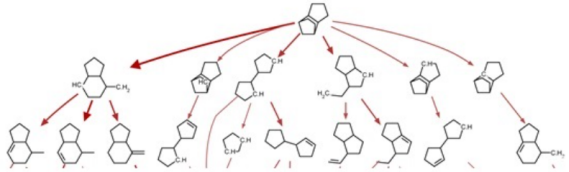
GREEN RESEARCH GROUP
FUNDAMENTAL AND APPLIED CHEMICAL KINETICS



Reaction Pathways of Cyclopentanone Oxidation Intermediates

Sarah Khanniche, William H. Green

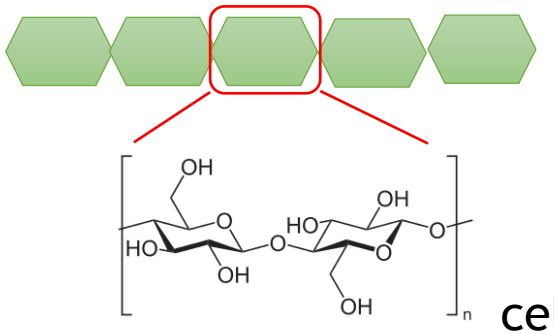
Wednesday, June 26 2019

ORLÉANS,
JUNE
23 - 27 2019

Cyclopentanone(CPO) as a Biofuel

Biomass

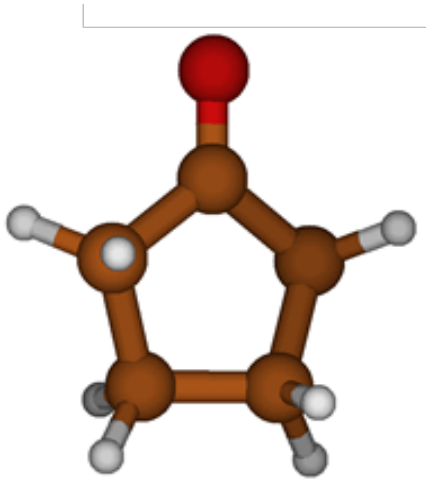
Chains of cellulose molecules



cellulose

Thermo-chemical decomposition

Biological digestion



Cyclic ketone
C_5H_8O

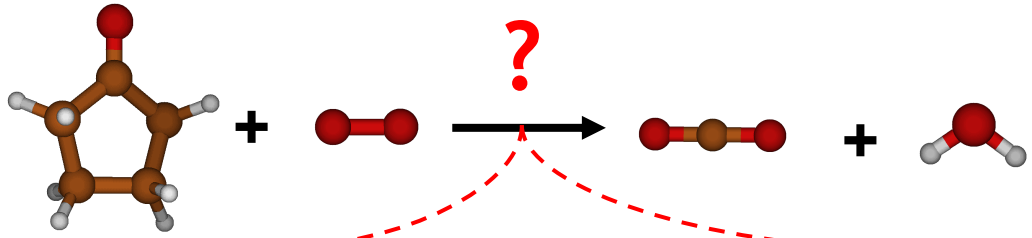
Resistance to autoignition

Low reactivity

High octane number

Aim of the project

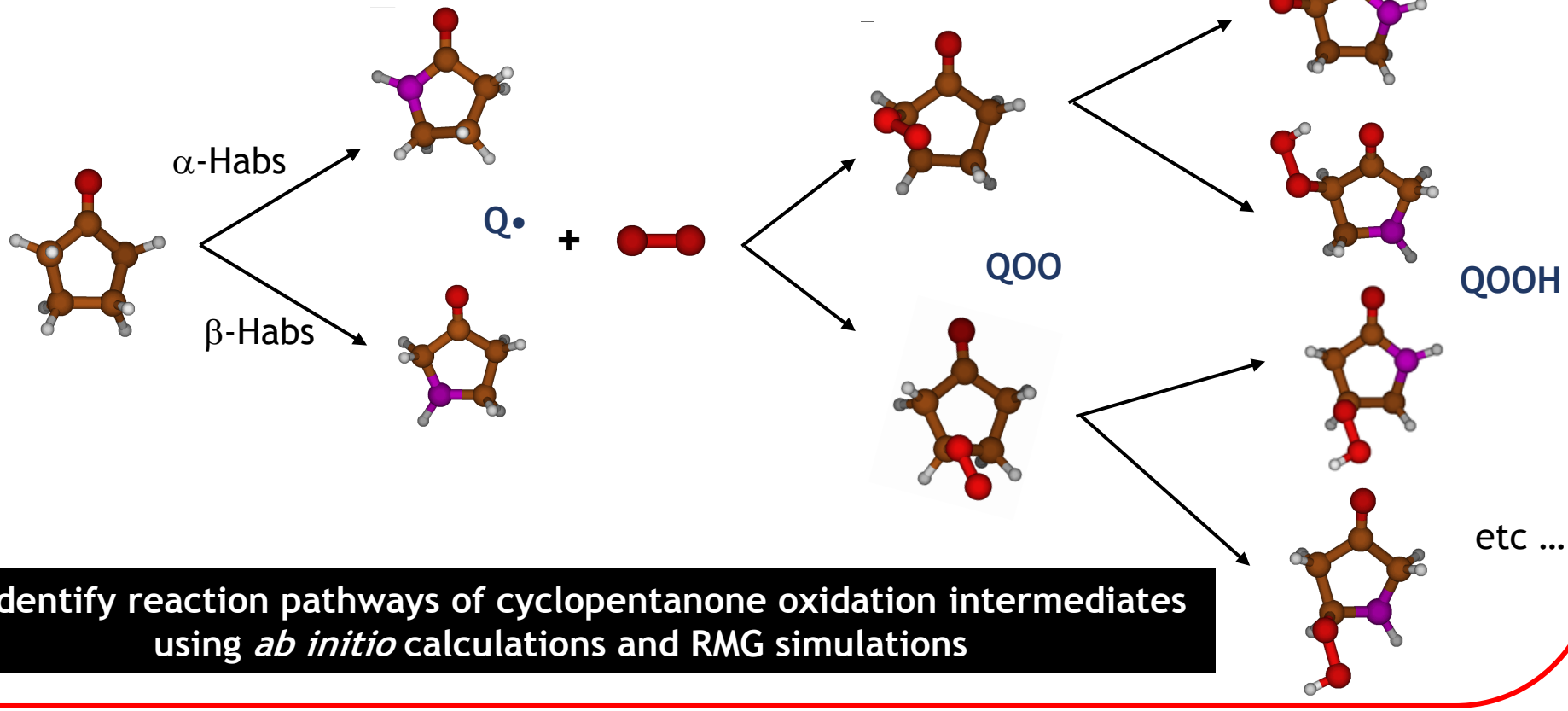
Combustion of CPO



What are the elementary reactions?
How fast are they?

Initiation reactions

Chain propagation reactions



To identify reaction pathways of cyclopentanone oxidation intermediates using *ab initio* calculations and RMG simulations

RMG simulations

Rate-based Model Enlarging Algorithm
(flux-based algorithm)

Initial set of Species *j*

Database

Reactor Conditions (T, P, c_0)

Reaction Mechanism Generator (RMG)

List of reactions $j \overset{k}{\leftrightarrow} i$

Reactor simulations

$R_i = dC_i/dt$

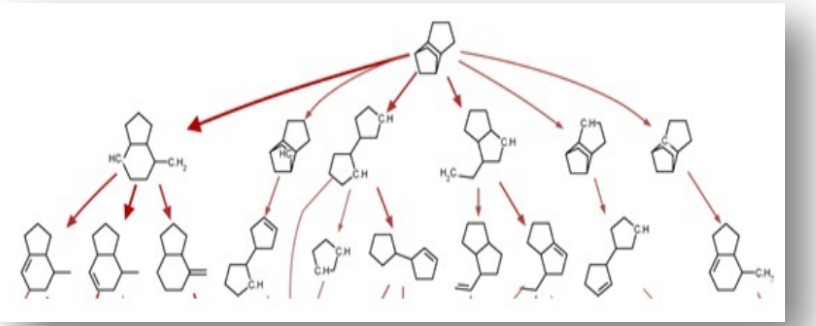
If $R_i > \varepsilon R_{char}$

Add species *i*

Iteration

Reaction Mechanism

Large set of Elementary reactions + Rate constants



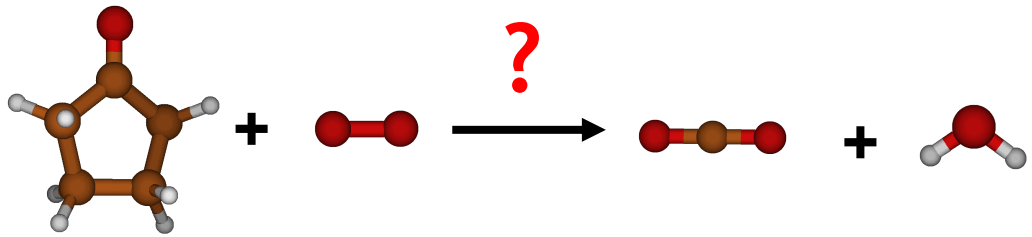
Fuel properties

$0.001 < \varepsilon < 0.1$

R_{char} = reaction system's characteristic rate

Outline of the talk

Combustion of CPO



1. ***Ab initio* calculations**
   - QOO: H-migration *vs* HO_2 elimination
   - QOOH: Ring opening *vs* cyclic ether formation

2. **RMG simulations**
   - Evolution of the system with time
   - Sensitivity analysis

Computational methods

Electronic structure calculations

Gaussian

Transition States characterized by one imaginary frequency

Intrinsic Reaction Coordinate (IRC) calculations

CO/OO/OH scans

CBS-QB3 high-level calculations

ThermoKinetic Calculations

Arkane

rigid rotor- harmonic oscillator approximation

hindered internal rotors

Thermochemical properties
$\Delta_f H°_{298K}$, $S°_{298K}$, $C_p(T)$

Kinetic parameters
HPL $k(T)$

TST
+ tunneling correction

RMG simulations

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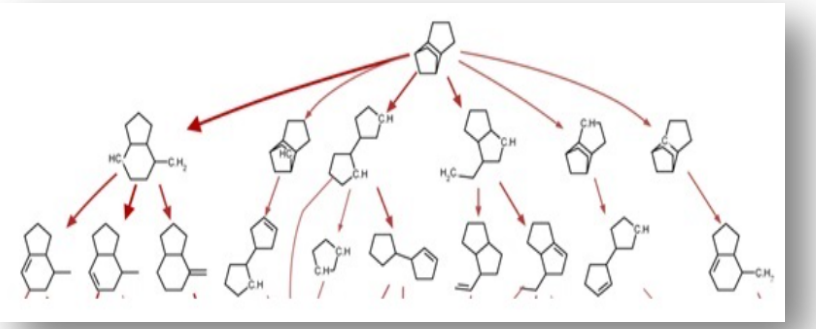

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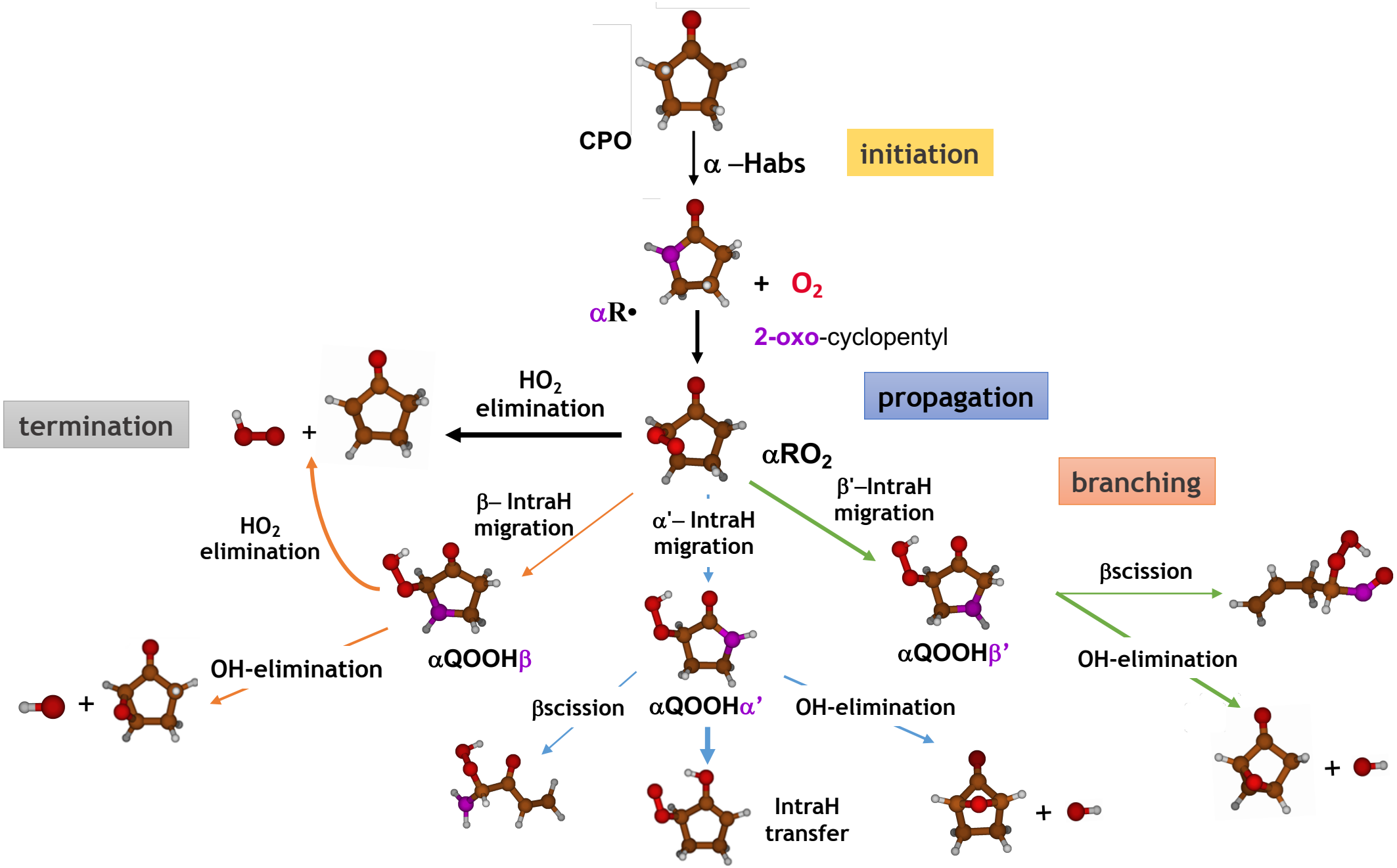
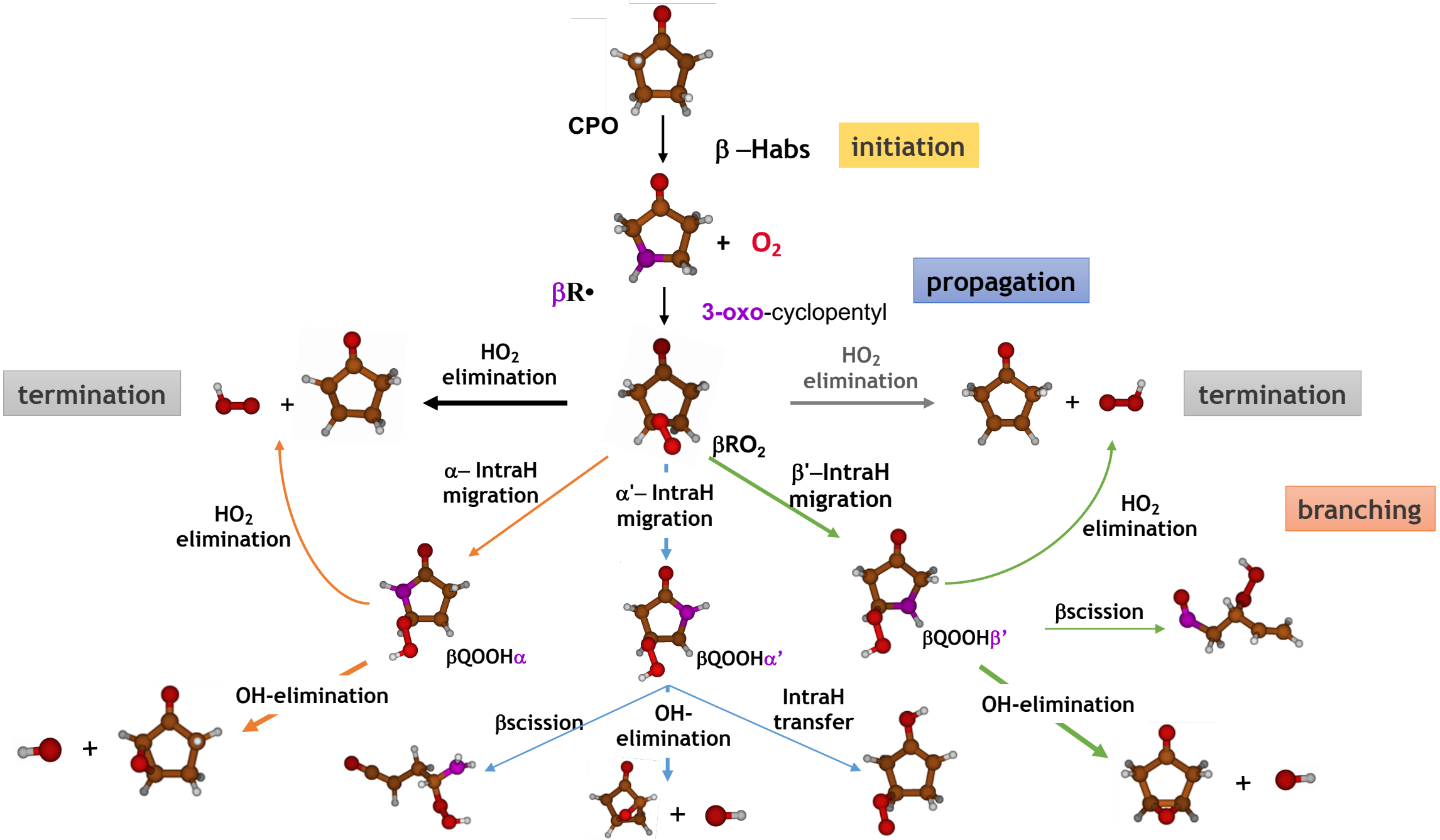
Oxidation of **2-oxo**-cyclopentyl

