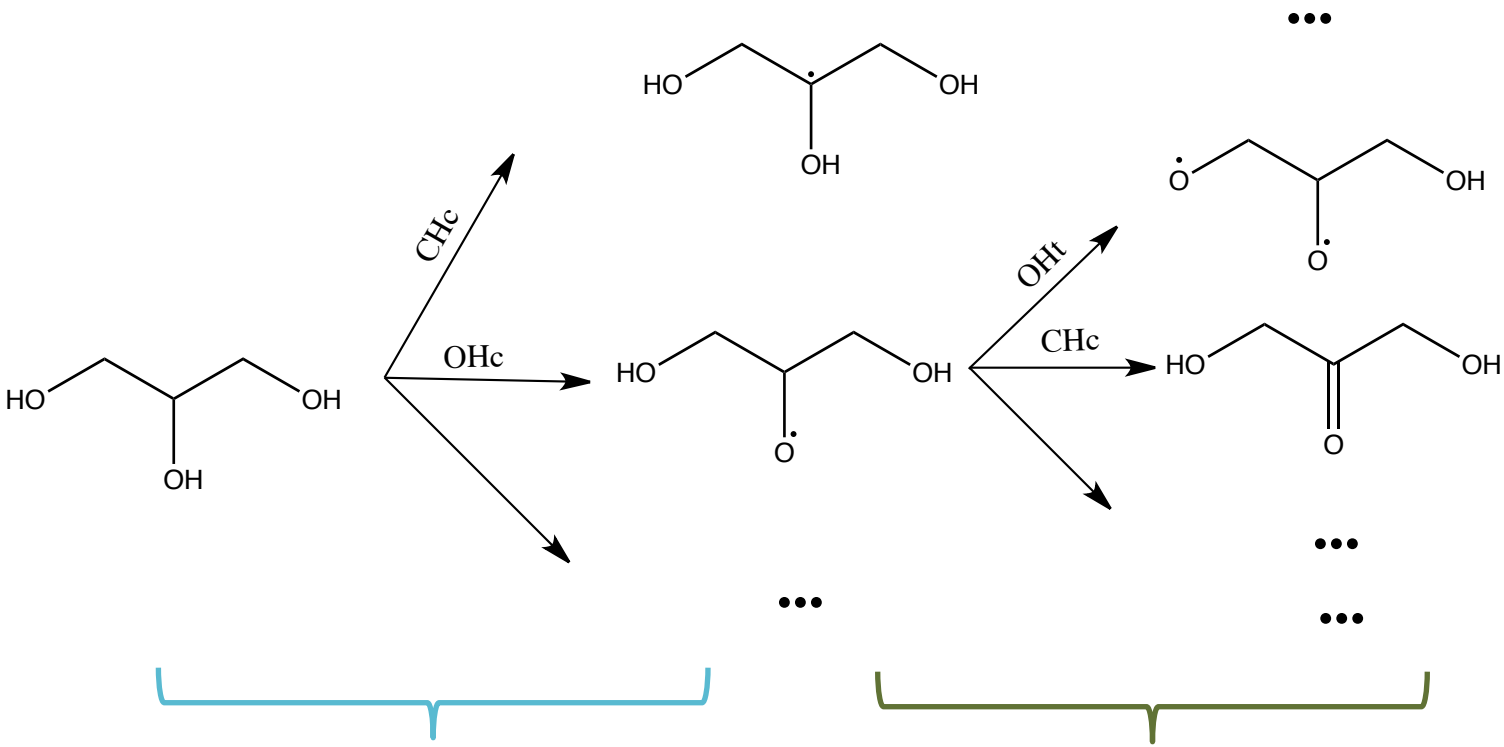
→ **OH:** $E_{TS} = \hat{E}_{TS} \pm 0.20$