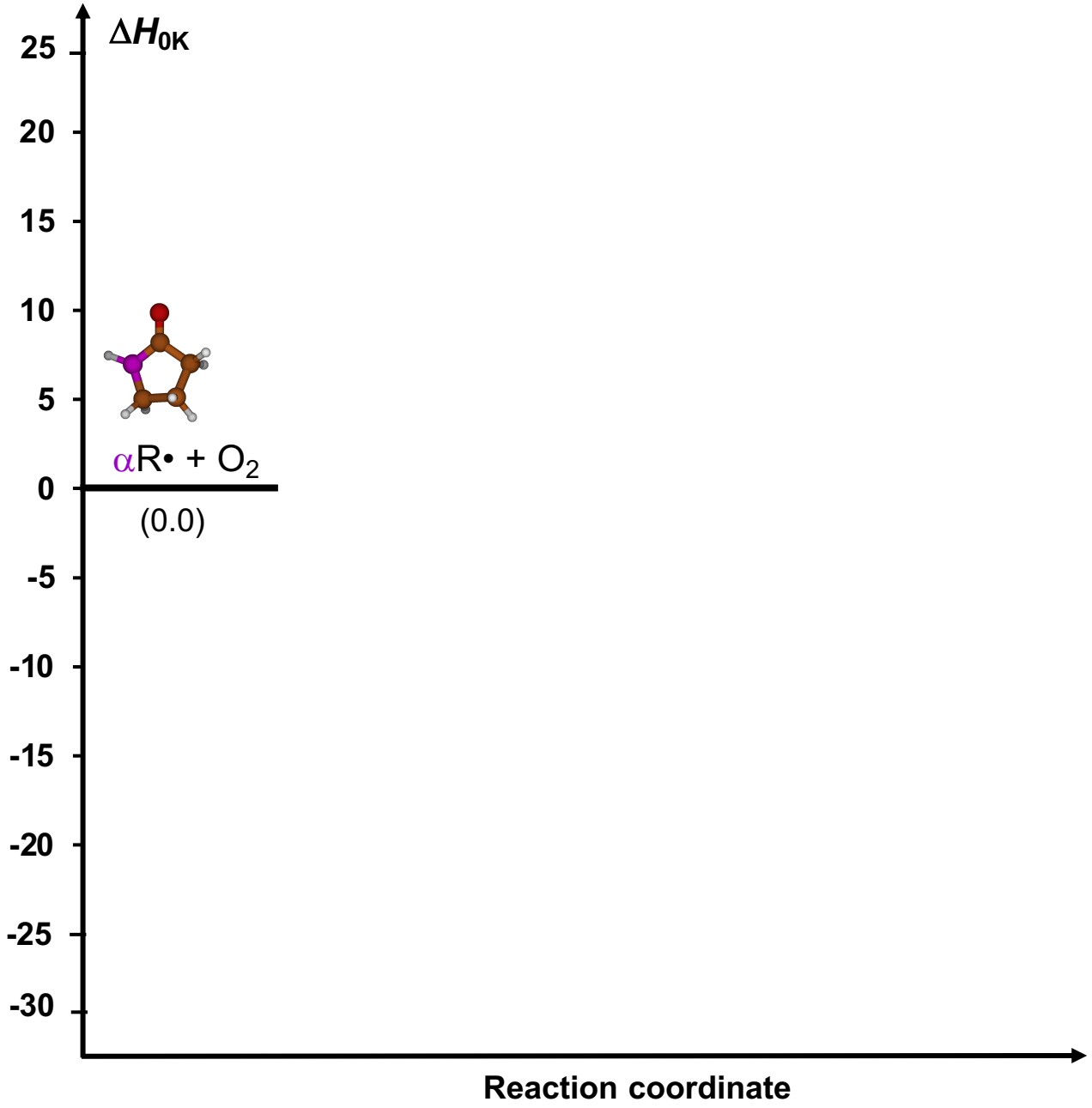


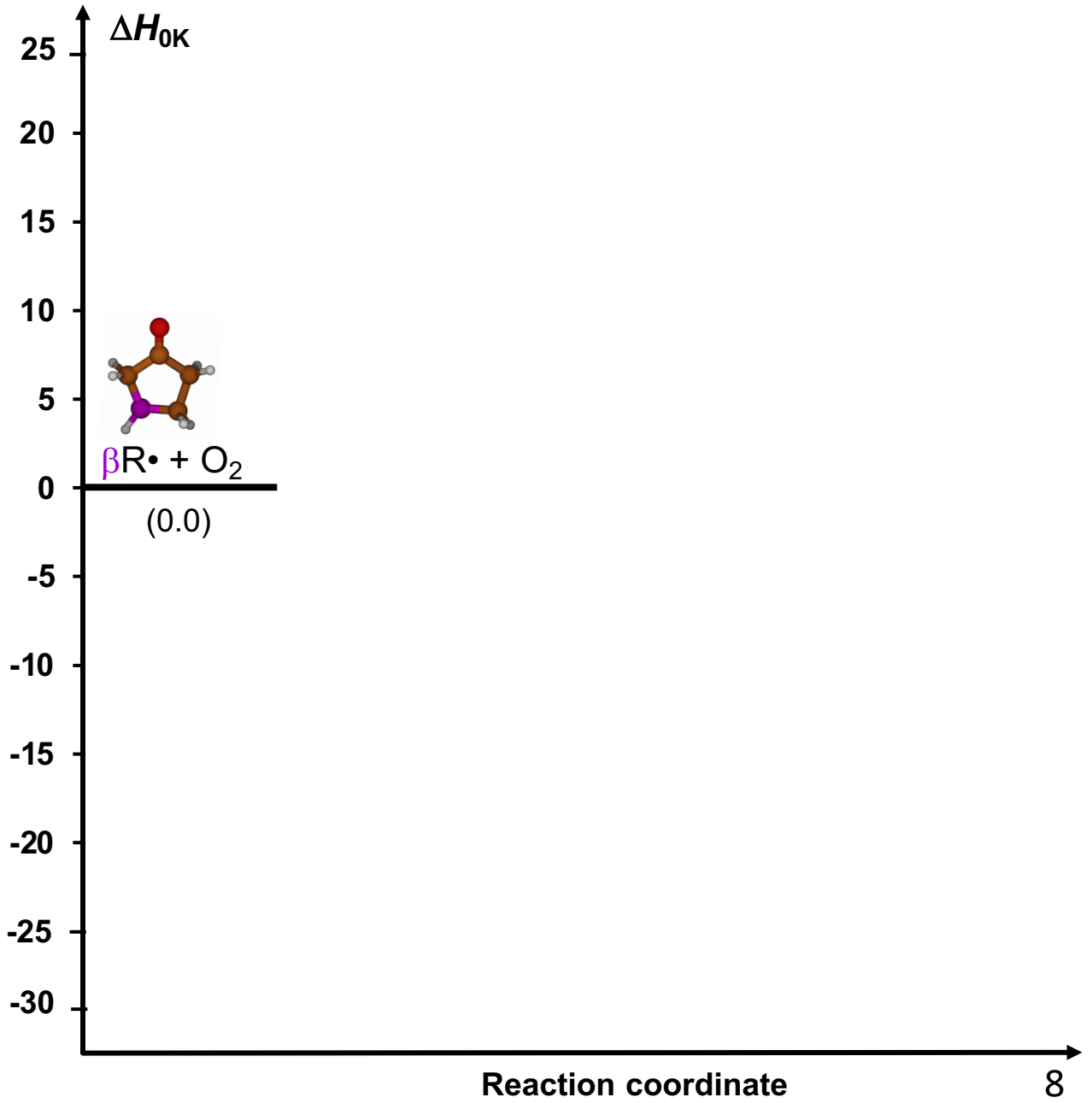
Oxidation of **3-oxo**-cyclopentyl



Oxidation of **2-oxo-** & **3-oxo**-cyclopentyl

ΔH_{0K} in kcal mol^{-1}





Oxidation of **2-oxo-** & **3-oxo-**cyclopentyl

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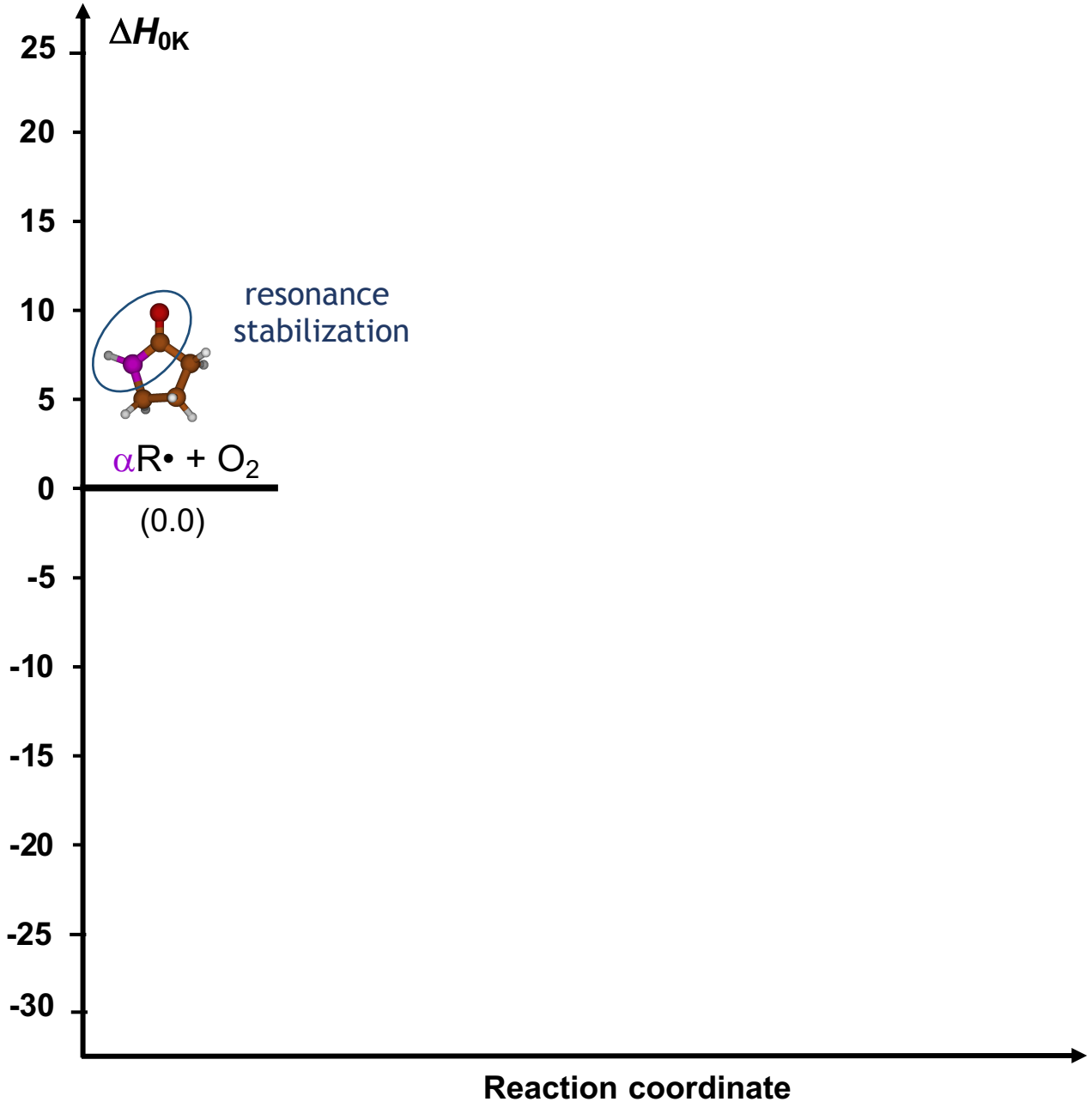

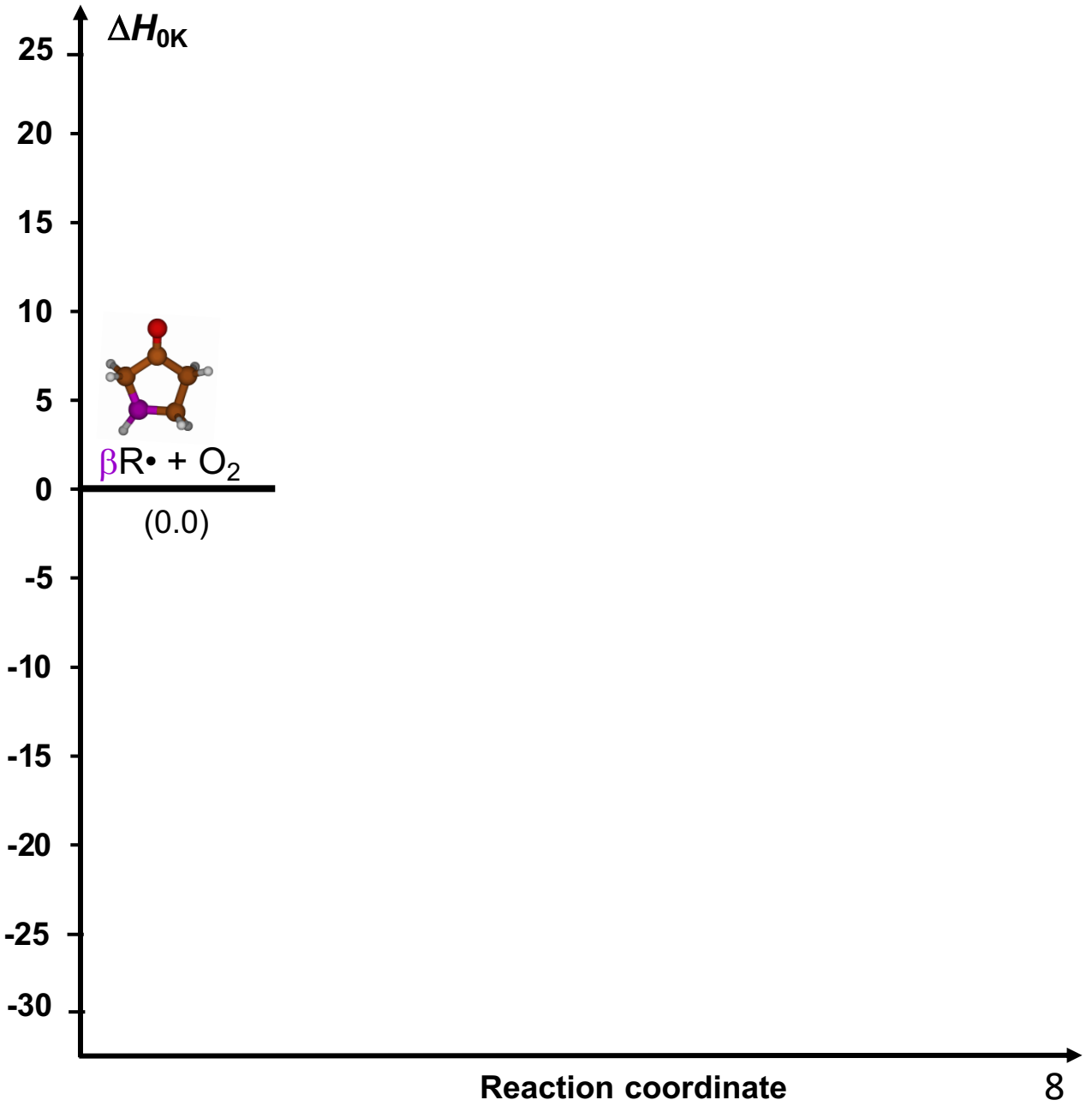

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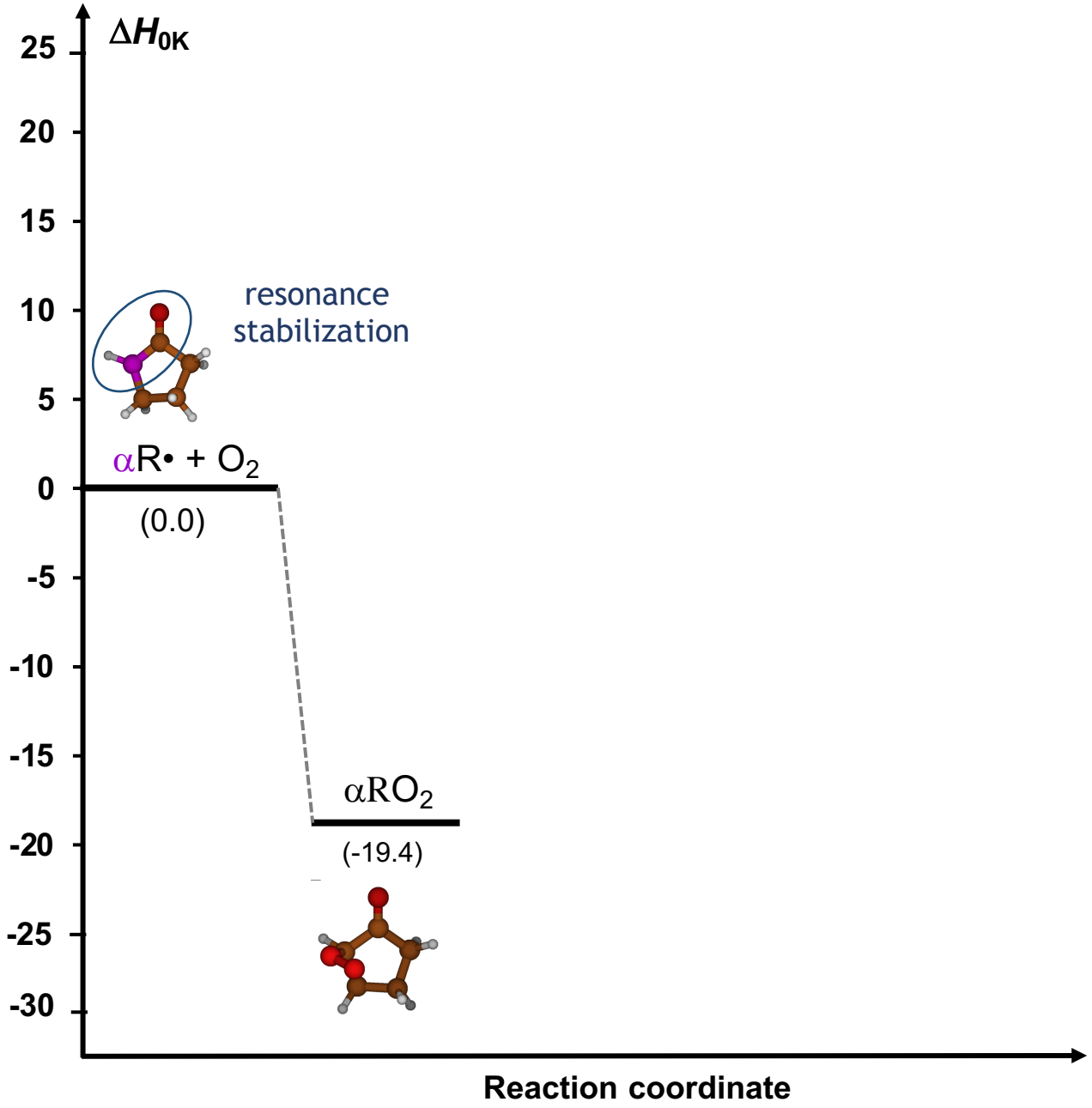
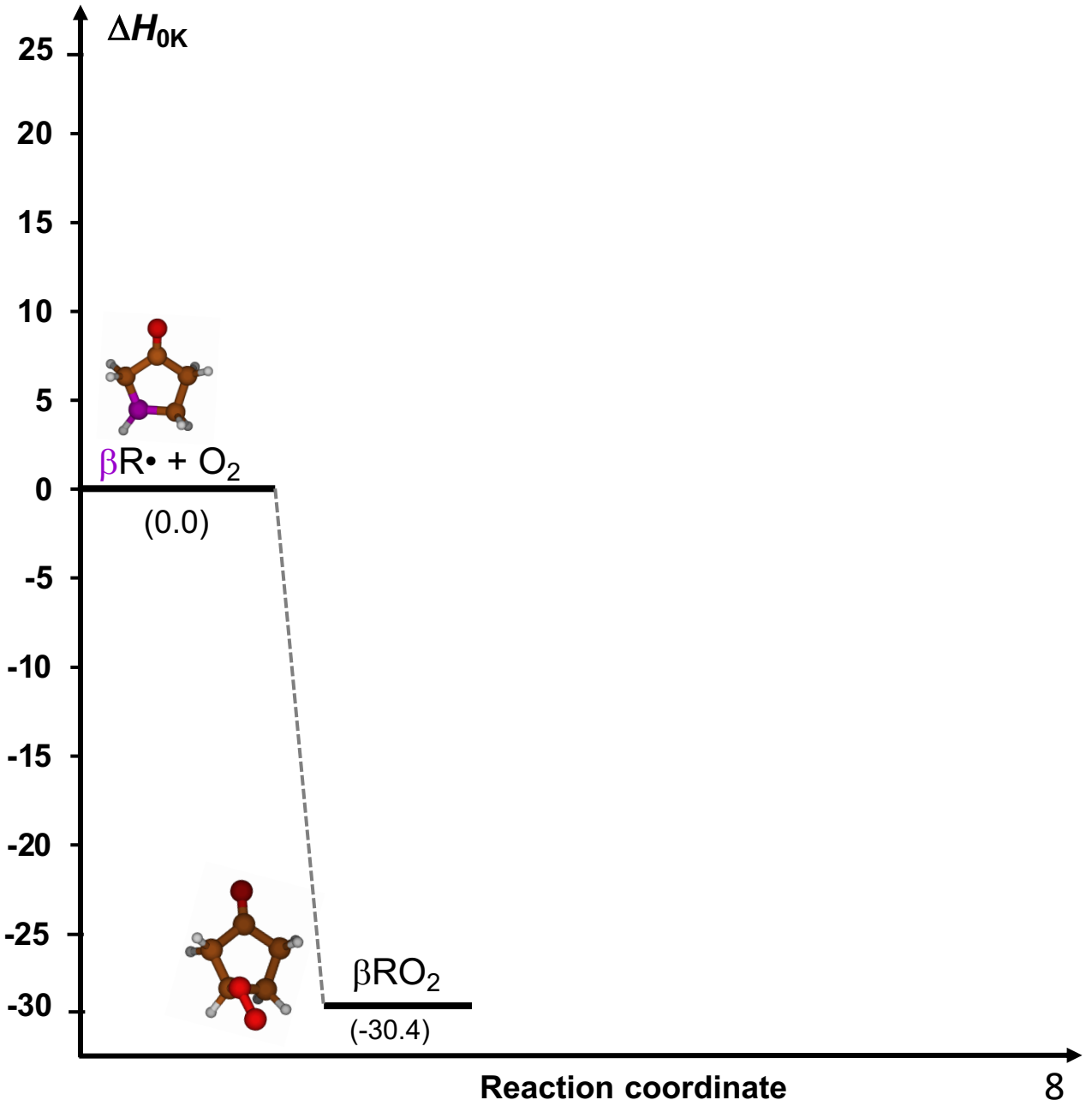
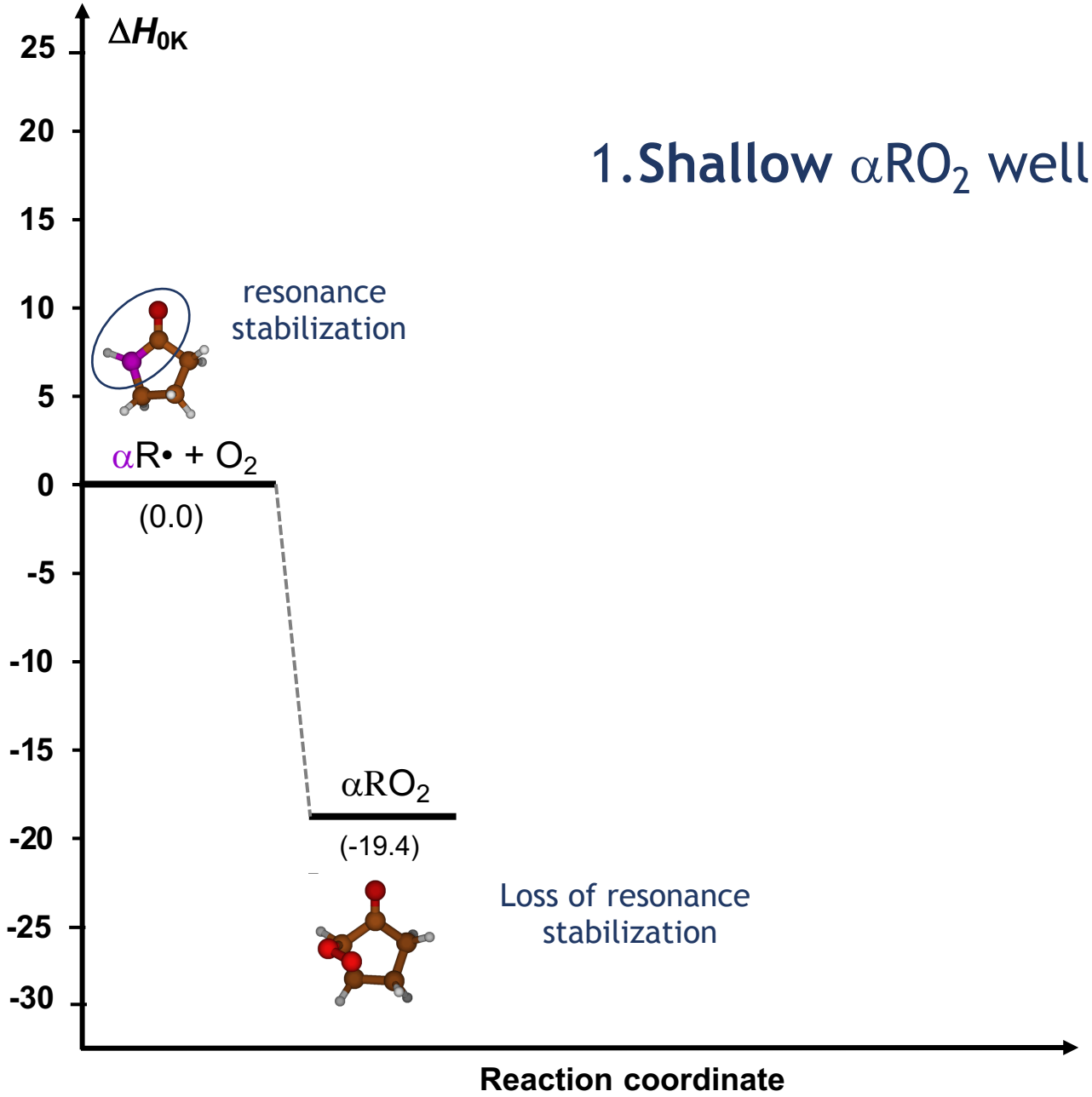