Further step

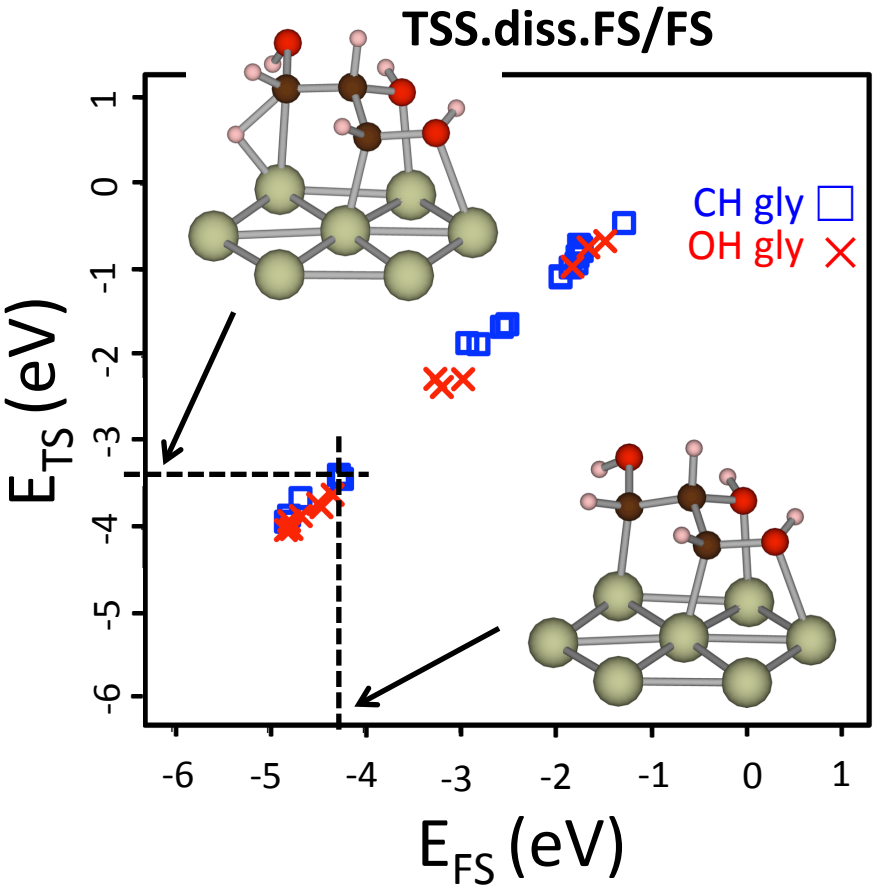


III- Glycerol dehydrogenation on Rh (111)

Elementary reactions



Can we predict glycerol reactivity from simple alcohols models?

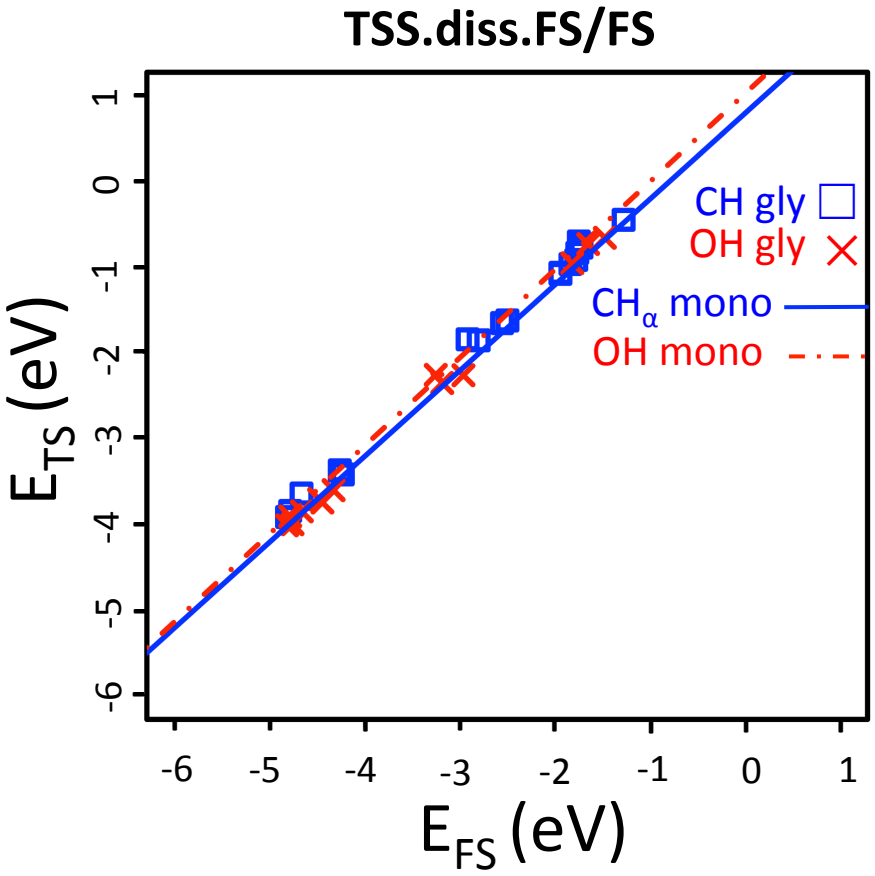


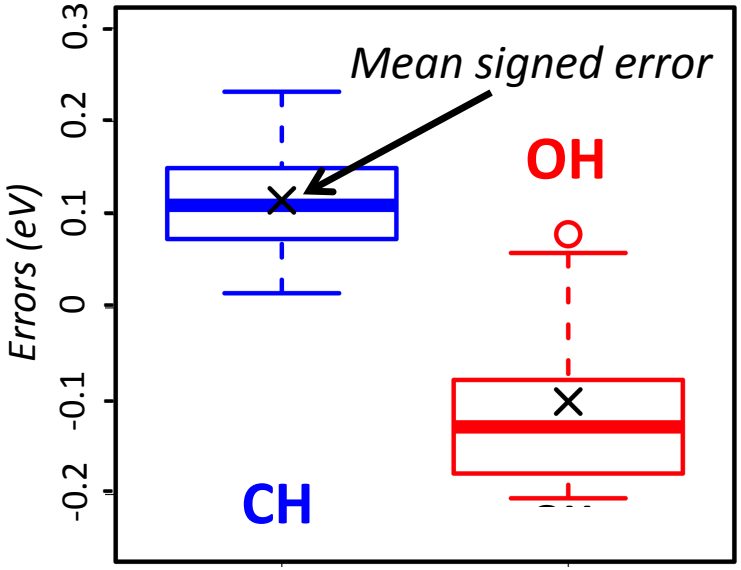
Glycerol vs. monoalcohols	slope	intercept
CH(gly)/CHα(mono)	6.53E-02	3.98E-01
OH(gly)/OH(mono)	6.21E-01	9.10E-01

*For both slope **and** intercept p-value >0.05*
➔ *the models are **statistically identical***

Can we predict glycerol reactivity from simple alcohols models?

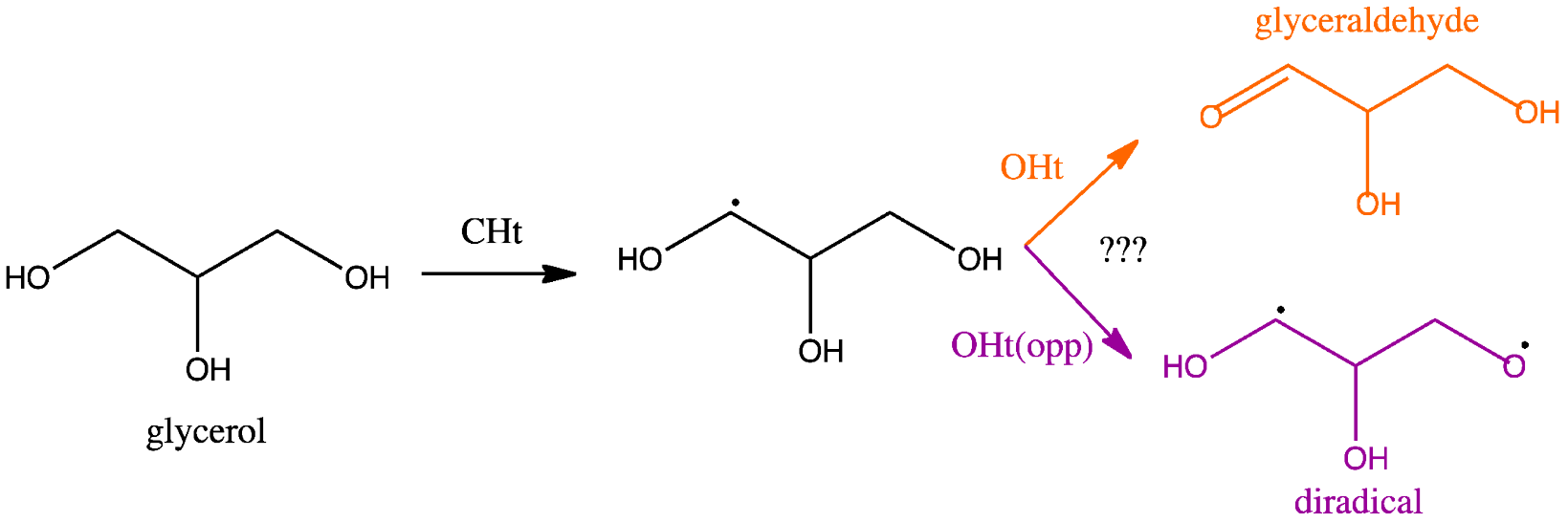
YES we can!