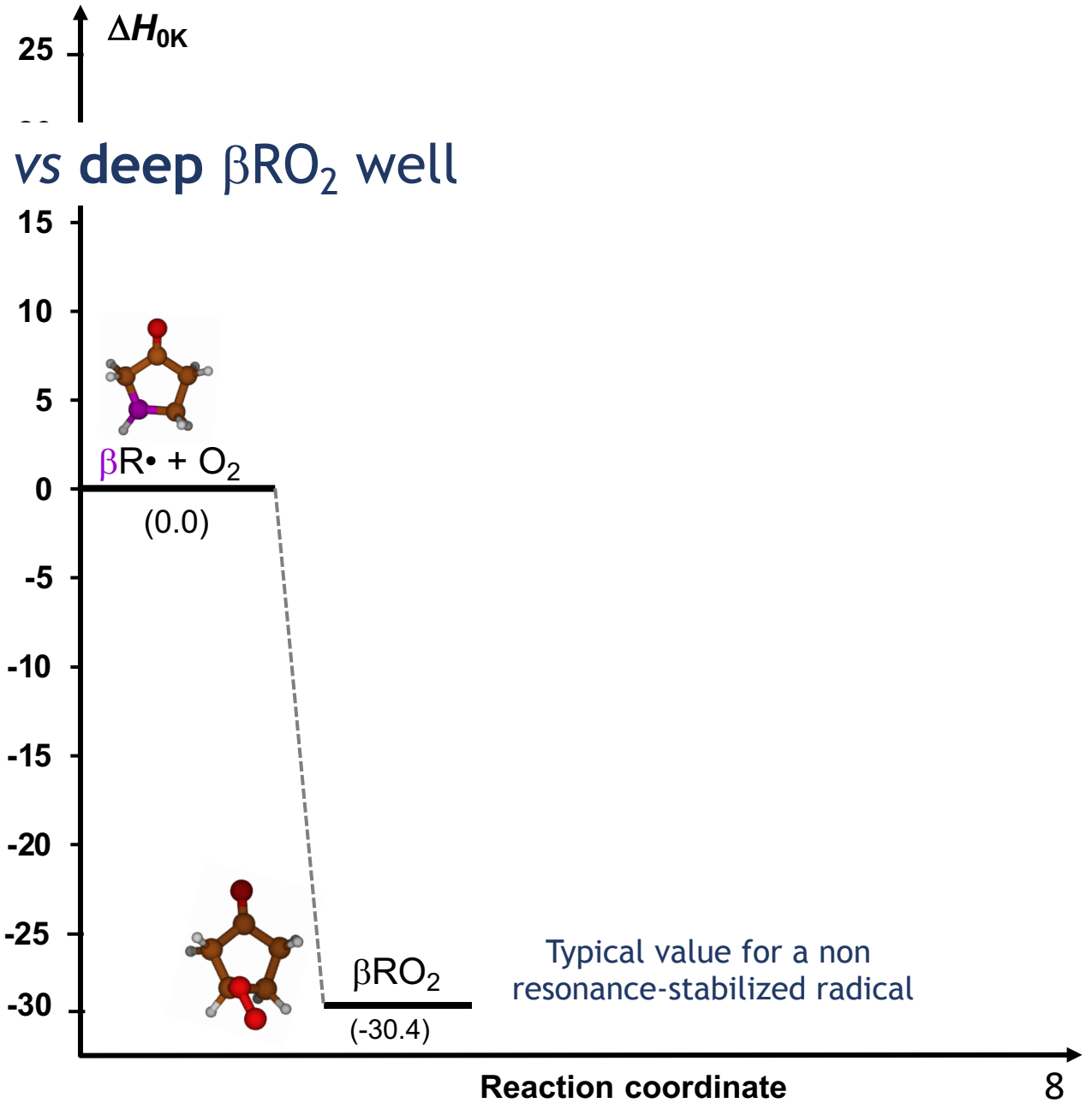


Oxidation of **2-oxo-** & **3-oxo**-cyclopentyl

ΔH_{0K} in kcal mol^{-1}

1. **Shallow** αRO_2 well *vs* **deep** βRO_2 well





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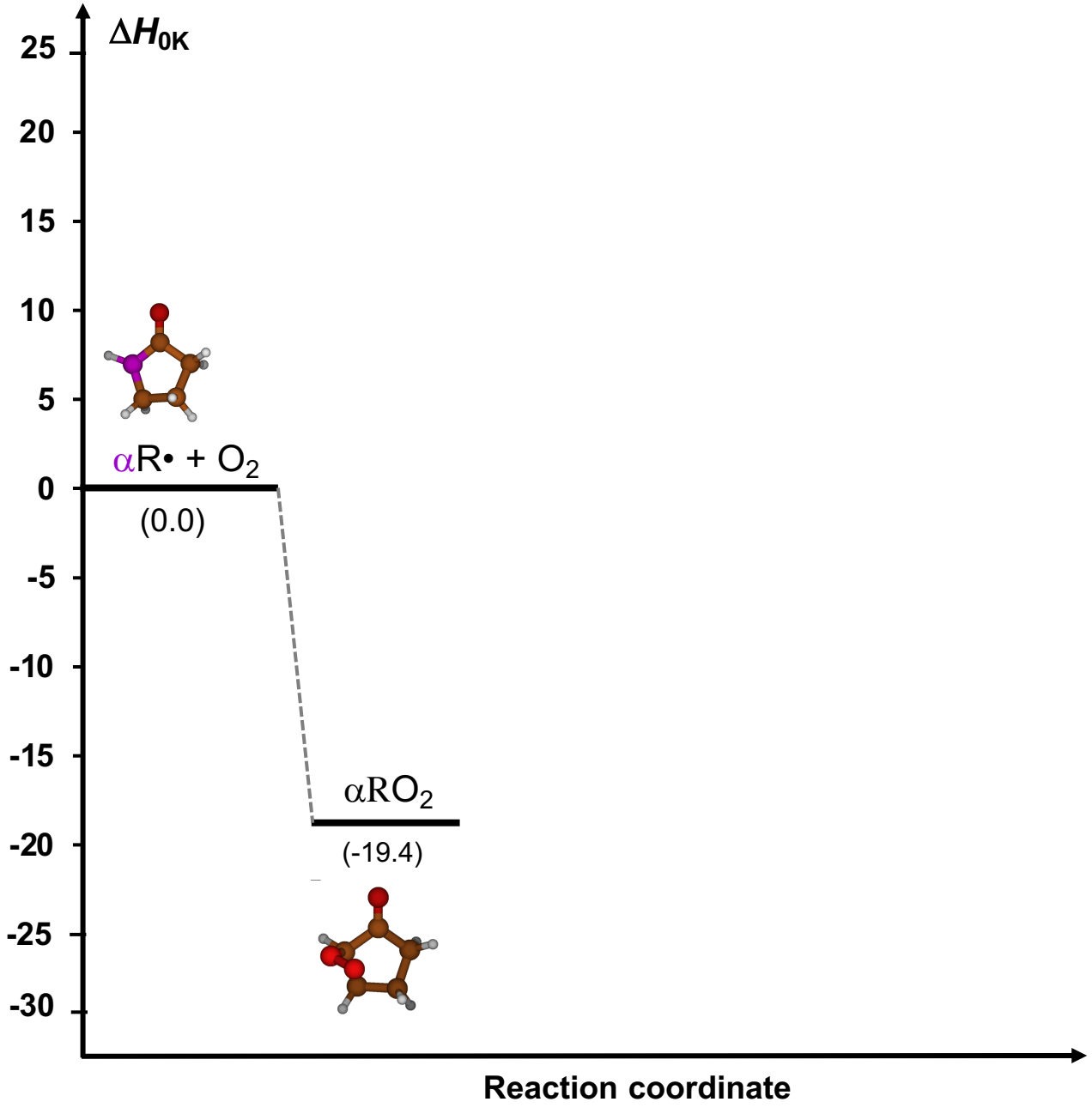

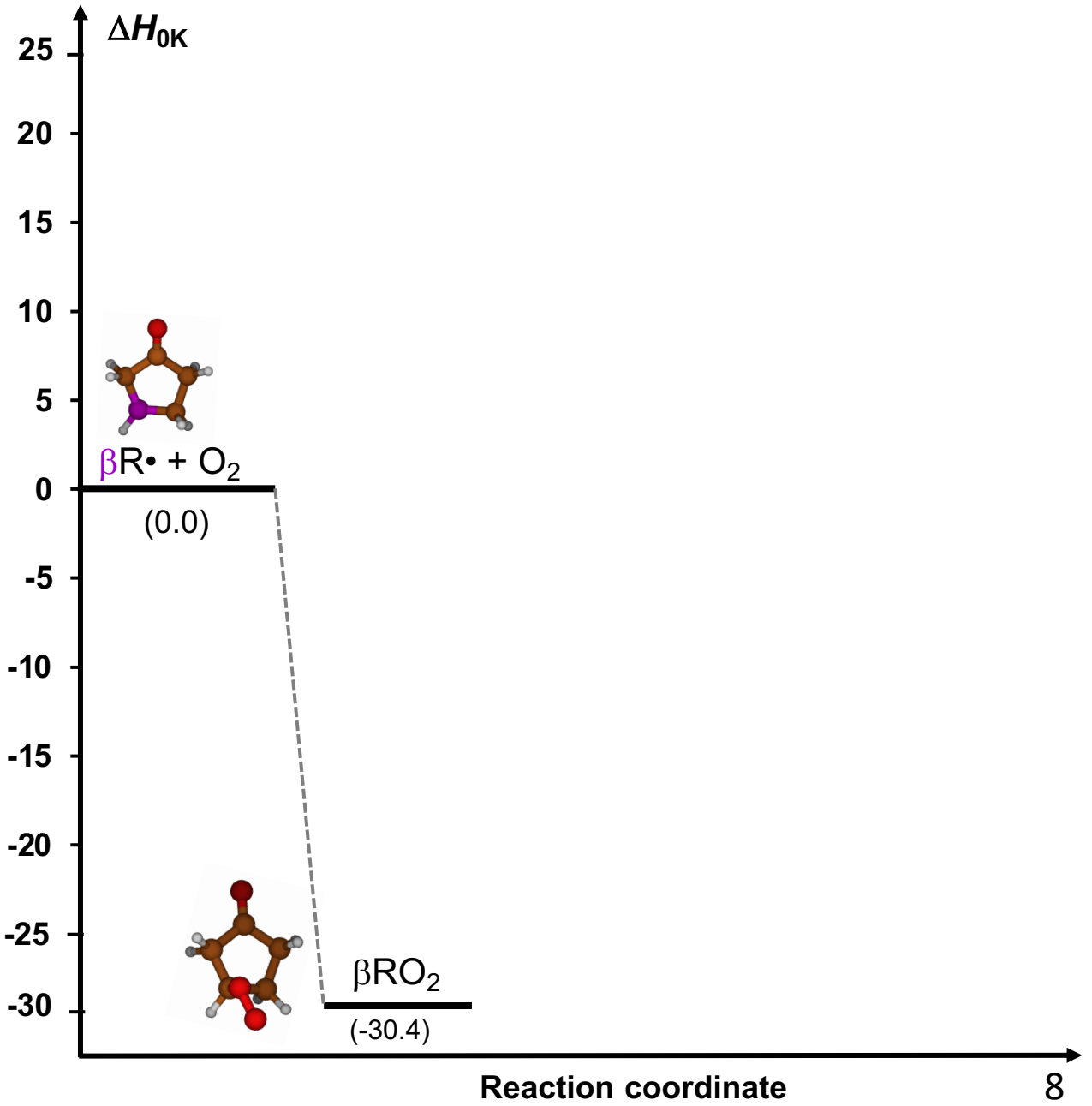

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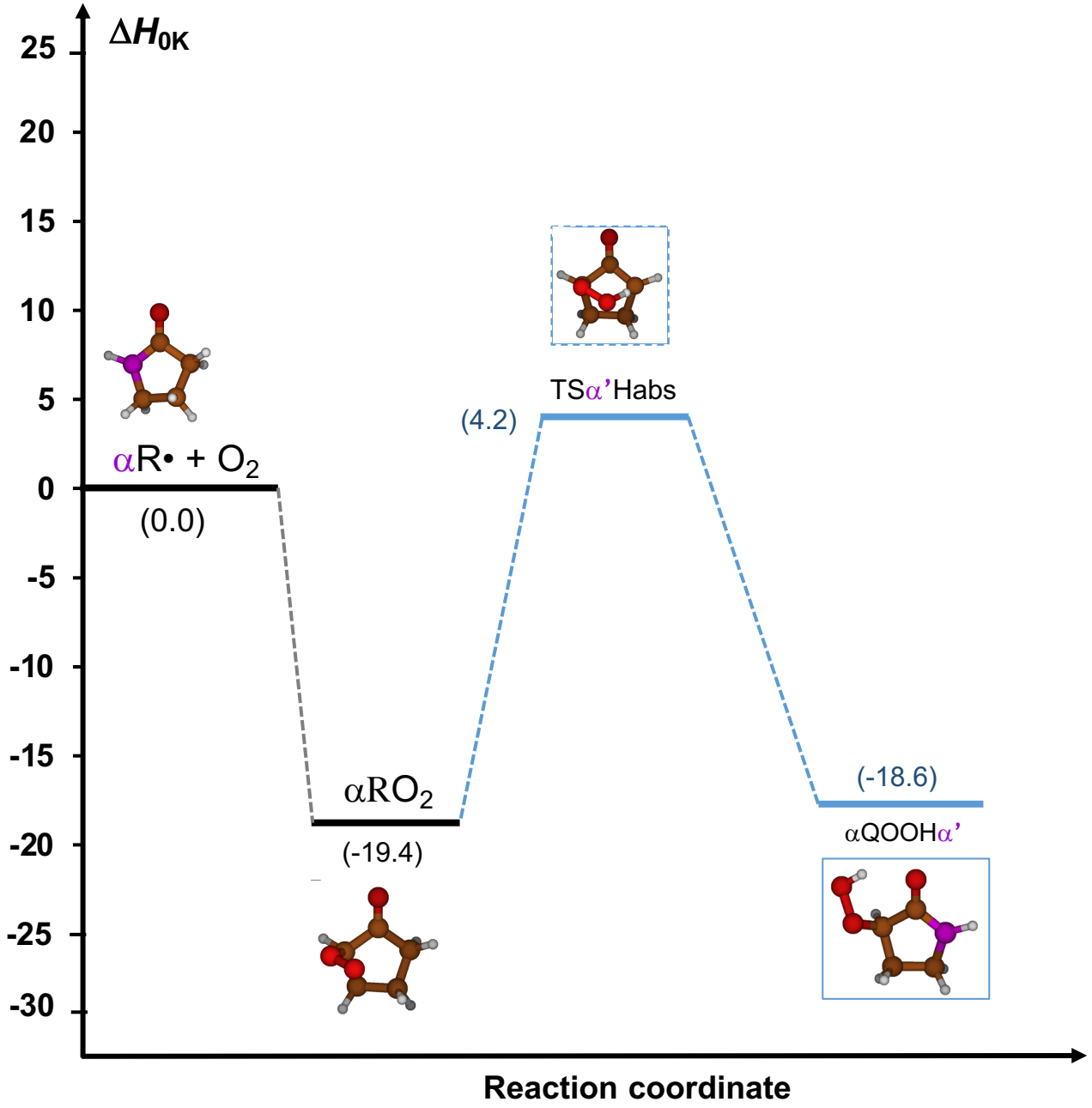