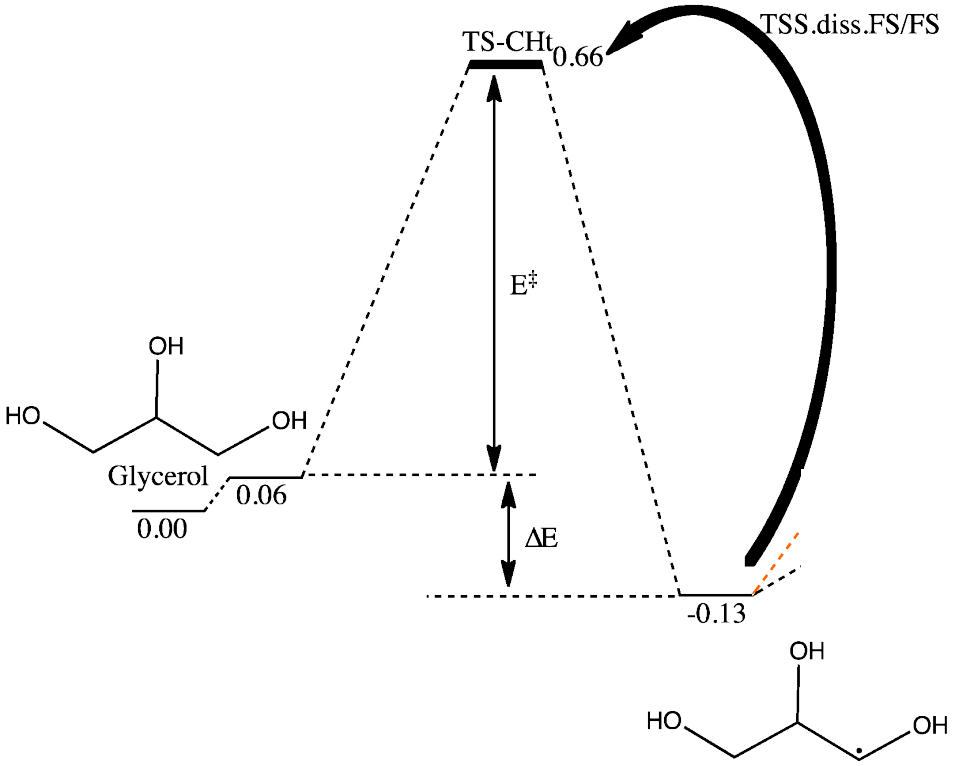
Using of the model

Glyceraldehyde or diradical?