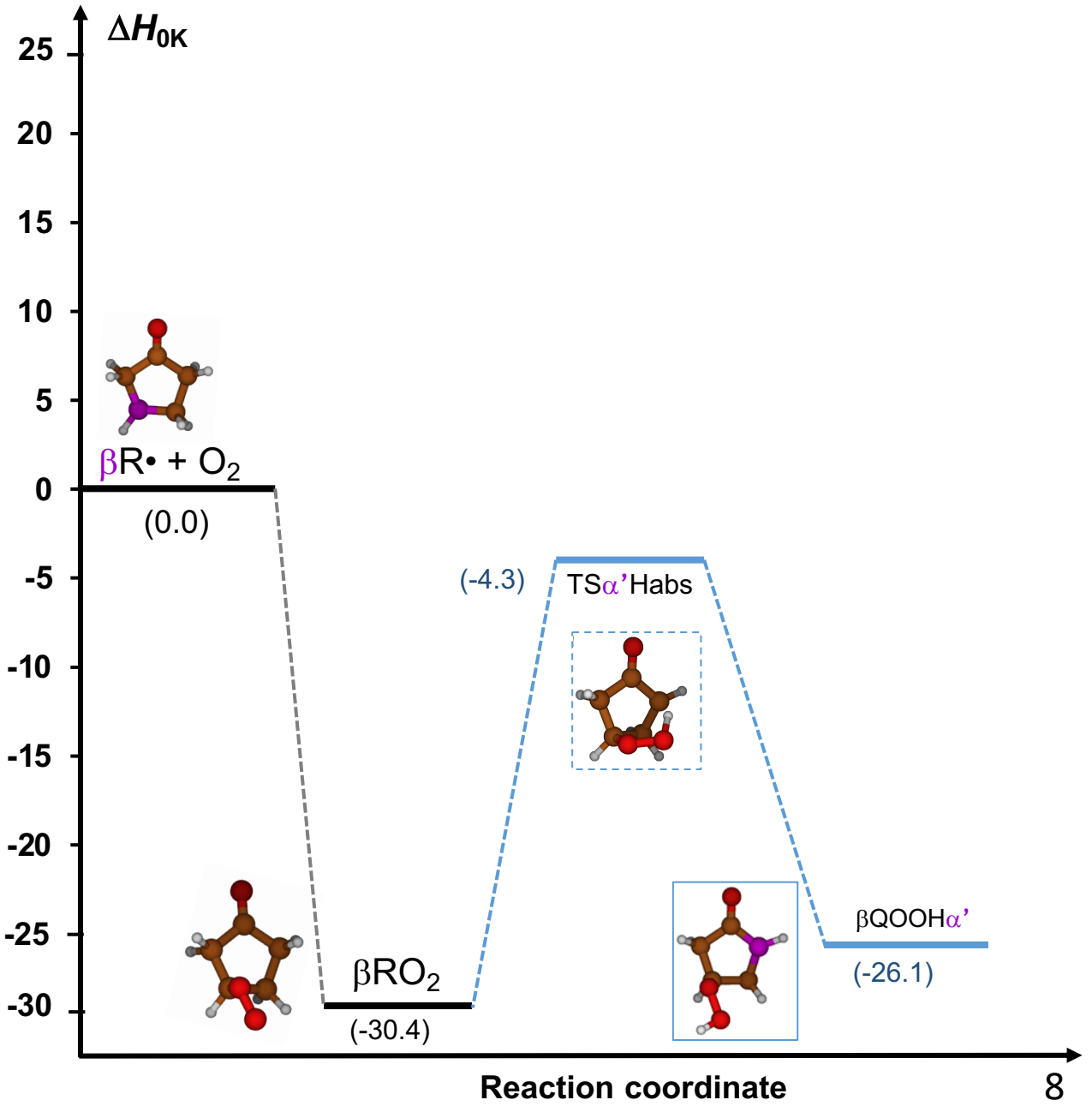

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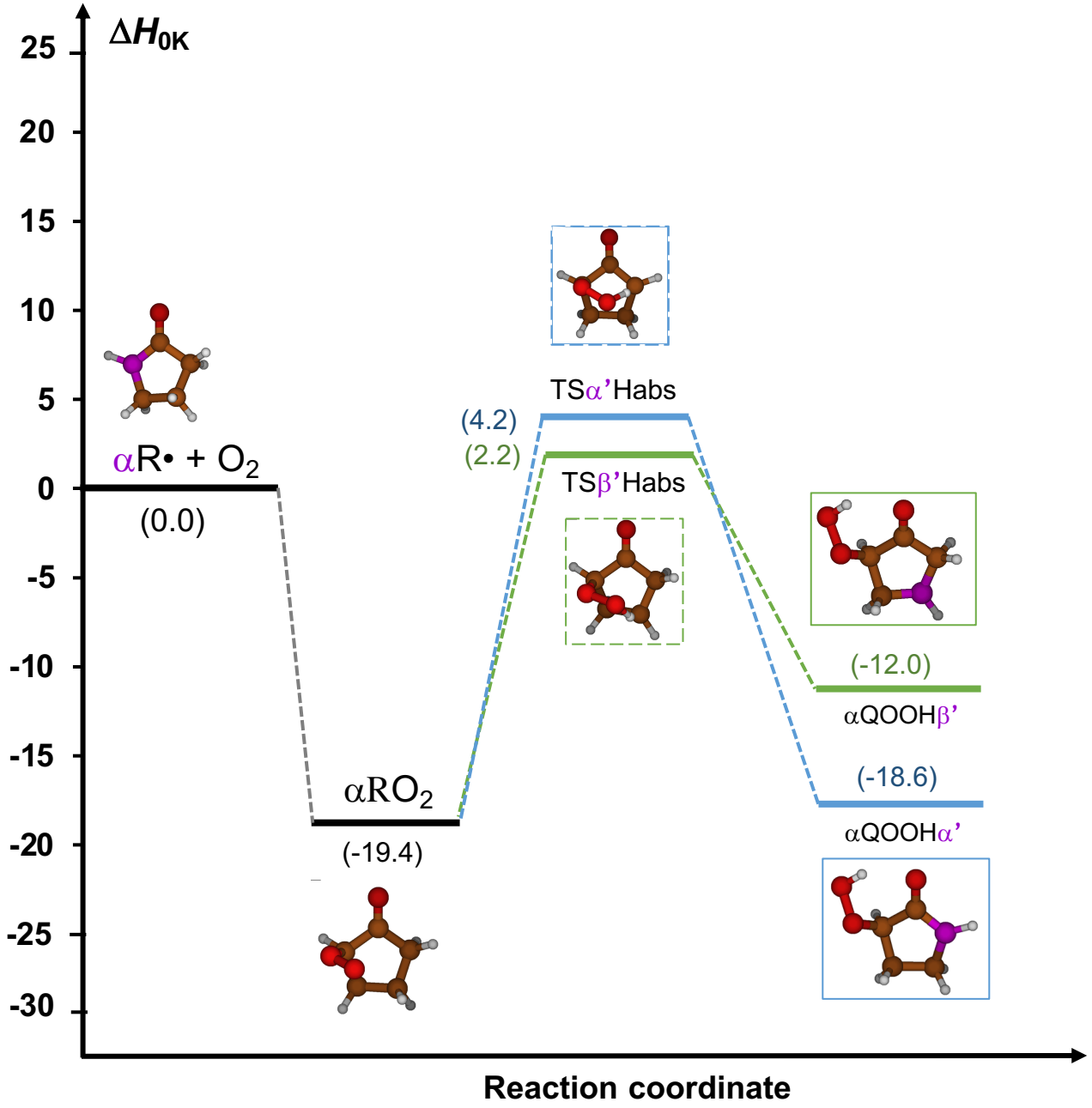
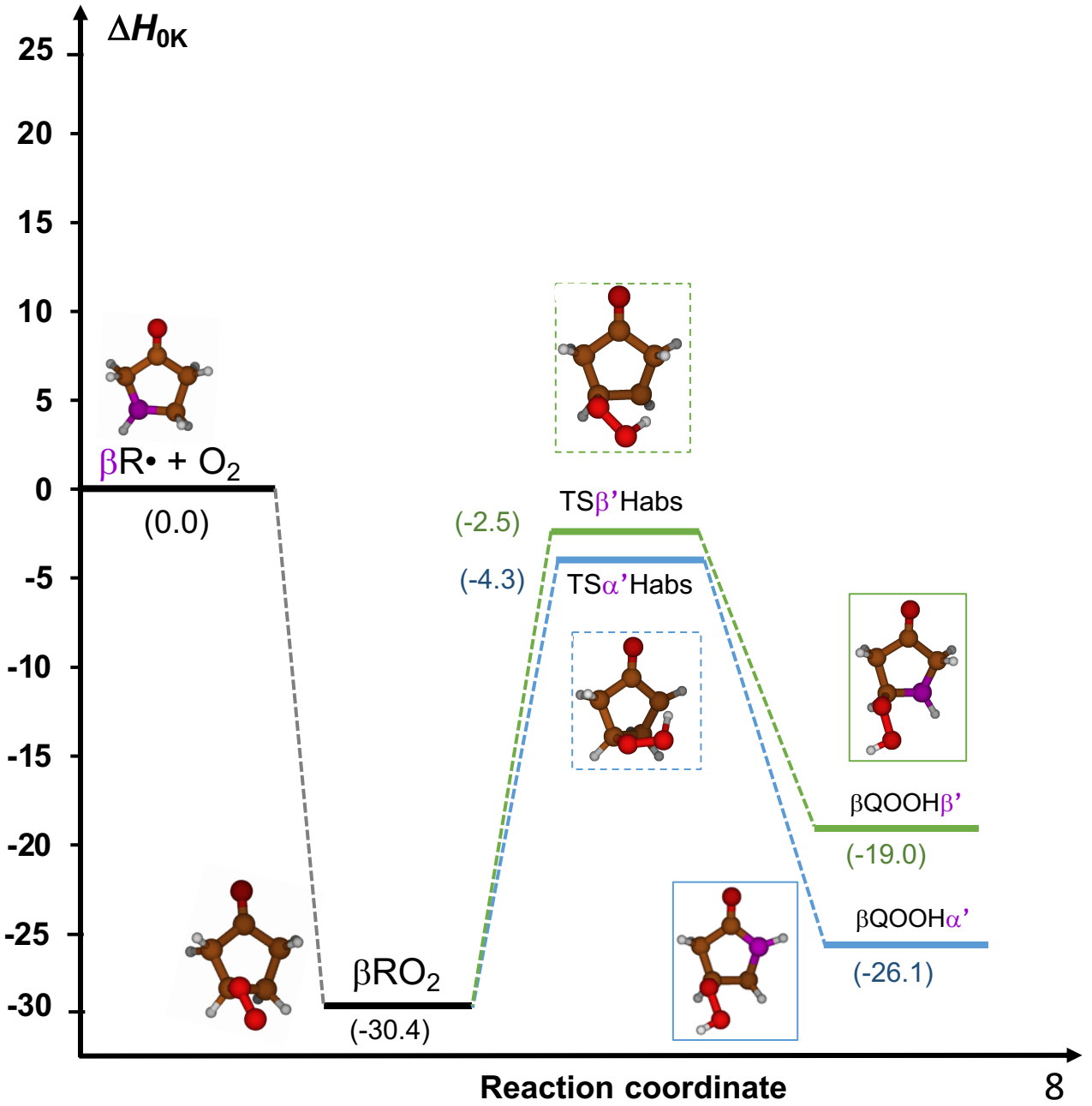
ΔH_{0K} in kcal mol^{-1}

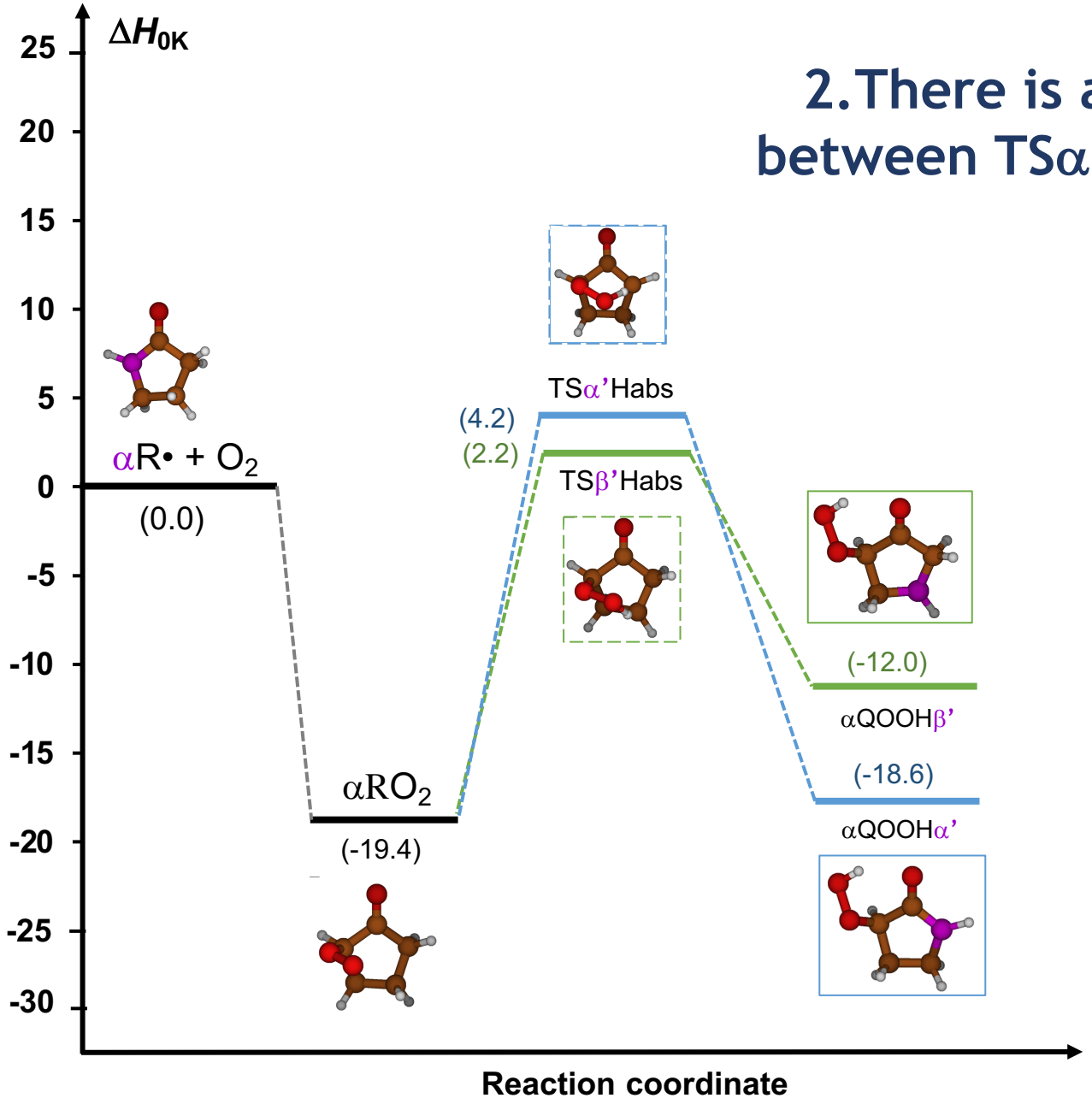


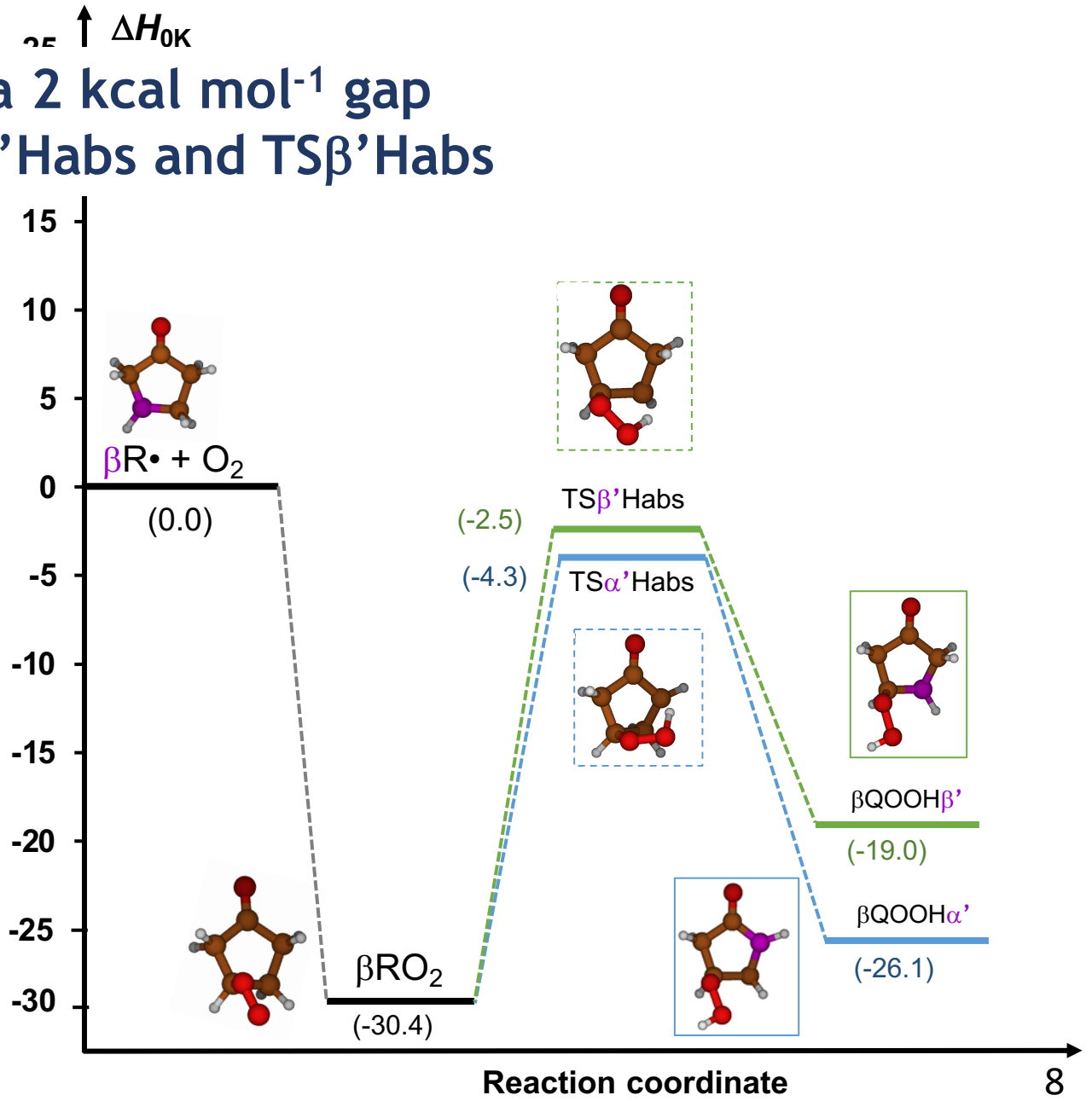


Oxidation of 2-oxo- & 3-oxo-cyclopentyl

ΔH_{0K} in kcal mol^{-1}

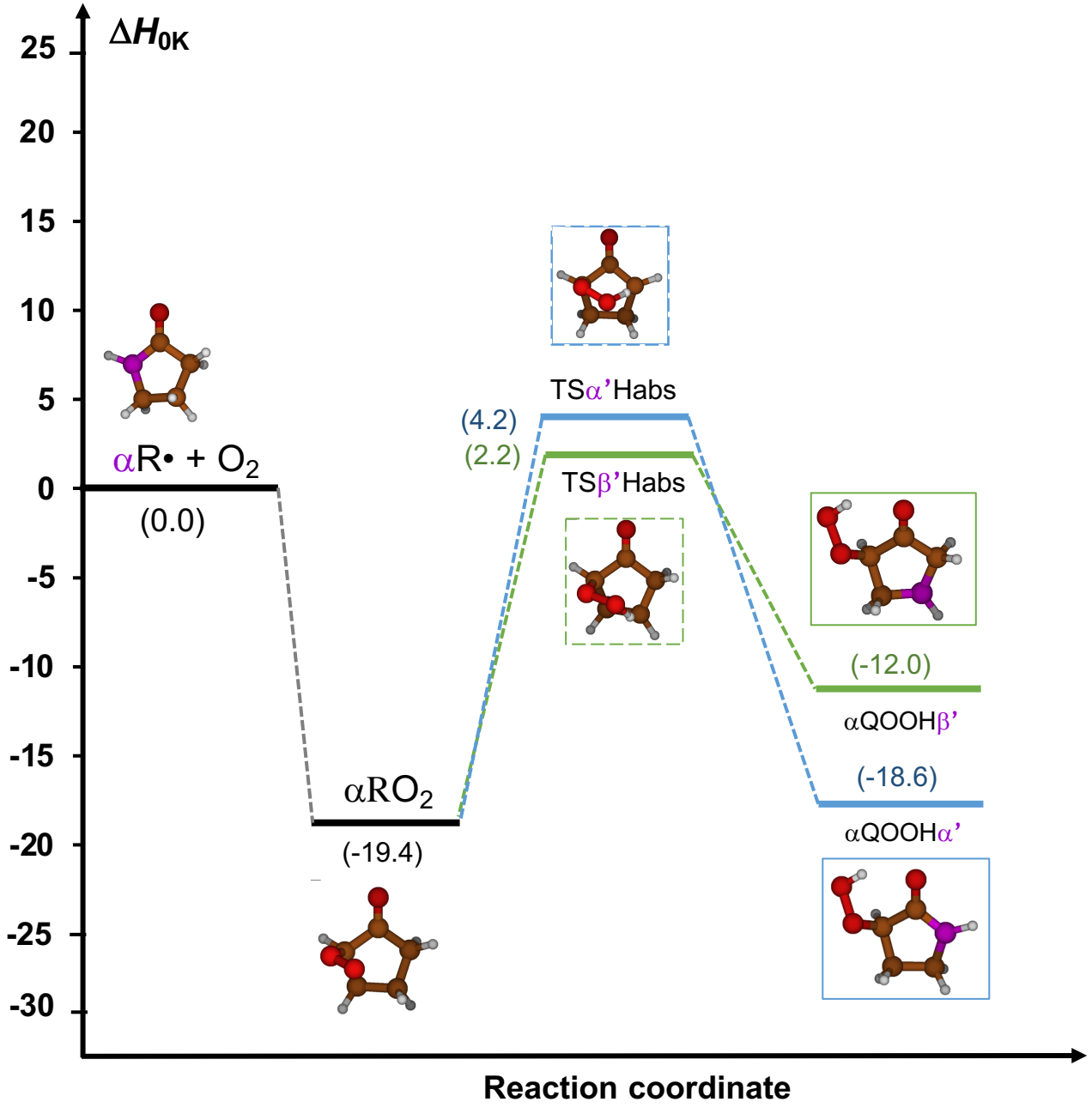
2. There is a 2 kcal mol^{-1} gap between TSα'Habs and TSβ'Habs