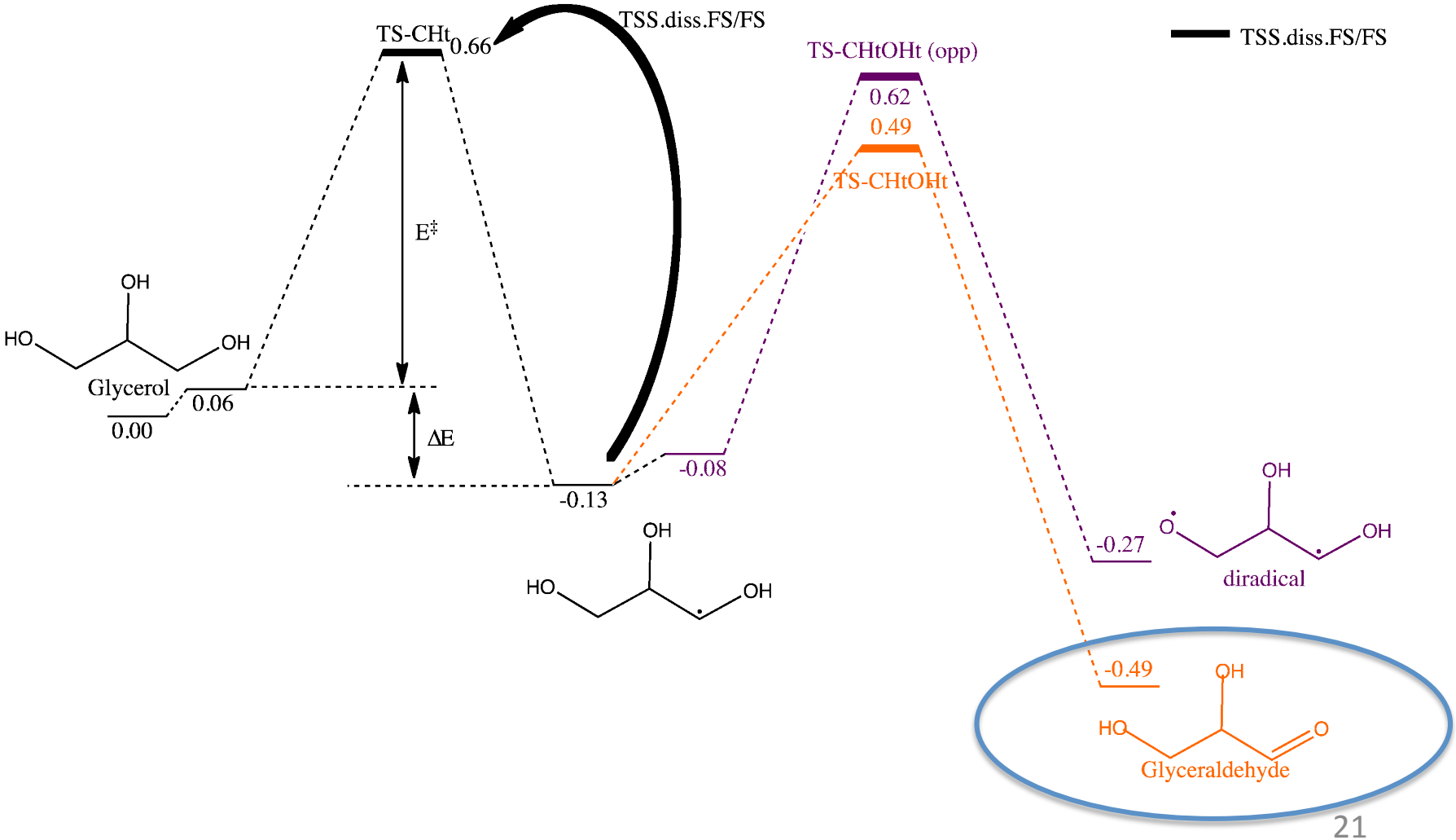
Using of the model

Glyceraldehyde or diradical?