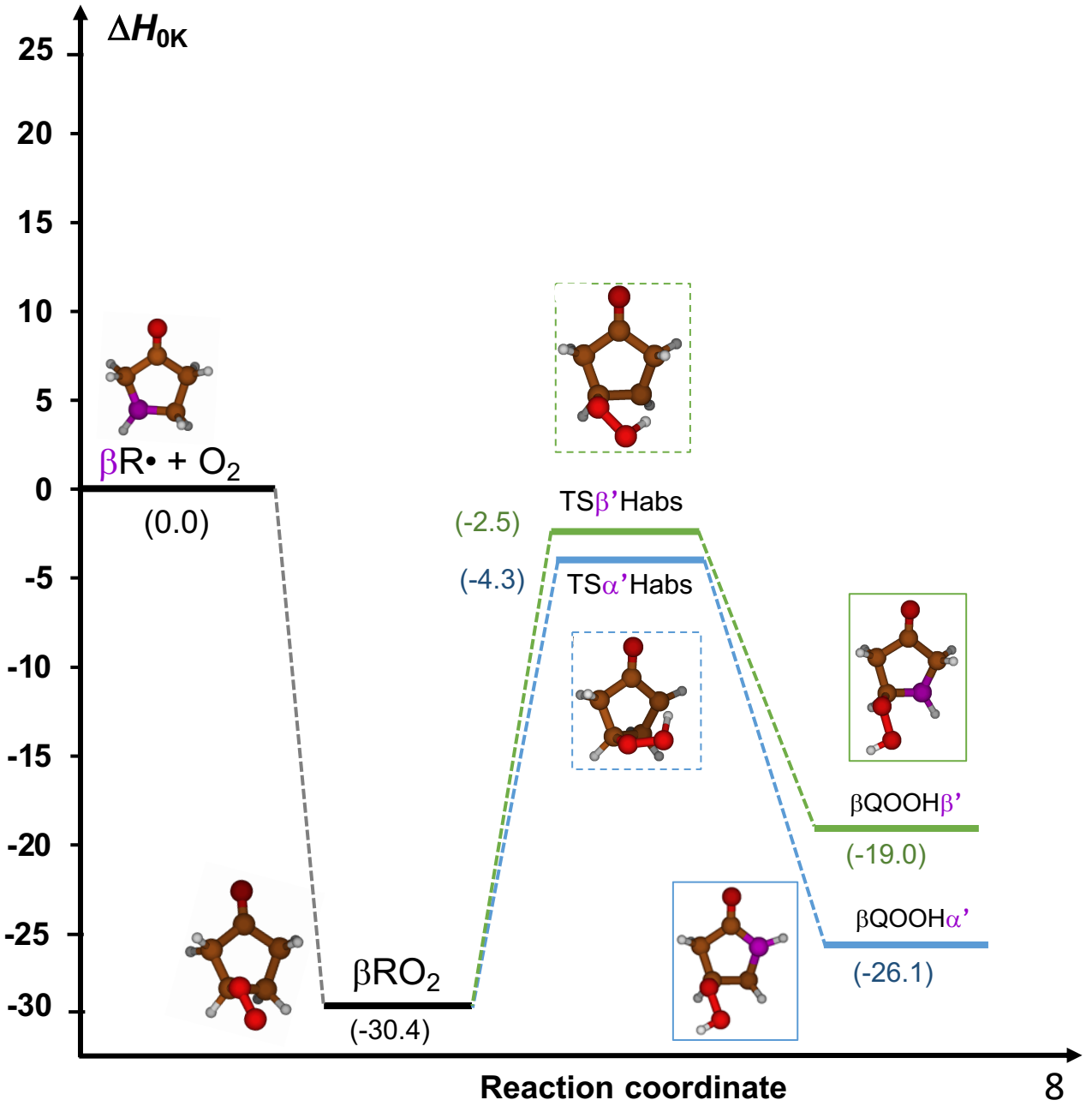




Oxidation of 2-oxo- & 3-oxo-cyclopentyl

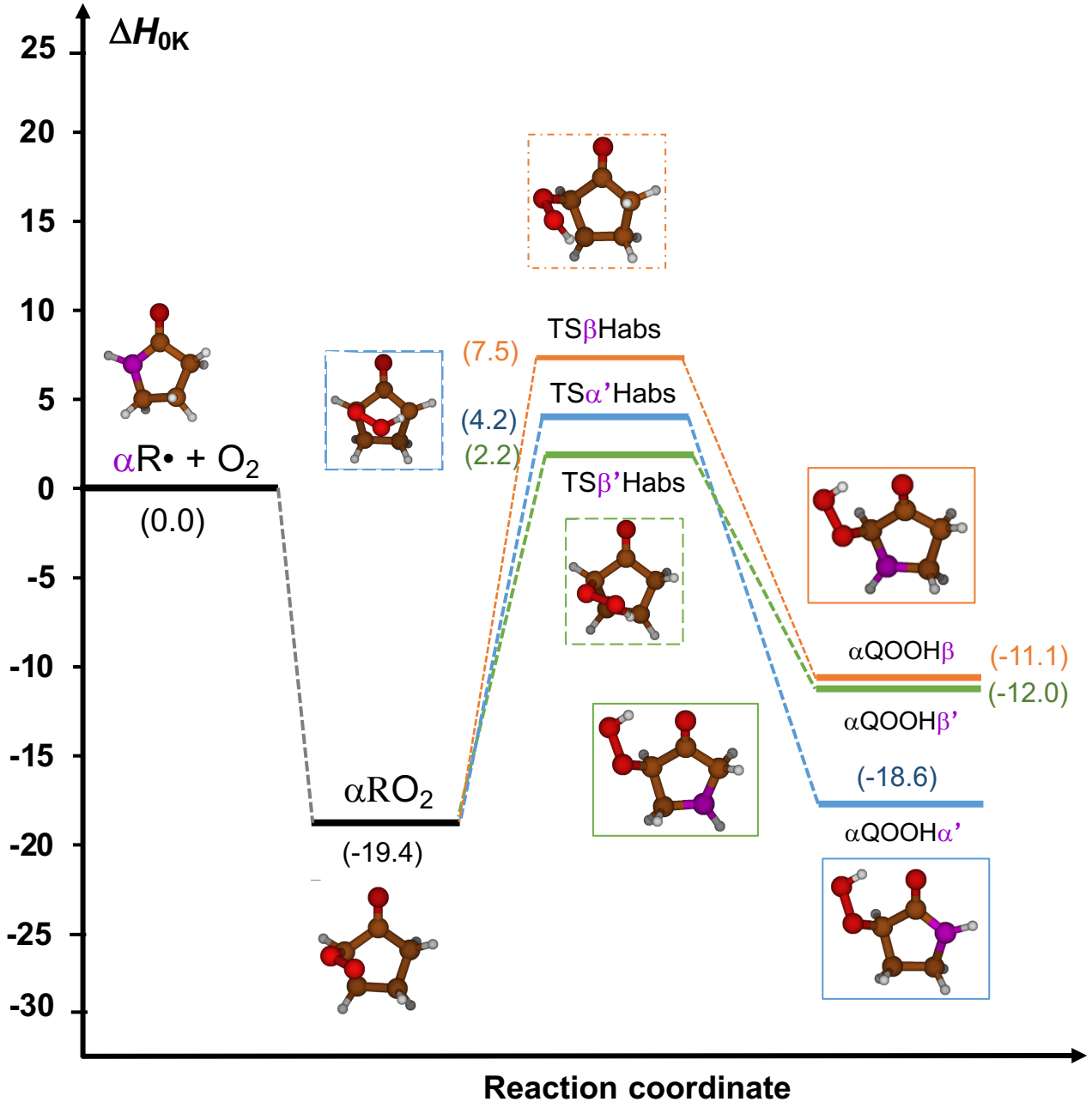
ΔH_{0K} in kcal mol^{-1}

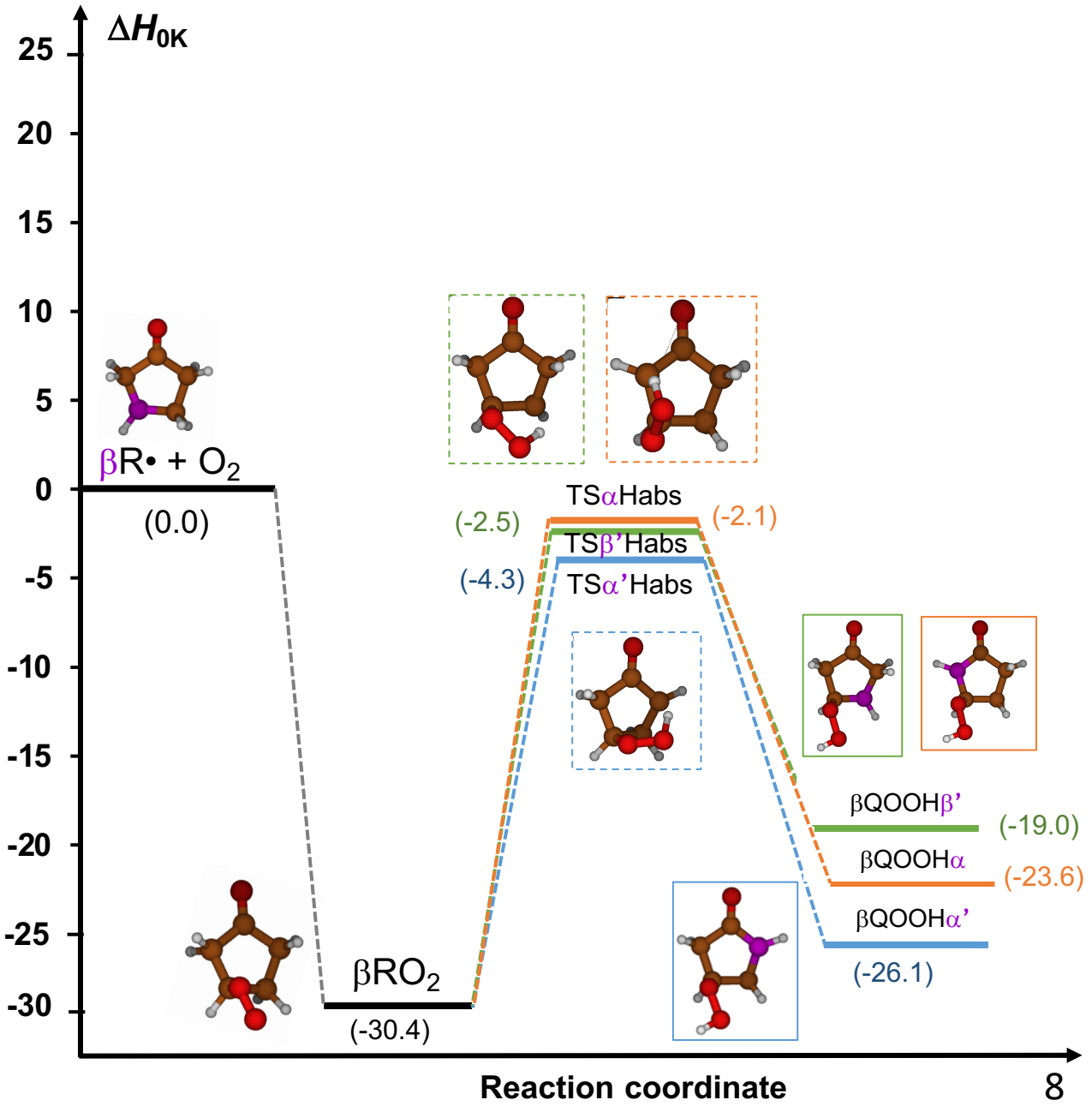




Oxidation of 2-oxo- & 3-oxo-cyclopentyl

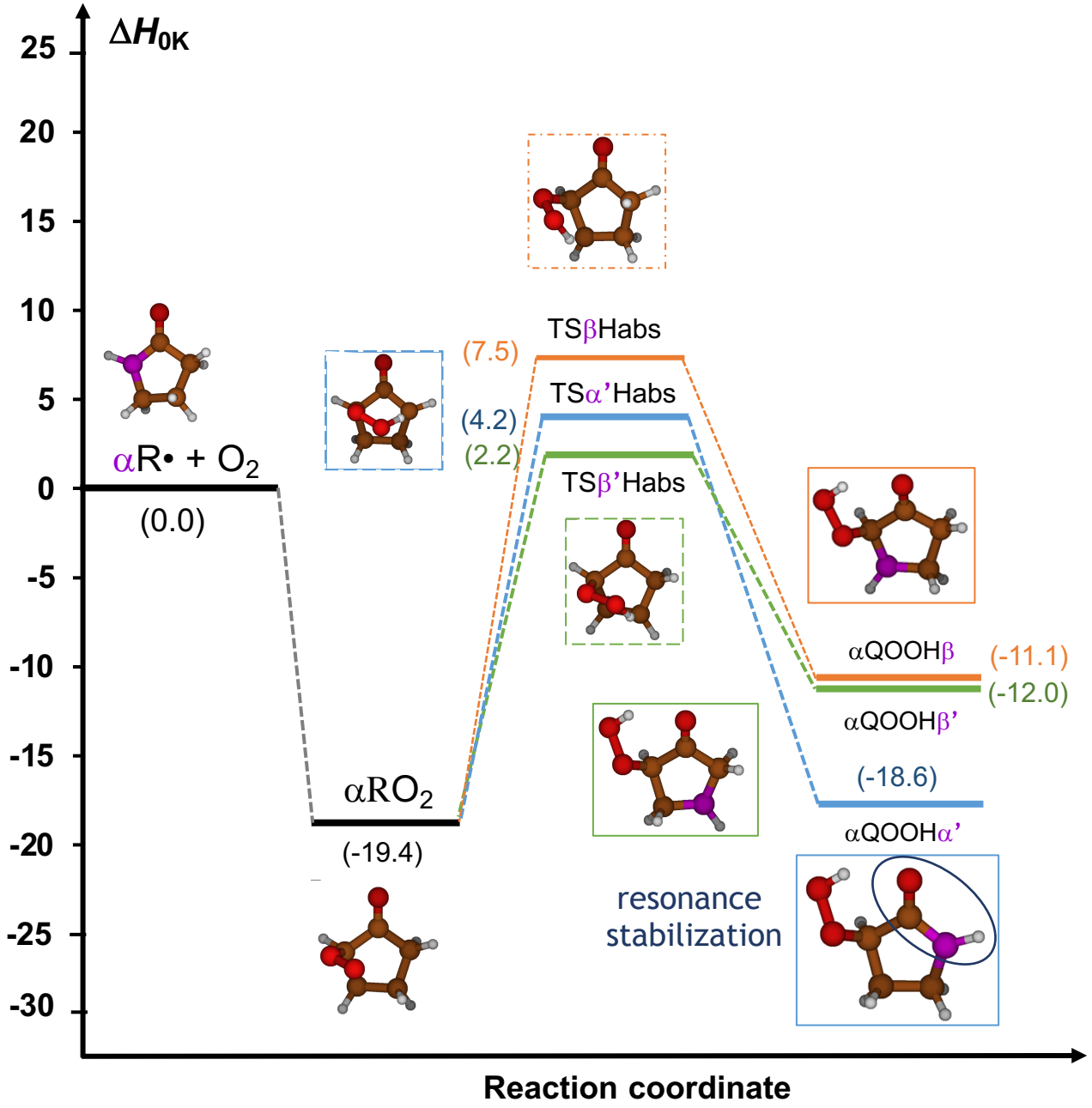
ΔH_{0K} in kcal mol^{-1}

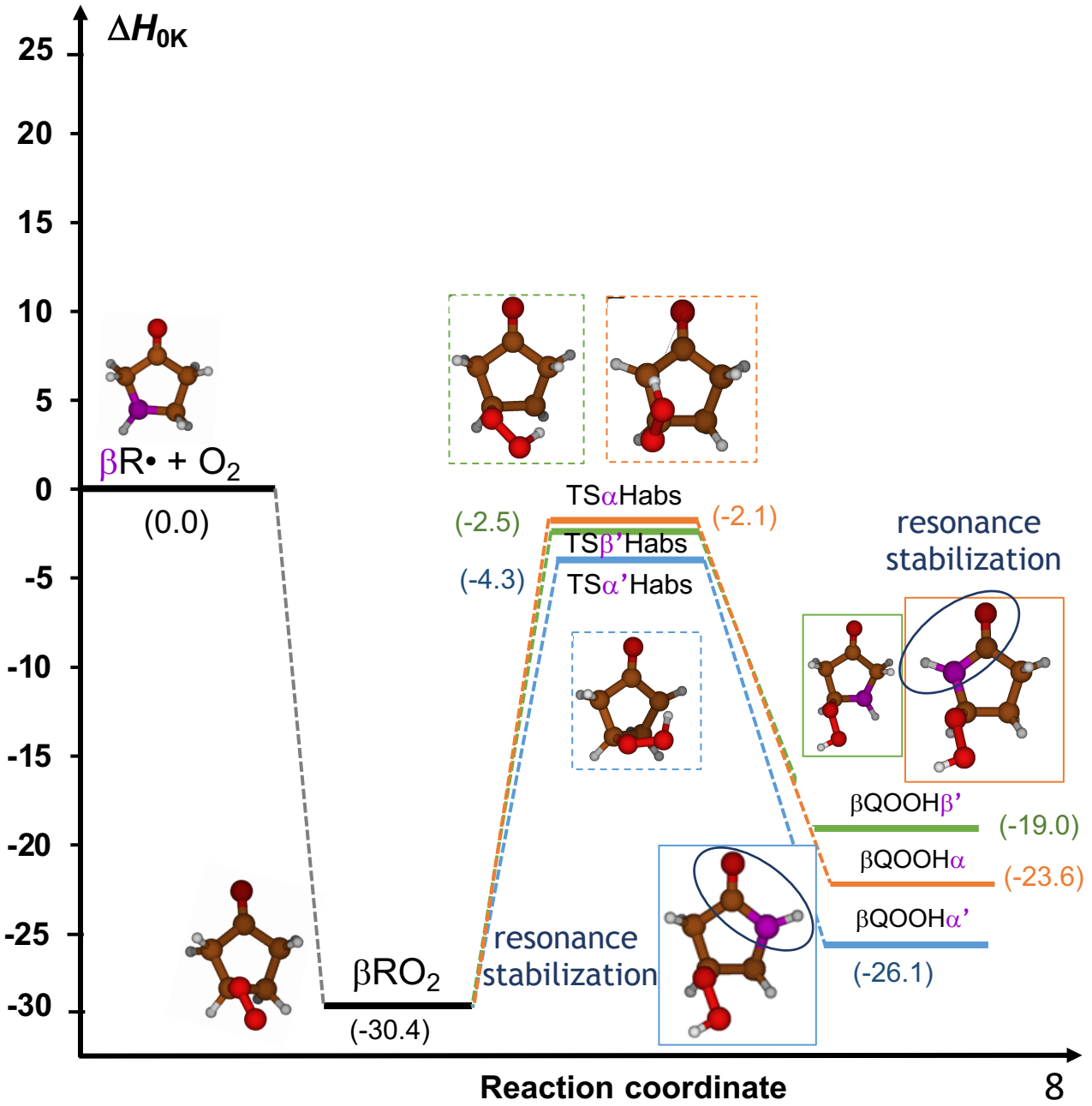




Oxidation of 2-oxo- & 3-oxo-cyclopentyl

ΔH_{0K} in kcal mol^{-1}

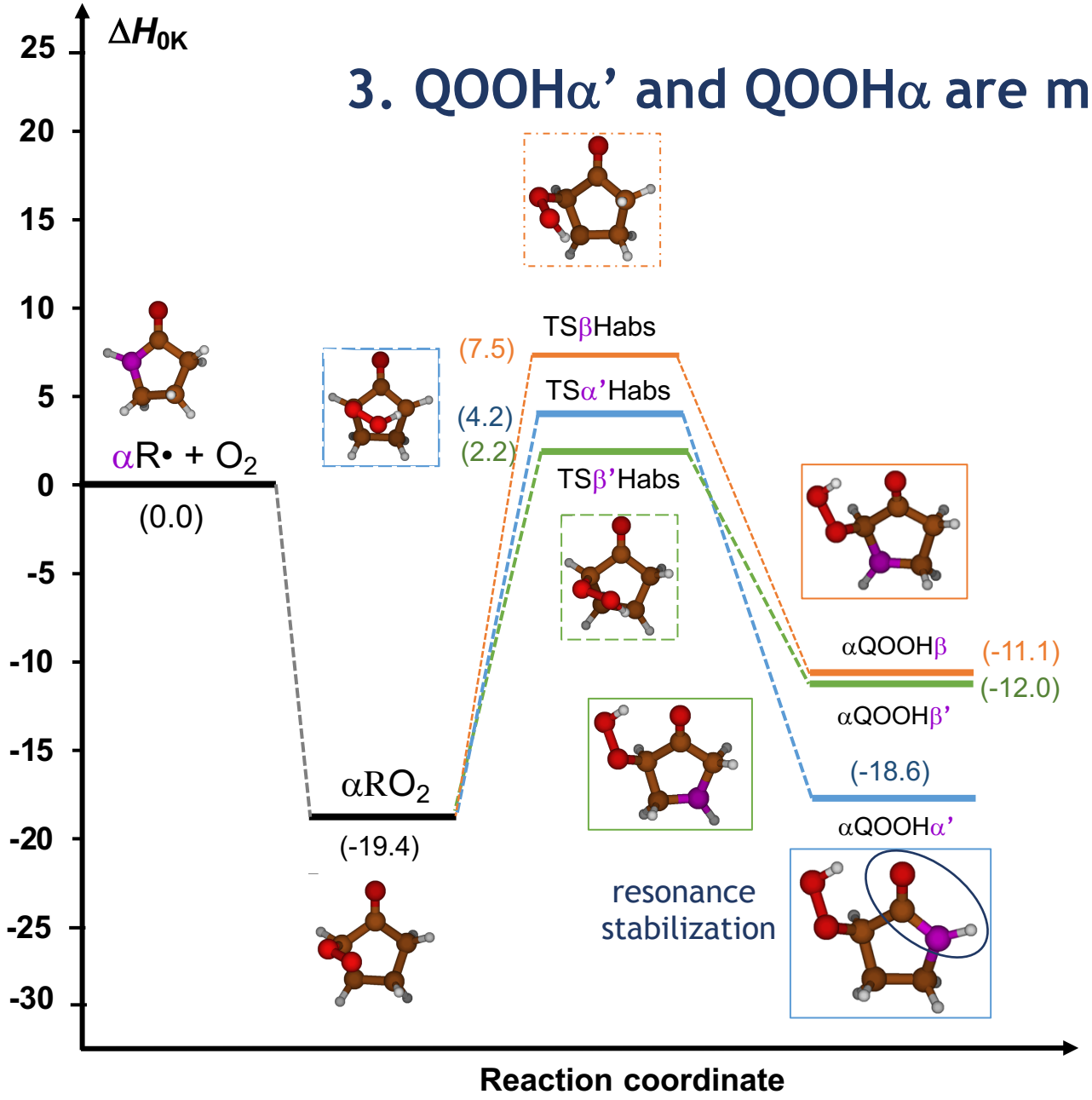


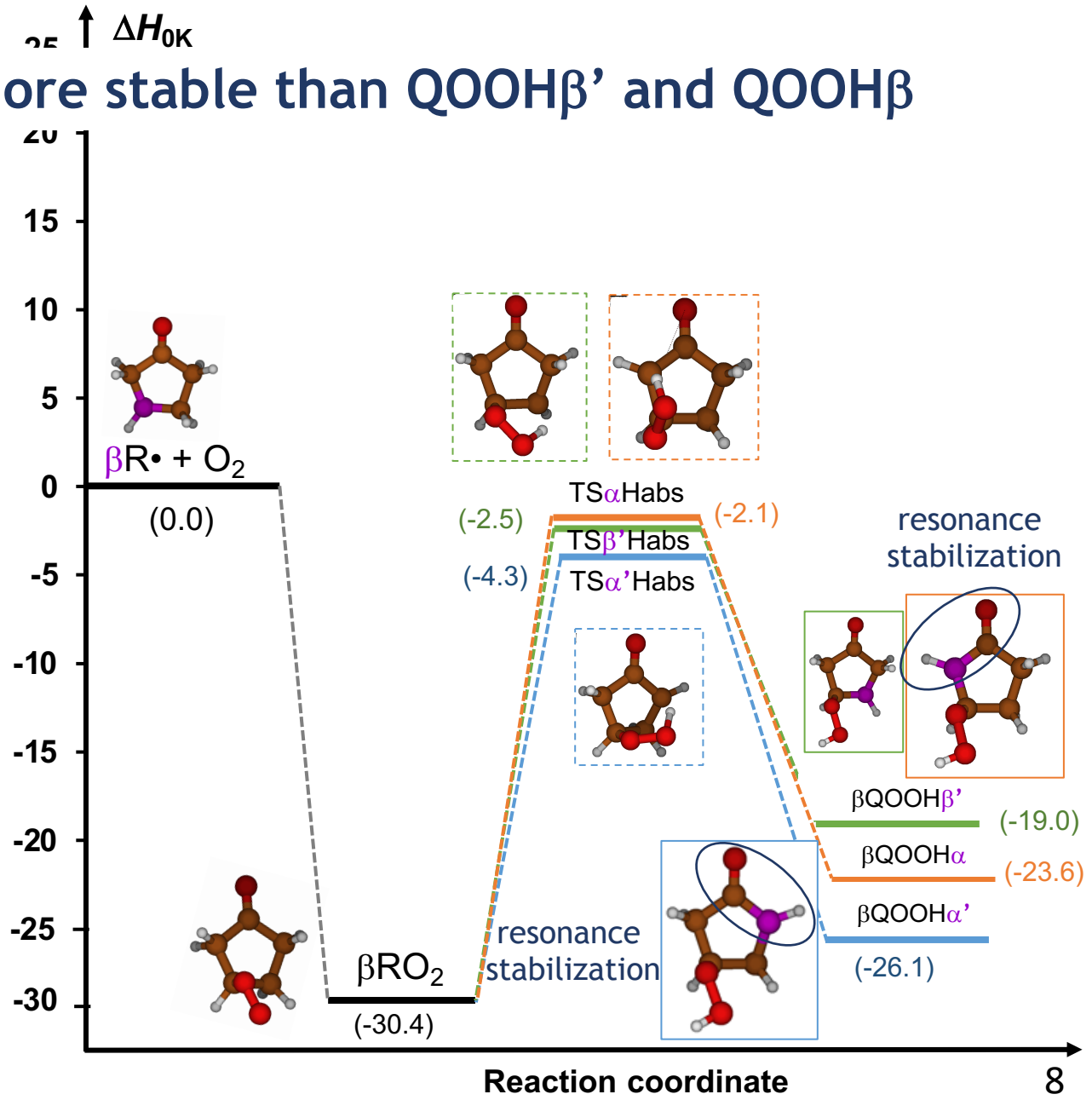