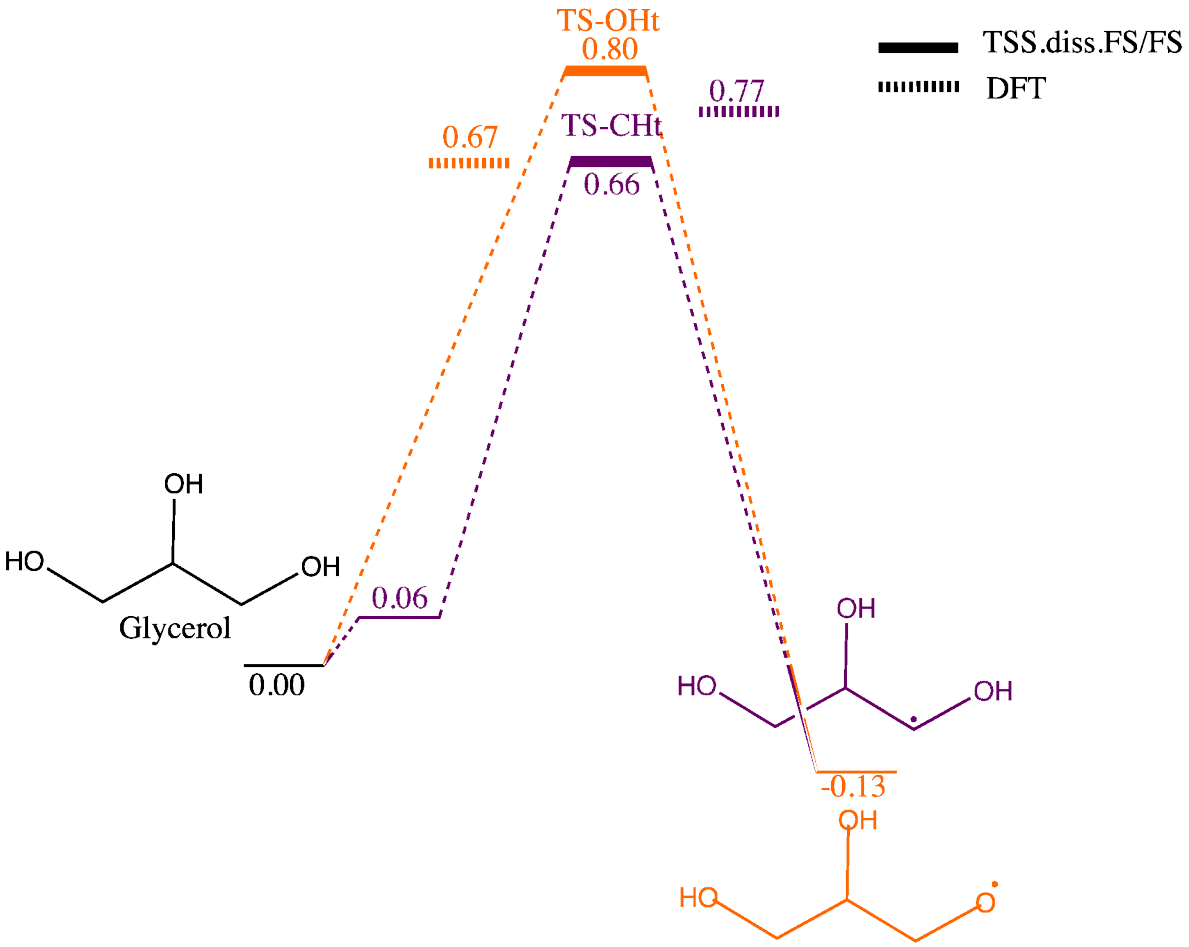
Using of the model

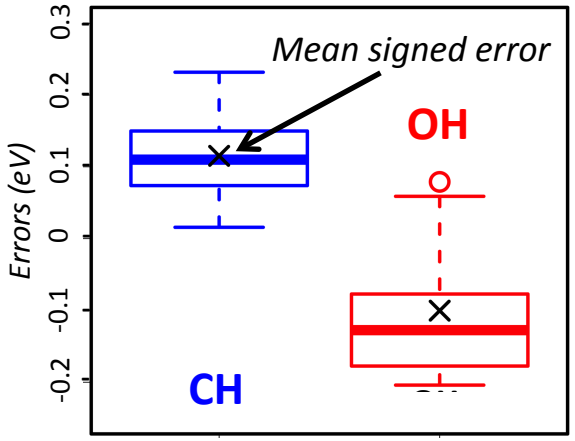
Glyceraldehyde or diradical?



Using of the model

A difficult example…





Errors distribution for glycerol via monoalcools using ***TSS.diss.FS/FS***

Summary & perspectives

Achievements…

- We established models to predict simple alcohols reactivity on Rh
- Those models have good quality but prediction interval is a bit high for OH dissociation compared to CH dissociation
- These models may be directly applied to complex alcohols such as glycerol

Predicting TS energies of…	Average errors
Simple alcohols	<0.10 eV
Glycerol	~±0.10 eV

Ongoing…

- Reduce the prediction intervals for simple alcohols linear regressions
- Justify quantitatively the systematic shift and eliminate it from the models
- Establish such models on various metallic catalysts

Acknowledgements

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Dr Françoise Delbecq

Calculation resources and software developers…

PSMN

CINES/IDRIS

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Dr David Loffreda

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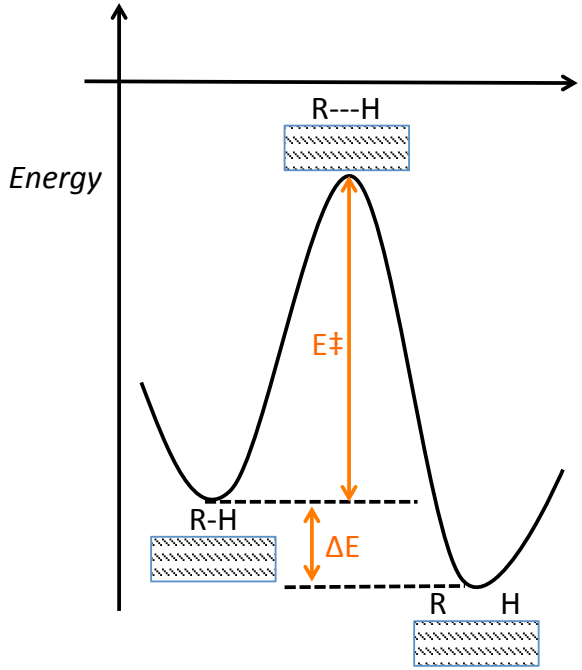
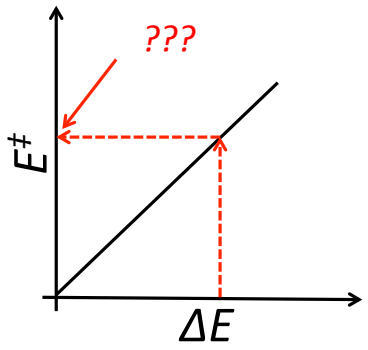
ANR

Annexes

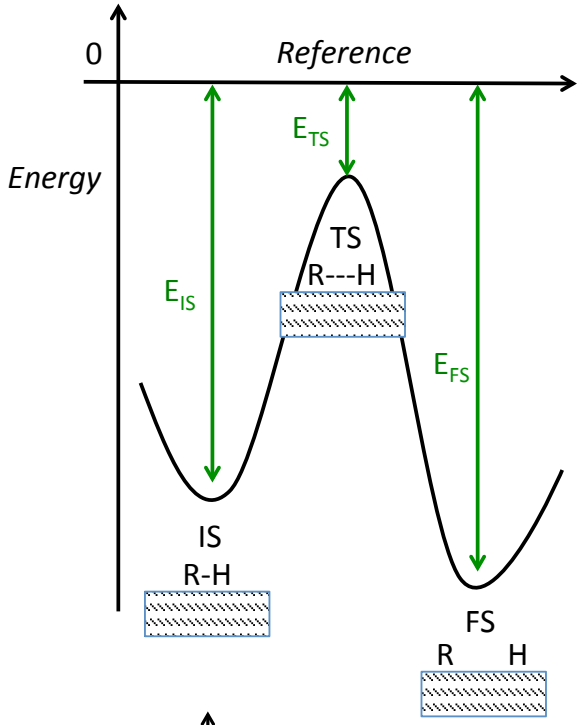
Various BEP type relationships

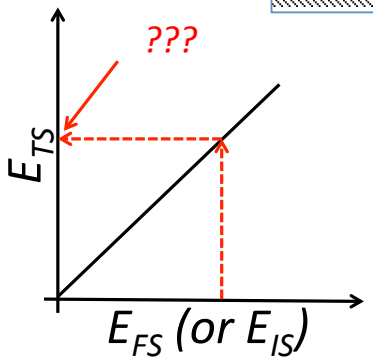
Brønsted-Evans-Polanyi (BEP)