Oxidation of 2-oxo- & 3-oxo-cyclopentyl

ΔH_{0K} in kcal mol^{-1}

3. QOOHα' and QOOHα are more stable than QOOHβ' and QOOHβ





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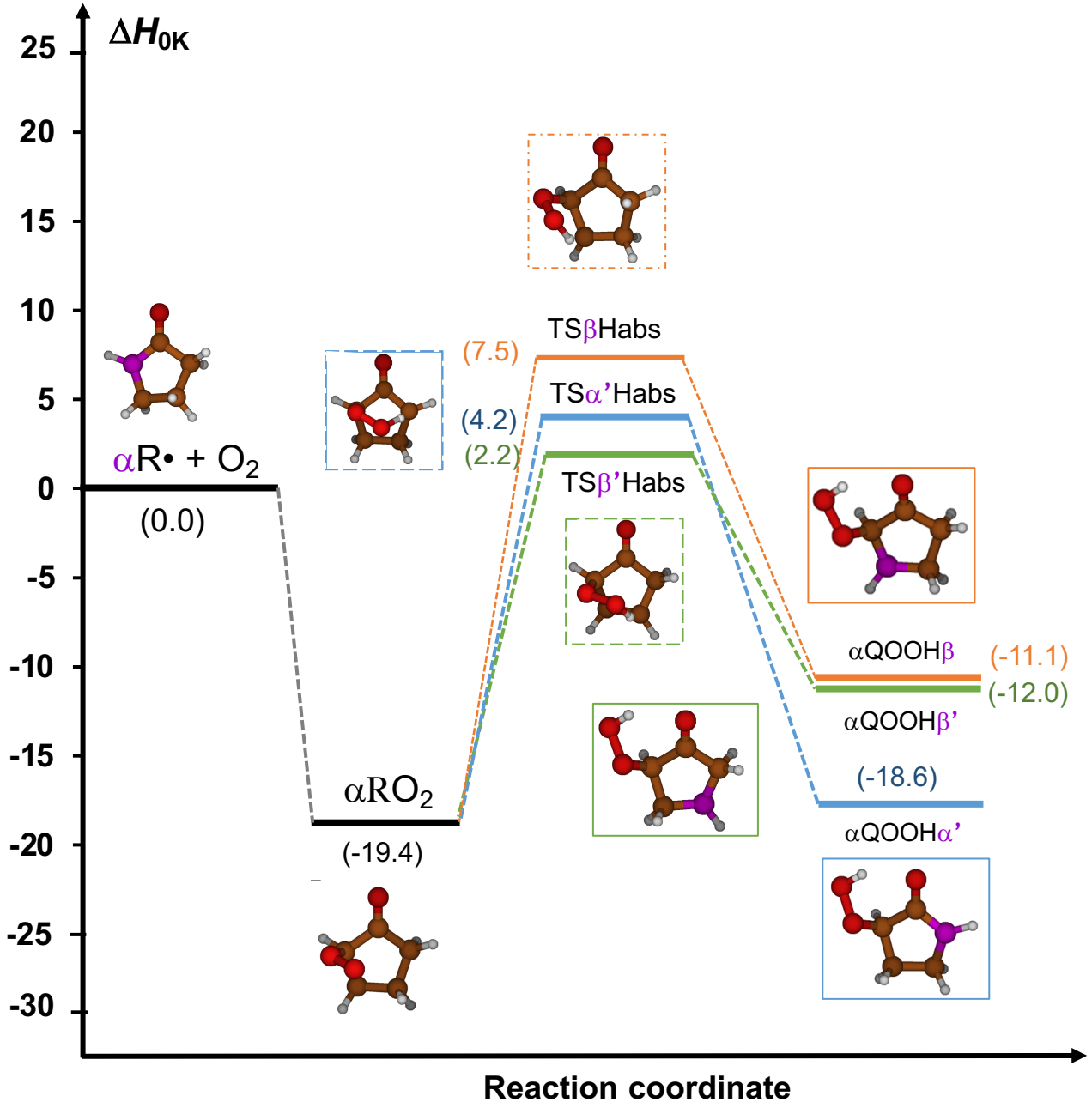
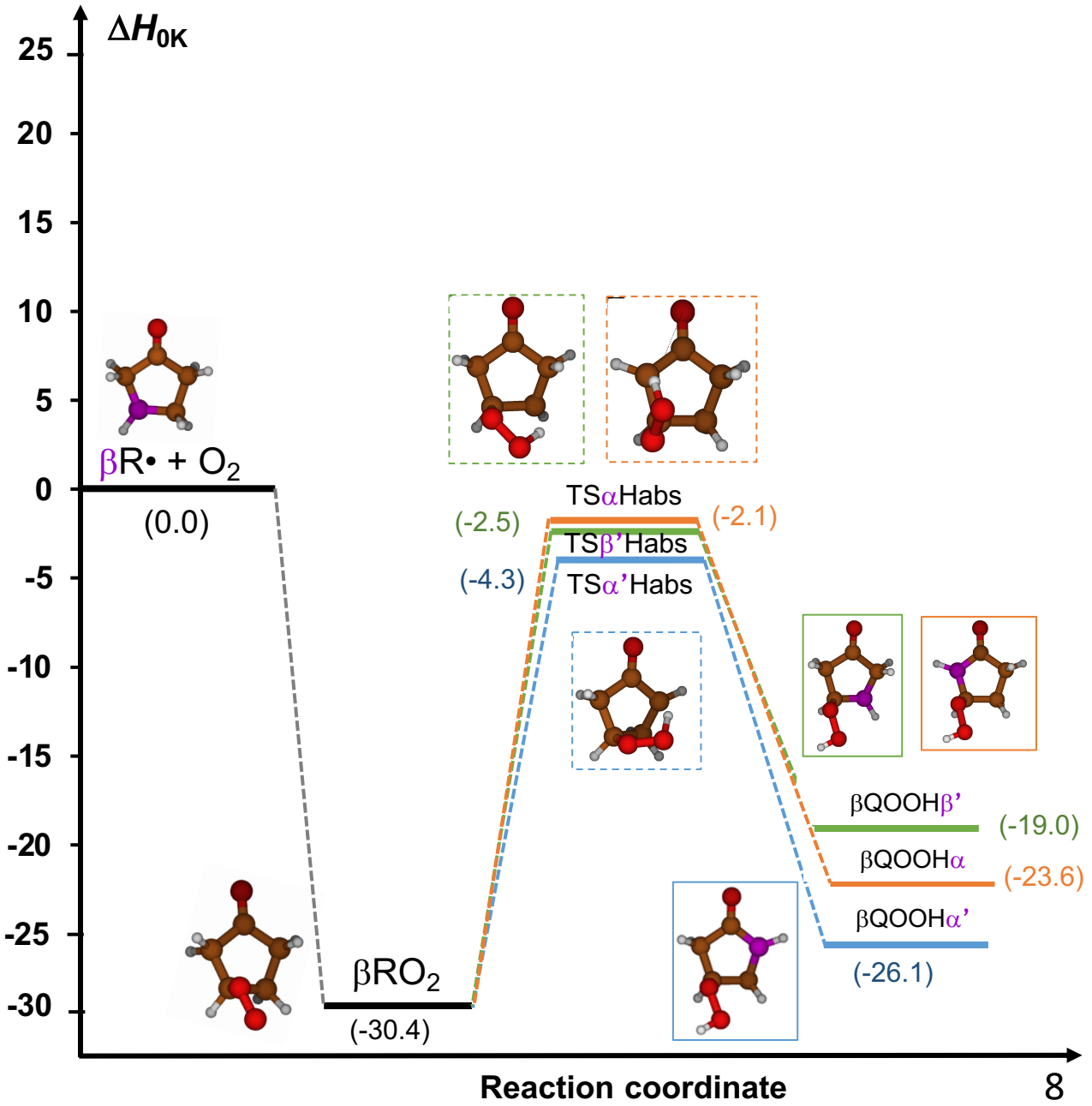
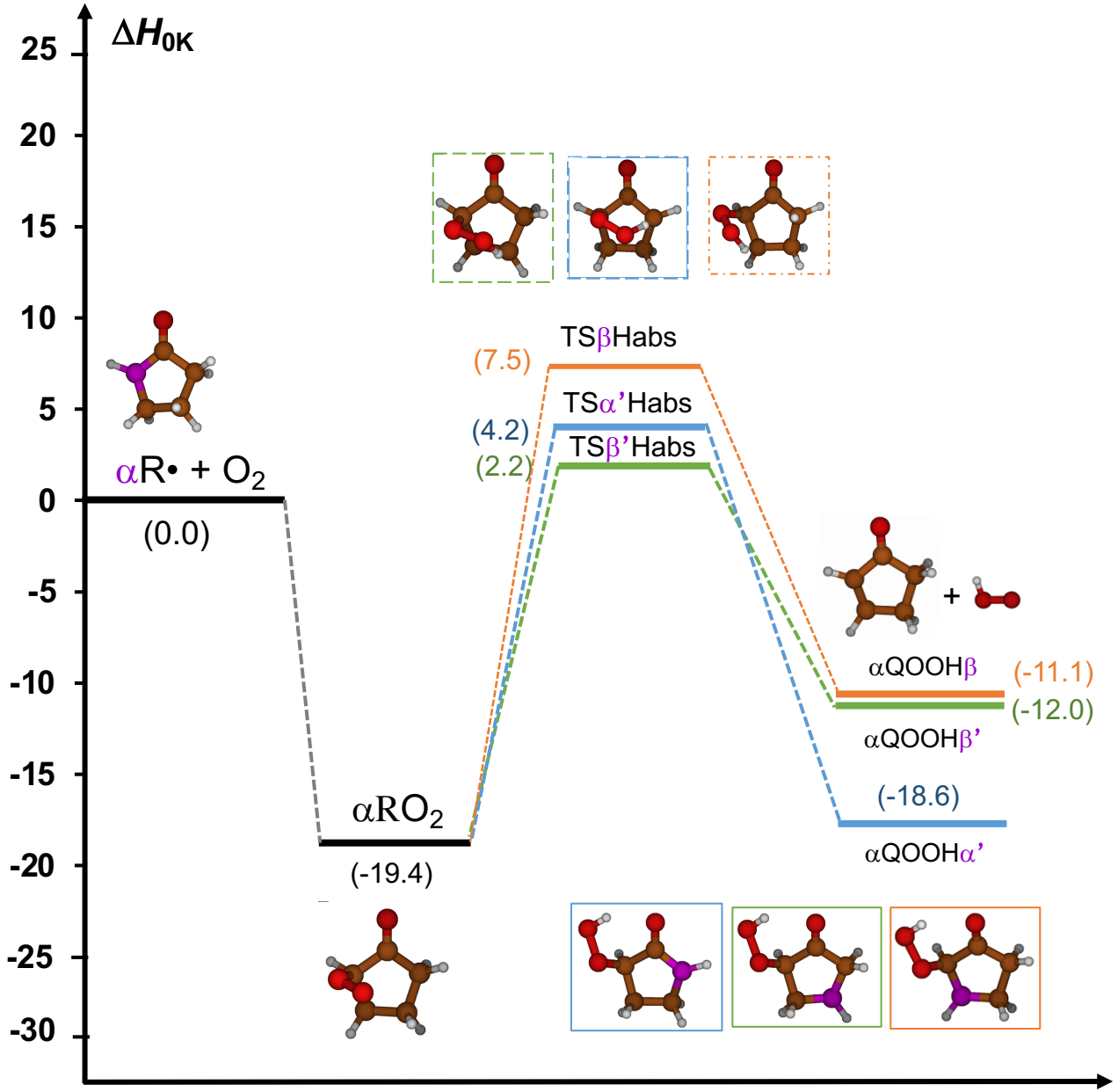
ΔH_{0K} in kcal mol^{-1}

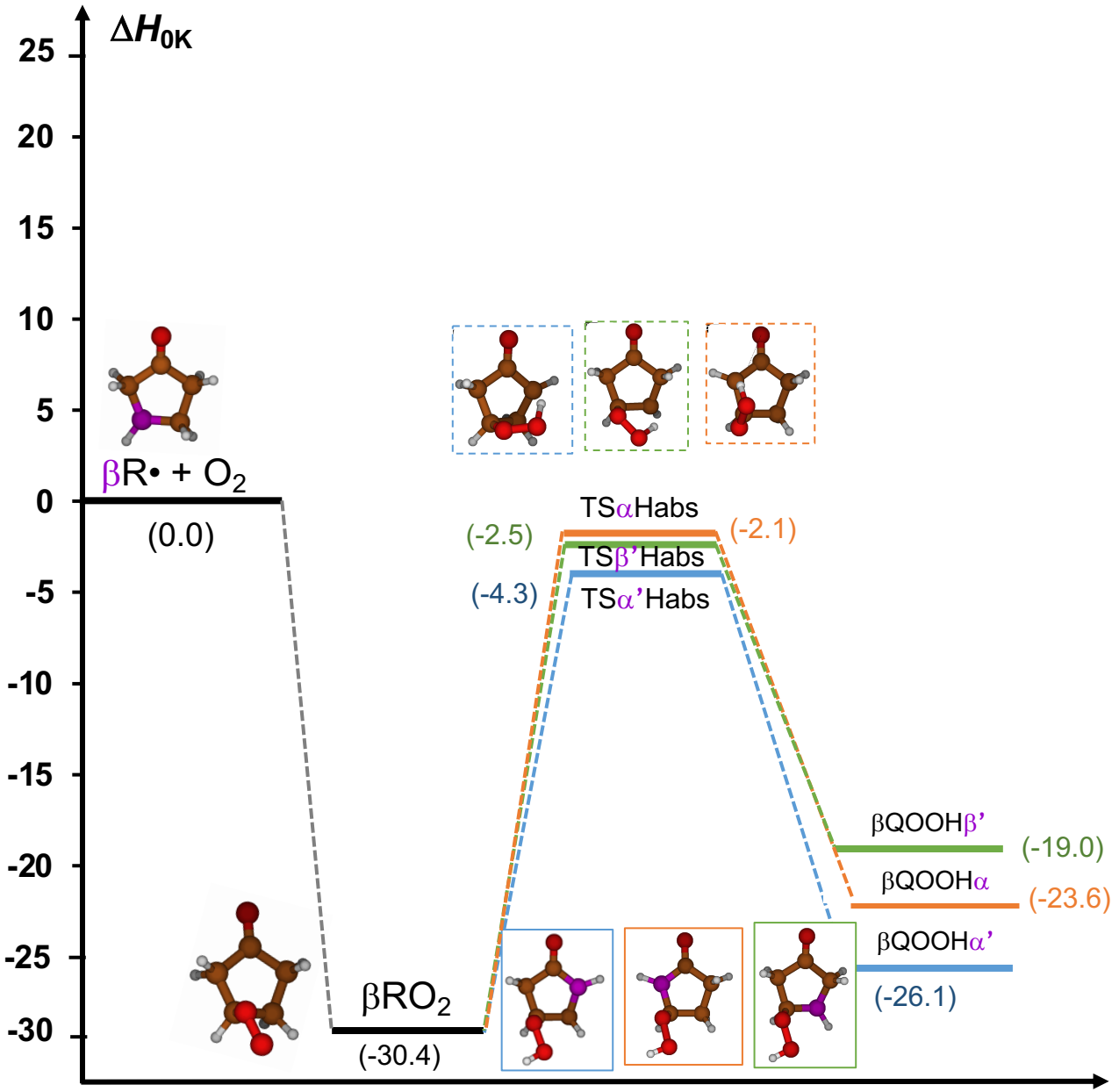




HO_2 elimination vs H-abstraction

ΔH_{0K} in kcal mol^{-1}





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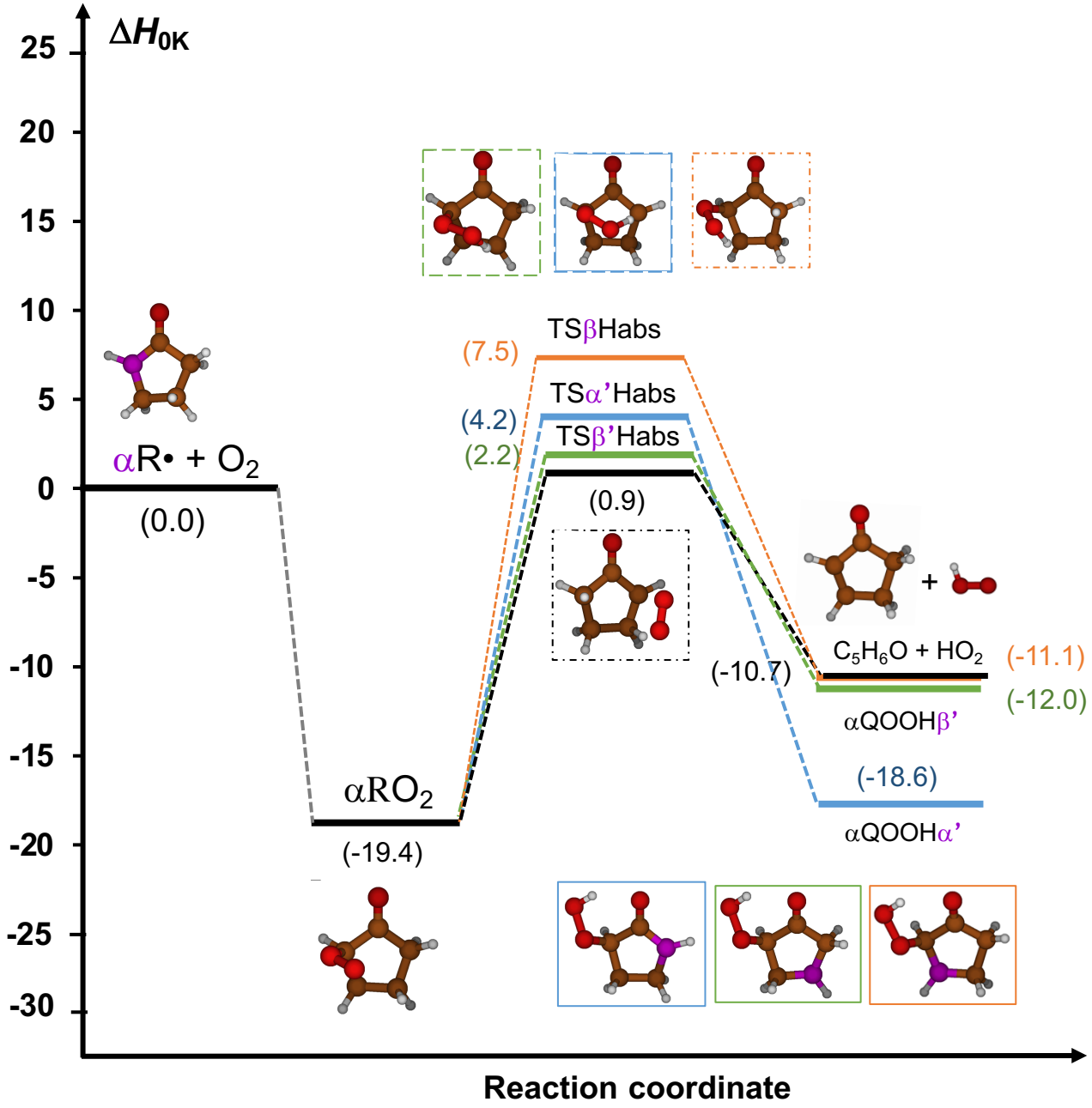