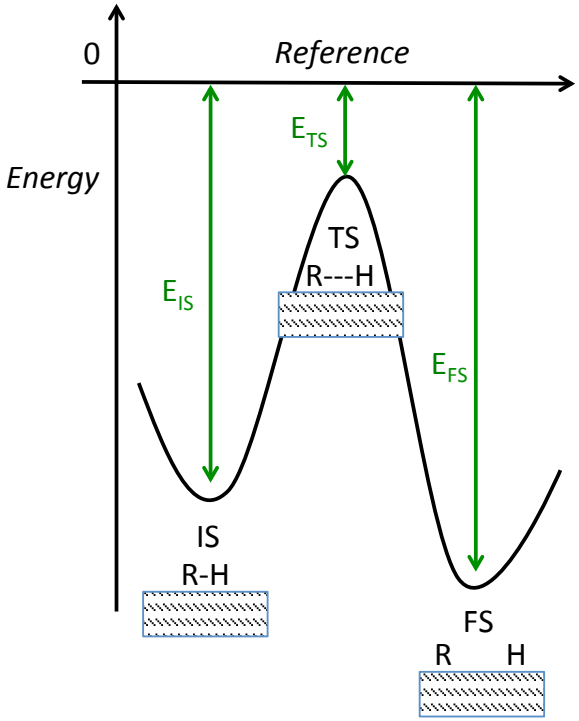


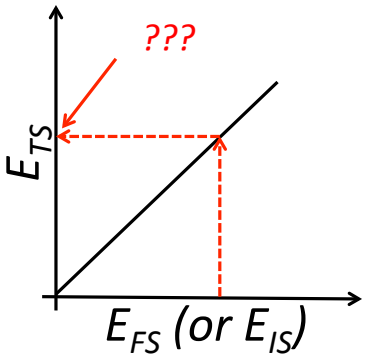
Transition State Scaling (TSS)





The TSS relationships



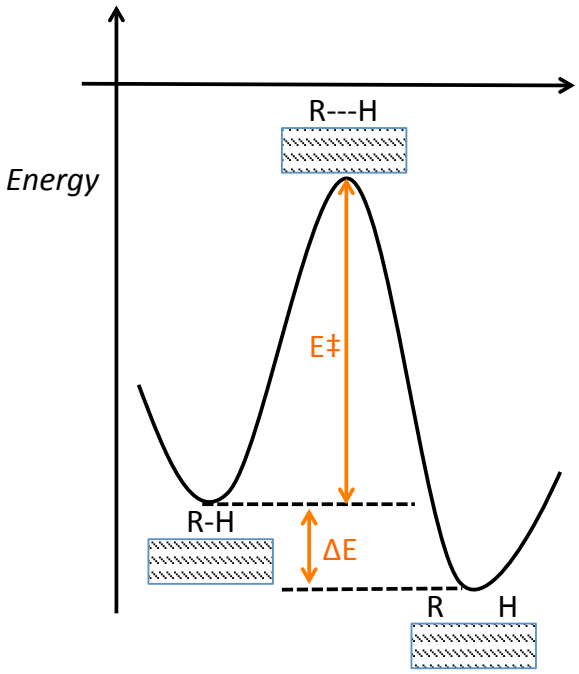


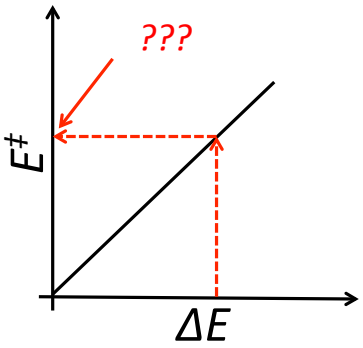
One can play on several parameters:

- Nature of the **independent variable** (E_{IS} or E_{FS})
- Energetic **reference** (IS or FS state)
- **Direction** of the reaction:
  - Defined with **structural** considerations (dissociation)
  - Defined with **energetic** considerations(exothermic)

➔ 8 modes of TSS correlations

The BEP relationships





One can play on:

- **Direction** of the reaction:
Association/dissociation or exothermic/endotermic

➔ 4 modes of TSS correlations

Equivalence of all the modes of correlation