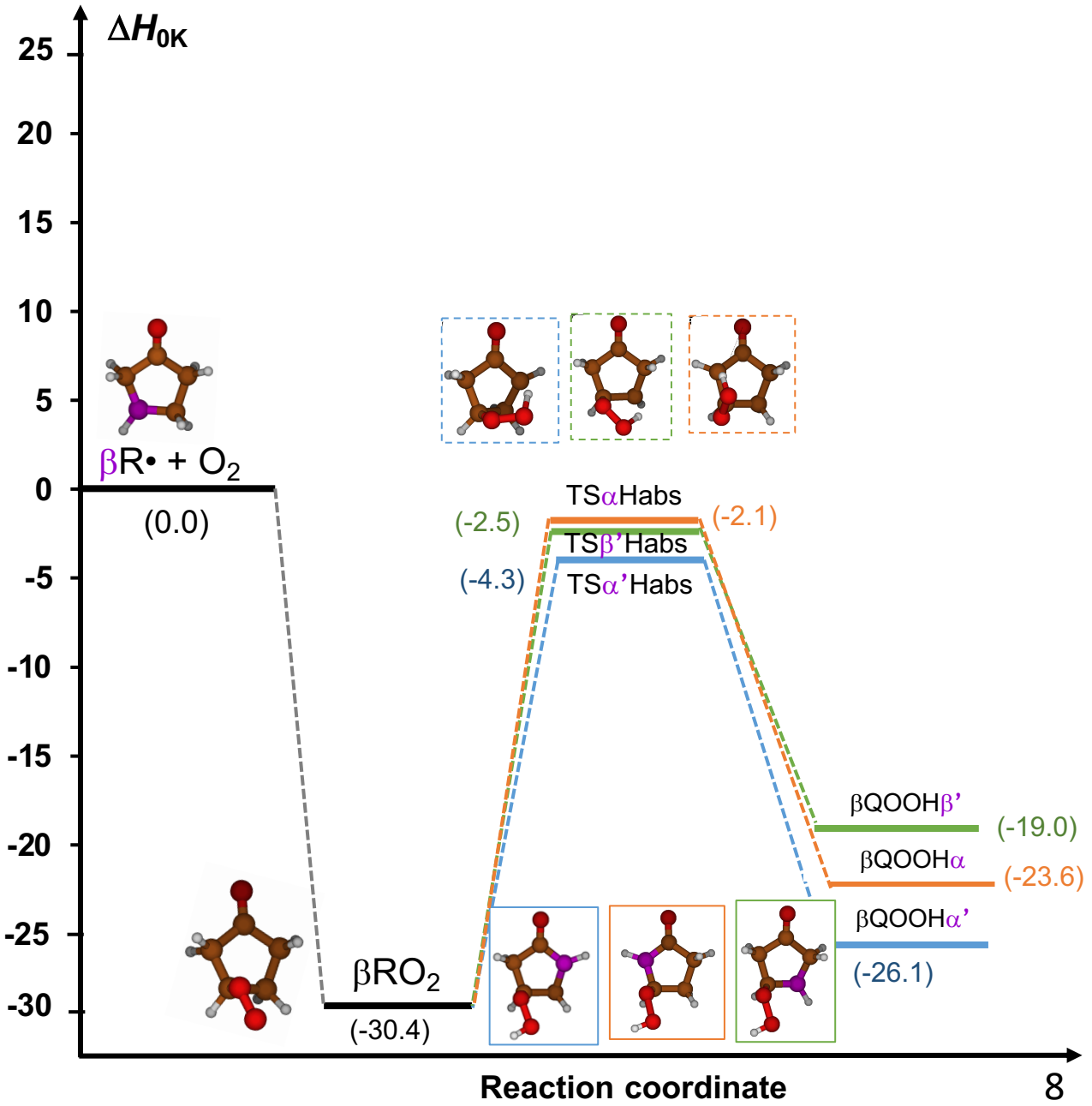

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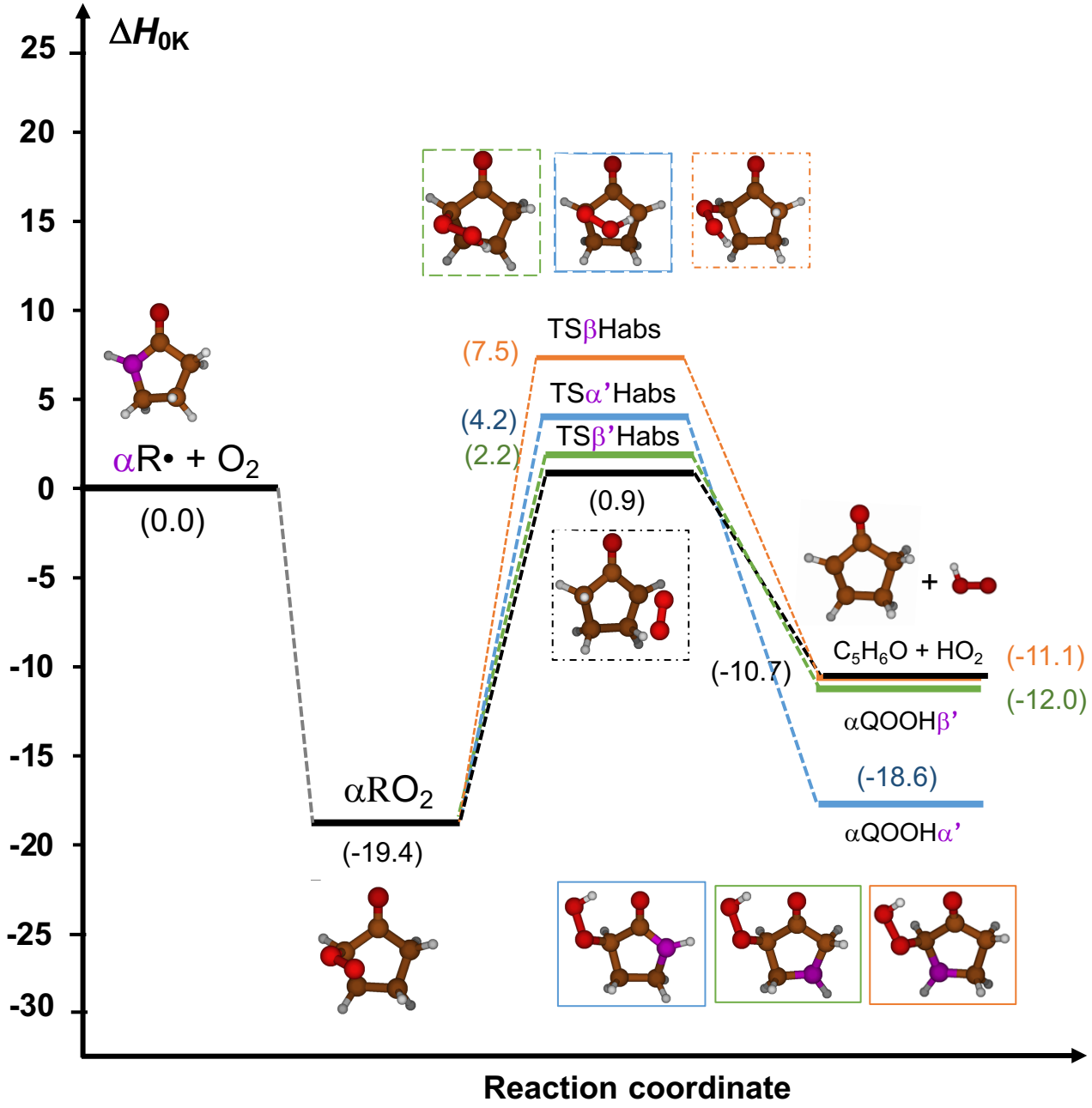

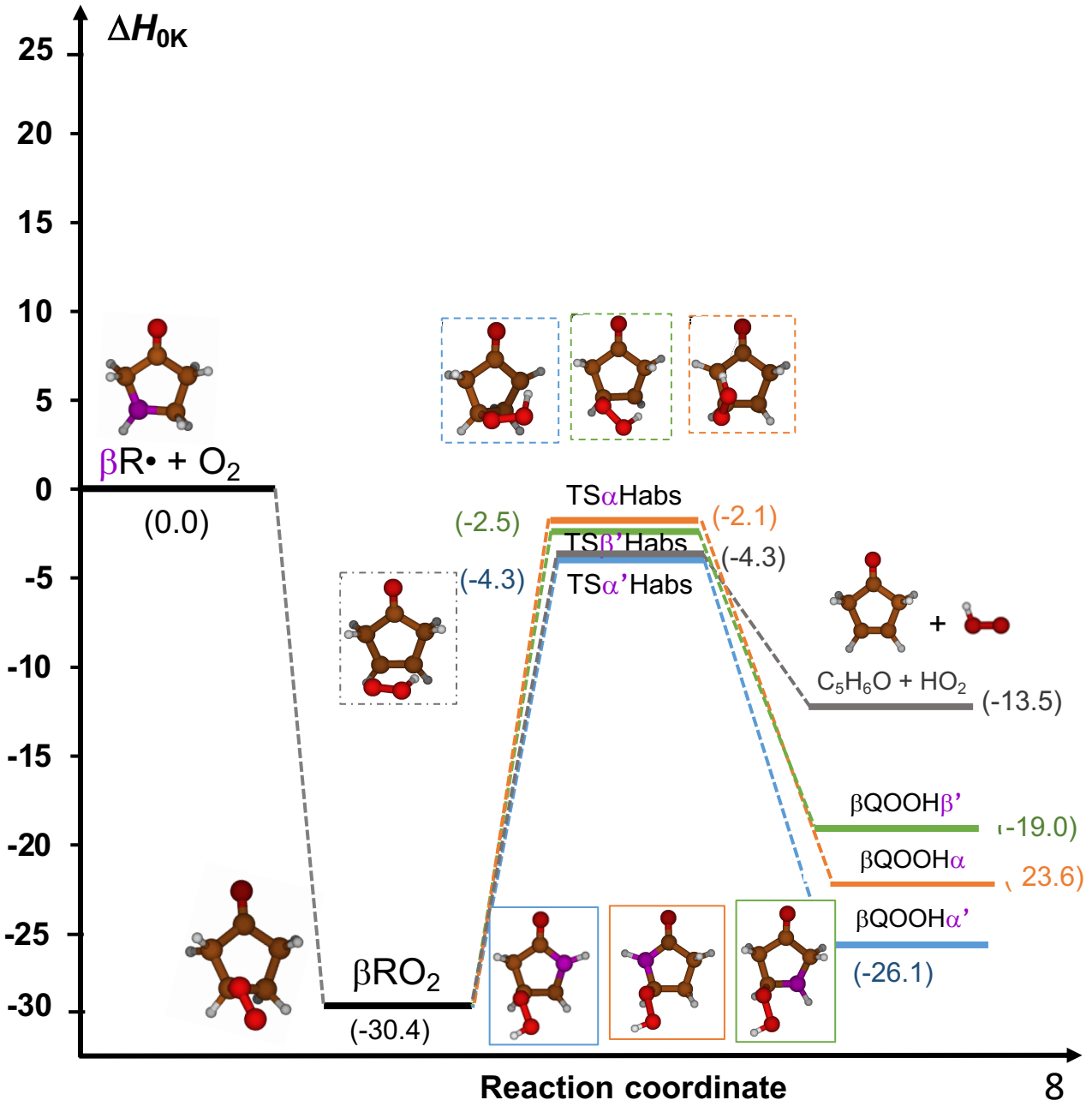

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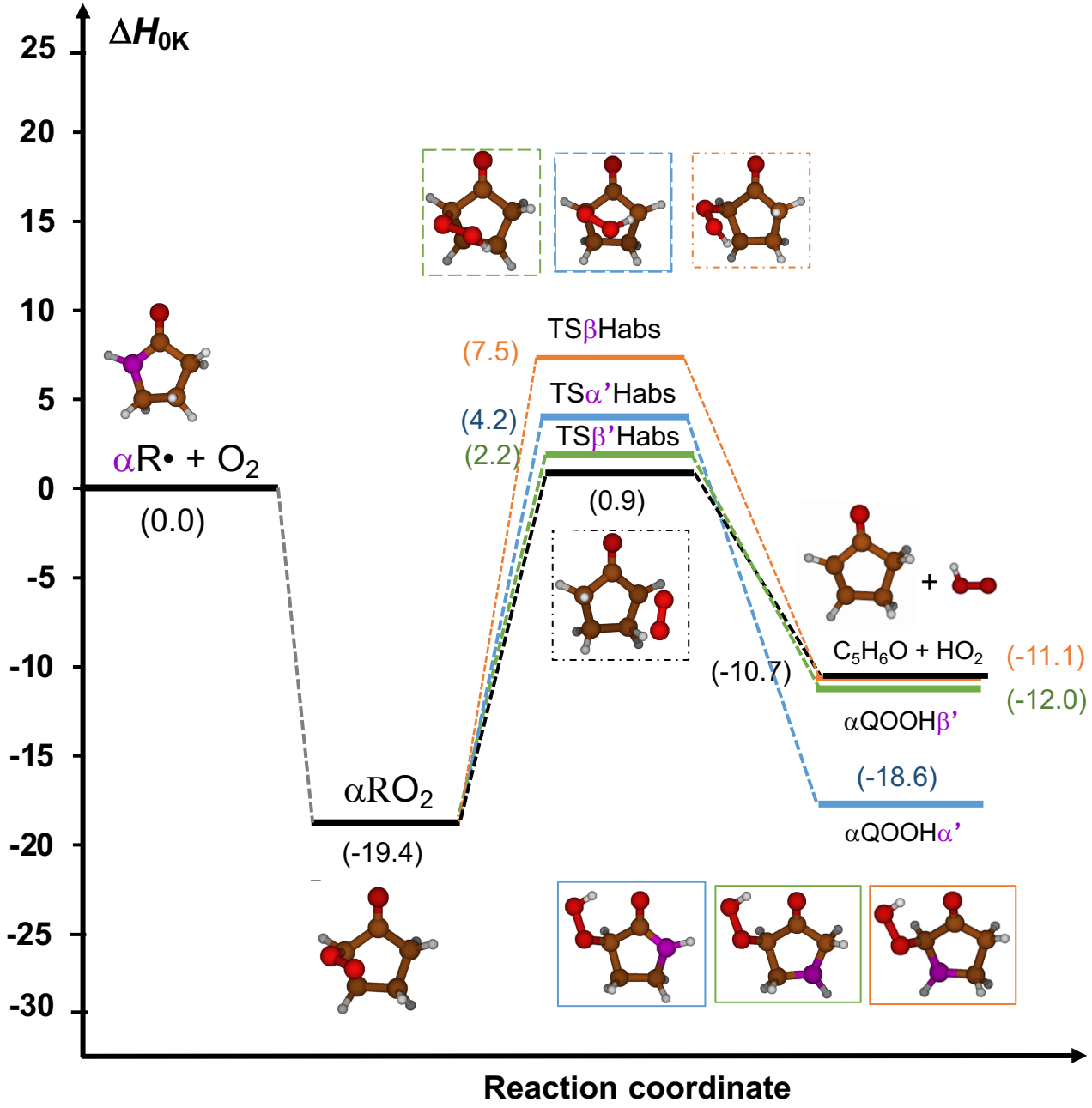
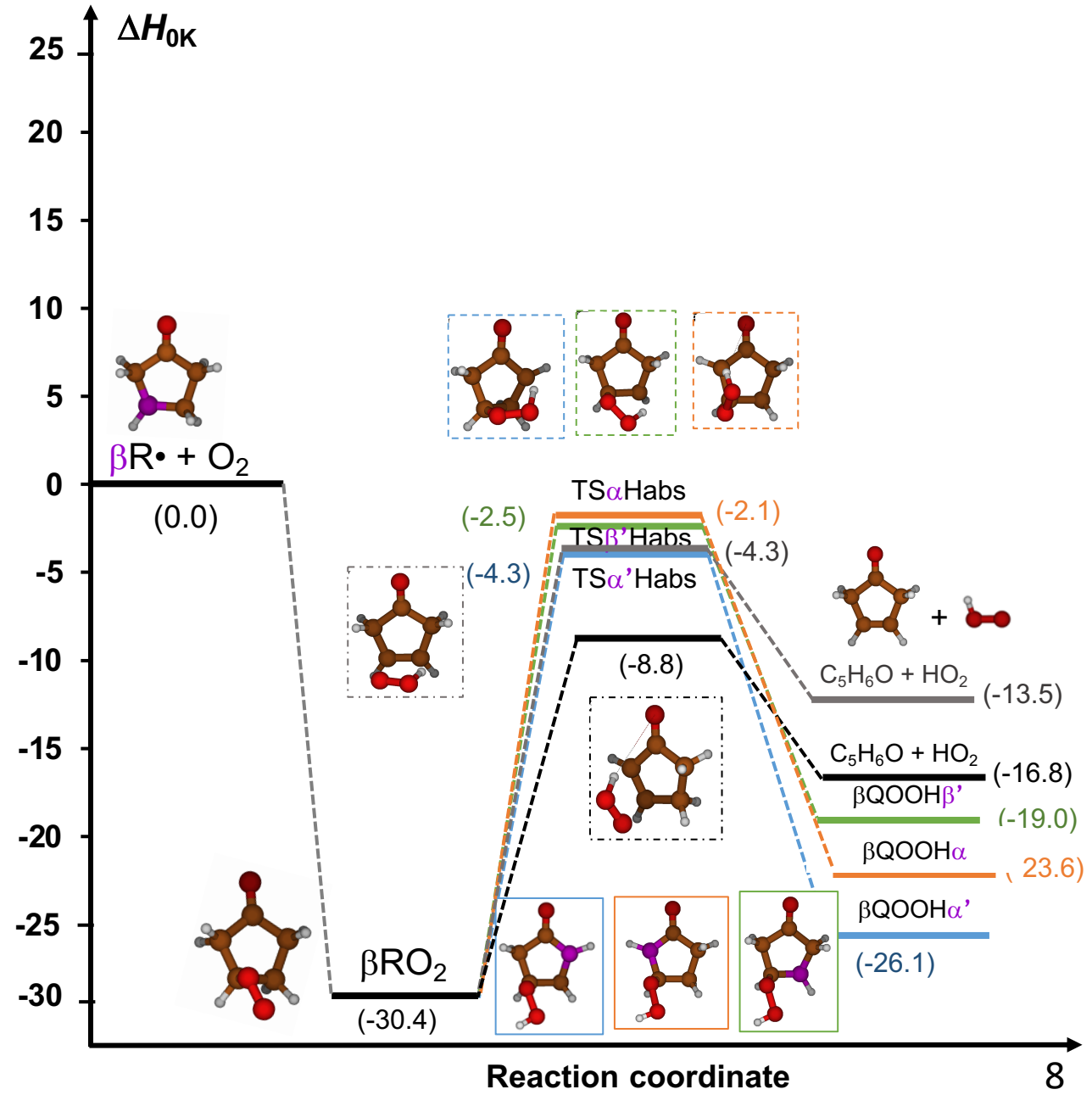
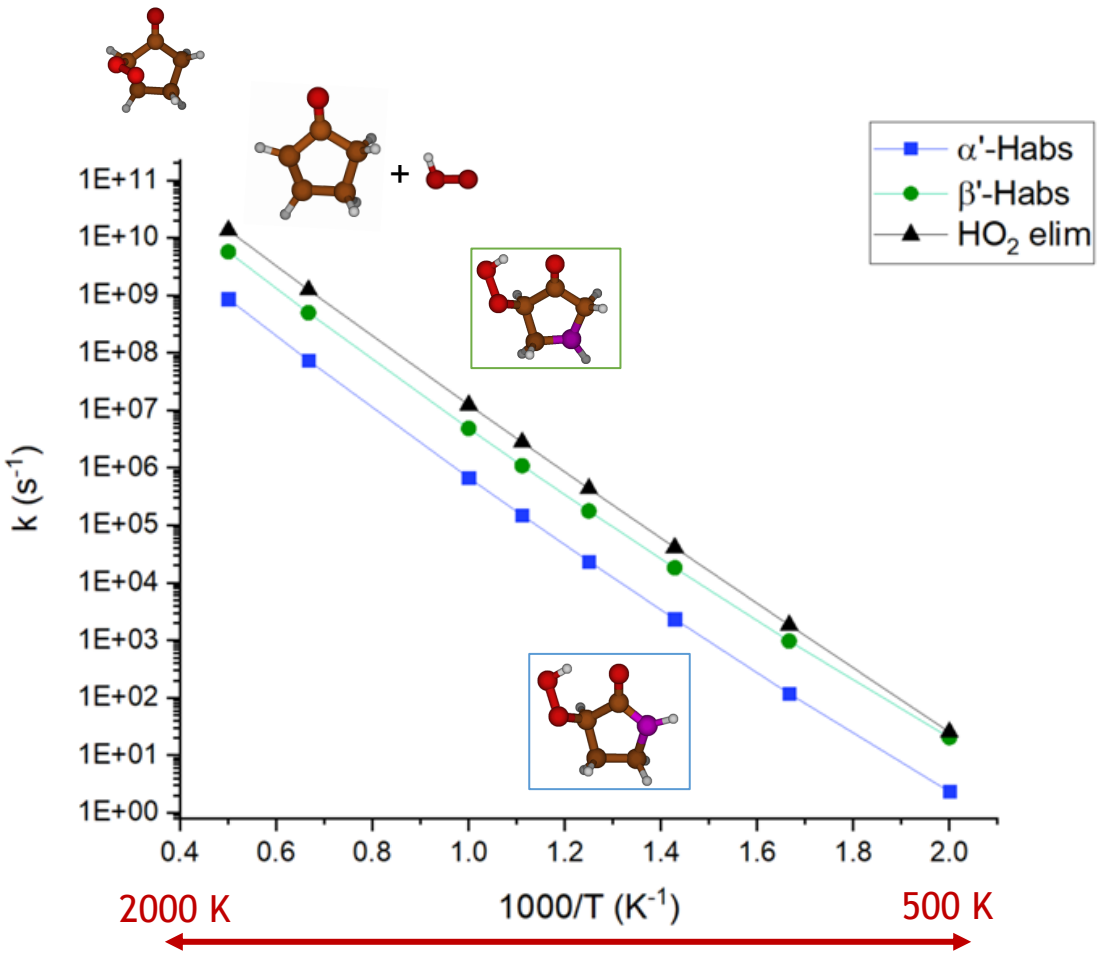
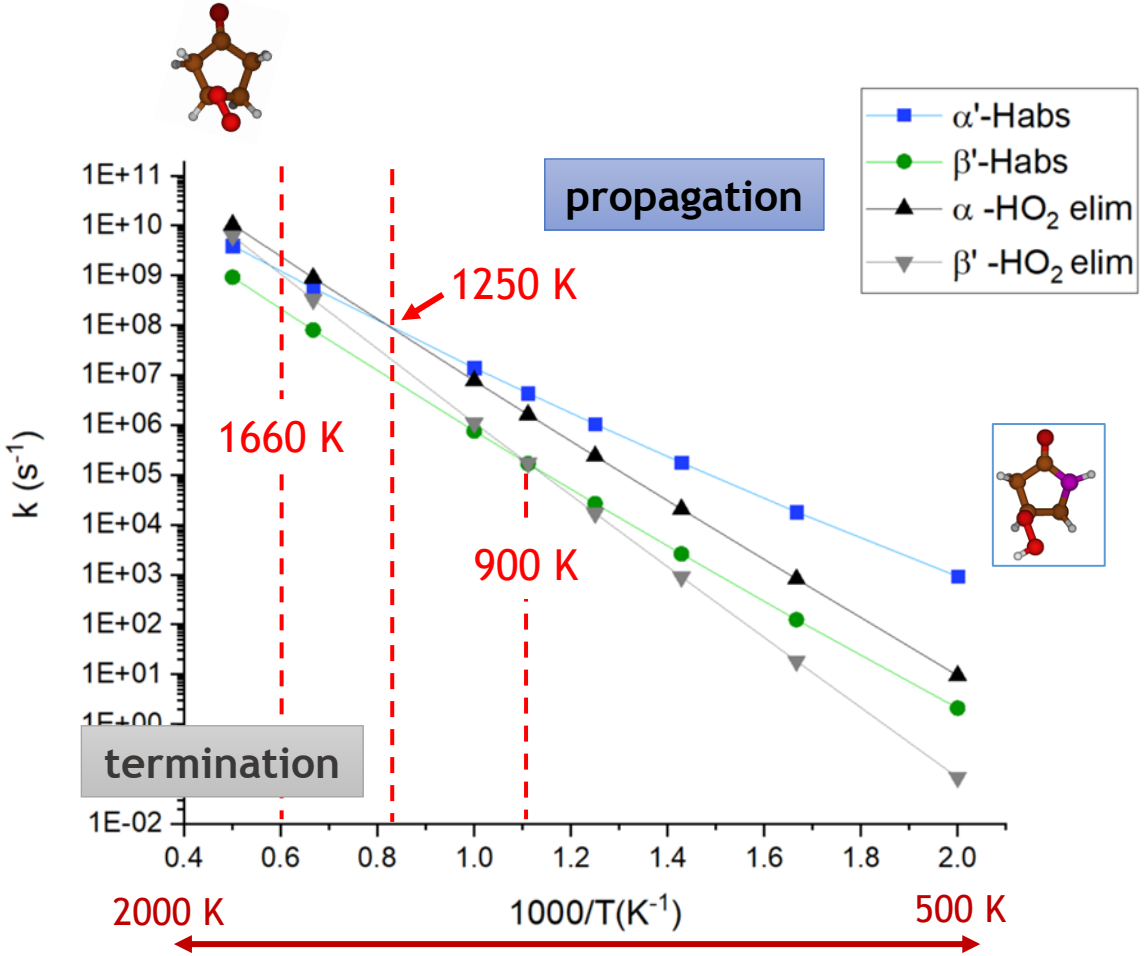




Kinetics, k_∞ (T)





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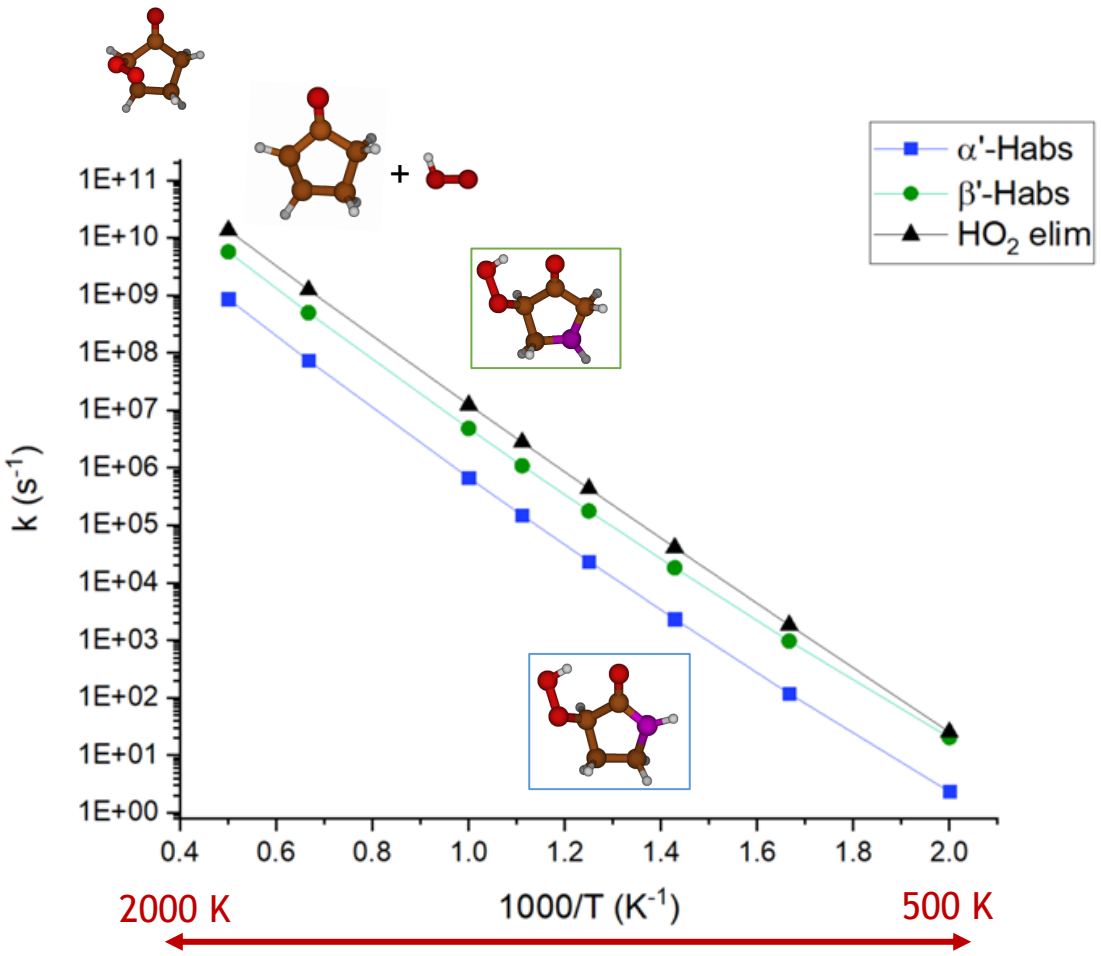
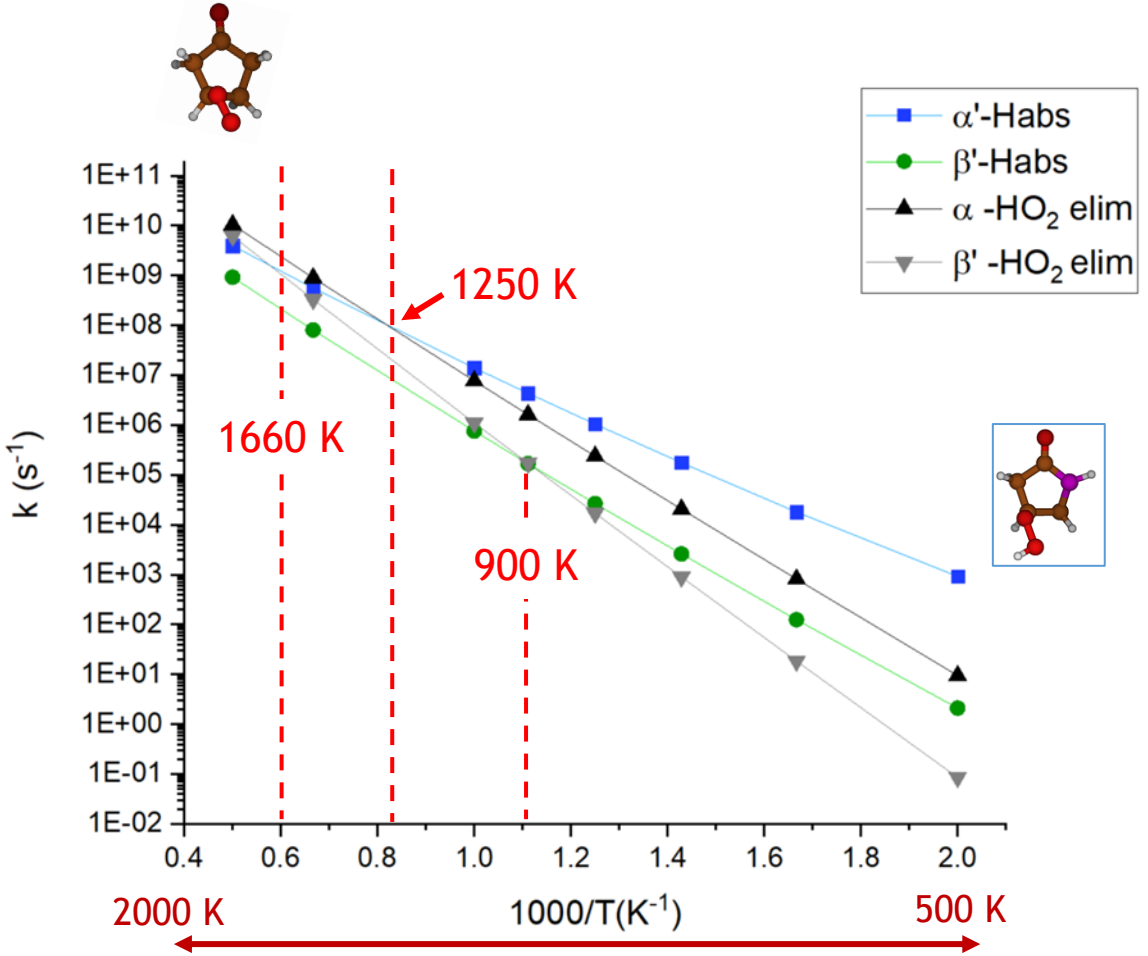




A = 1.9 x 10^3 s^{-1}
n = 2.45
Ea = 21.9 kcal mol^{-1}

A = 8.9 x 10^4 s^{-1}
n = 1.98
Ea = 21.3 kcal mol^{-1}

A = 4.0 x 10^8 s^{-1}
n = 1.27
Ea = 22.7 kcal mol^{-1}

$$k(T) = AT^n \exp(\frac{Ea}{RT})$$

A = 4.1 x 10^4 s^{-1}
n = 2.08
Ea = 20.4 kcal mol^{-1}

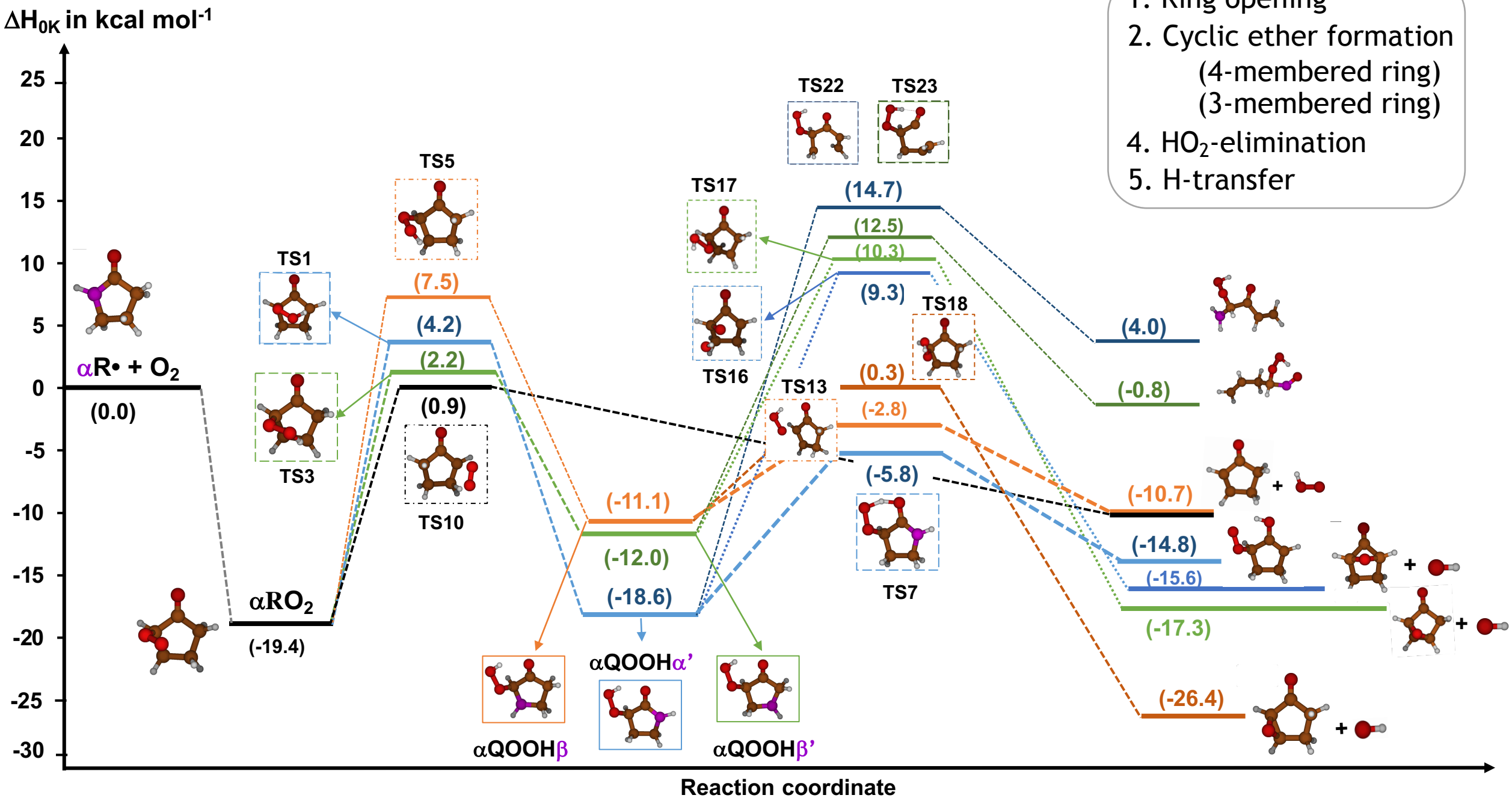
A = 1.0 x 10^5 s^{-1}
n = 2.51
Ea = 27.1 kcal mol^{-1}

A = 6.3 x 10^8 s^{-1}
n = 1.21
Ea = 23.7 kcal mol^{-1}

A = 7.9 x 10^8 s^{-1}
n = 1.29
Ea = 29.1 kcal mol^{-1}

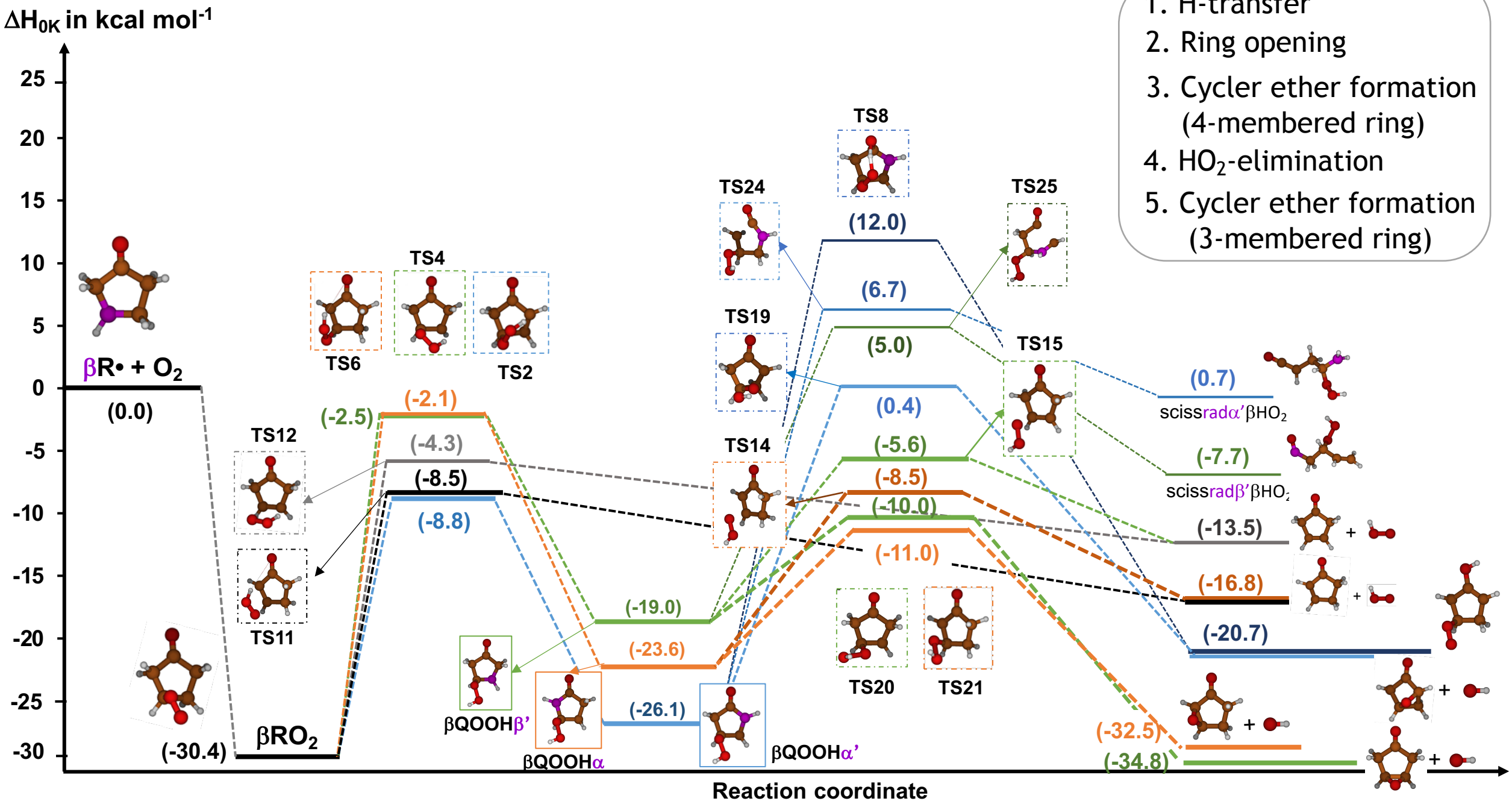
Oxidation of **2-oxo**-cyclopentyl

1. Ring opening
2. Cyclic ether formation
   (4-membered ring)
   (3-membered ring)
4. HO_2-elimination
5. H-transfer



Oxidation of **3-oxo**-cyclopentyl

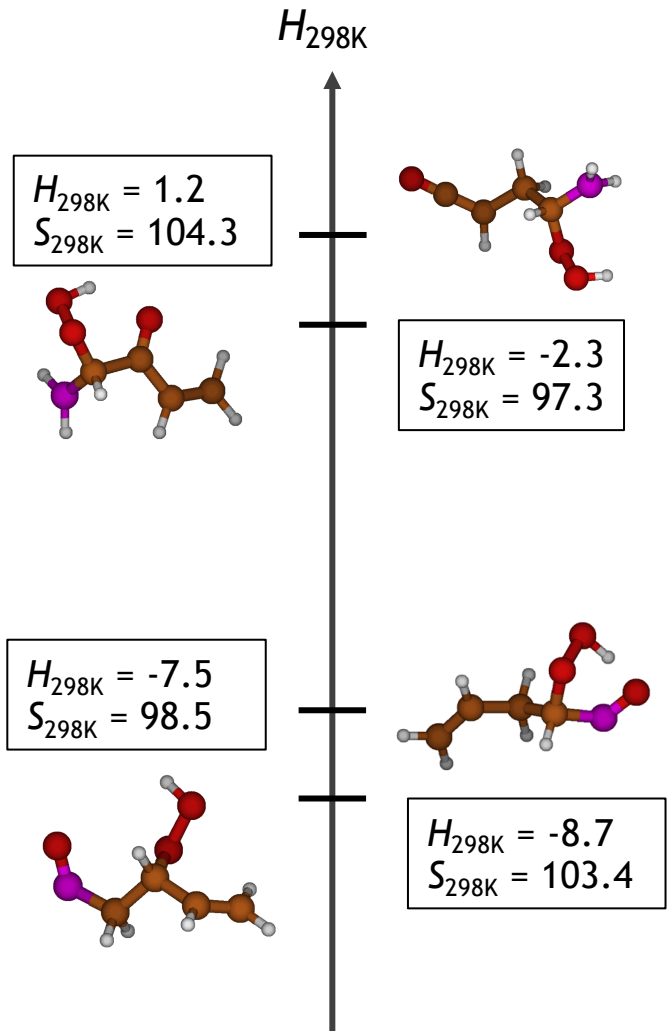
1. H-transfer
2. Ring opening
3. Cycler ether formation (4-membered ring)
4. HO_2-elimination
5. Cycler ether formation (3-membered ring)



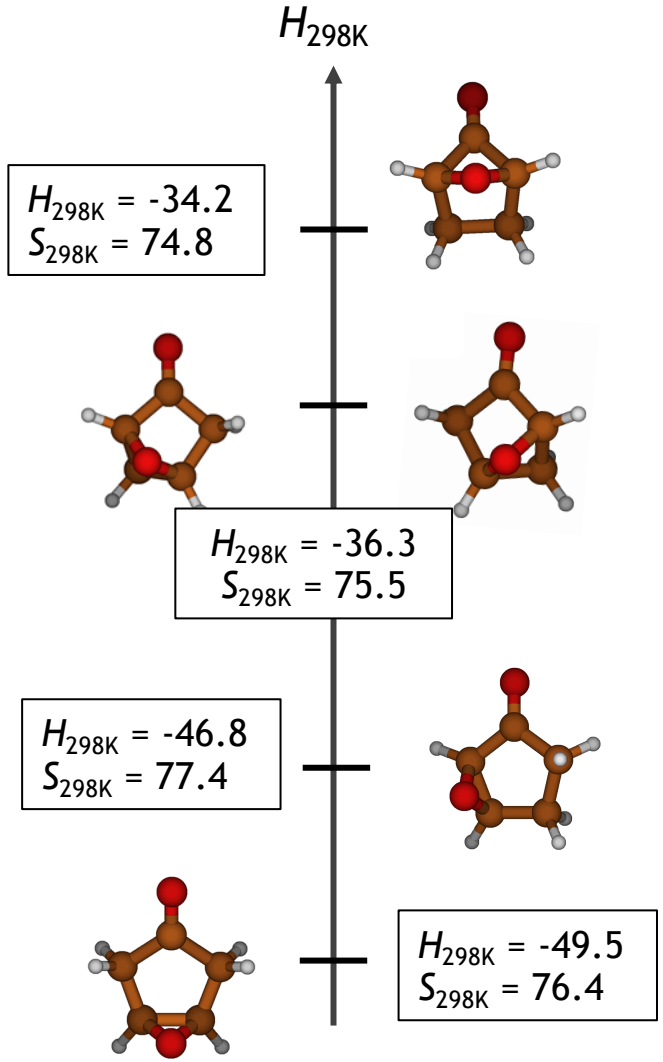
Thermodynamics

H_{298K} in kcal mol^{-1}
S_{298K} in cal mol^{-1} K^{-1}

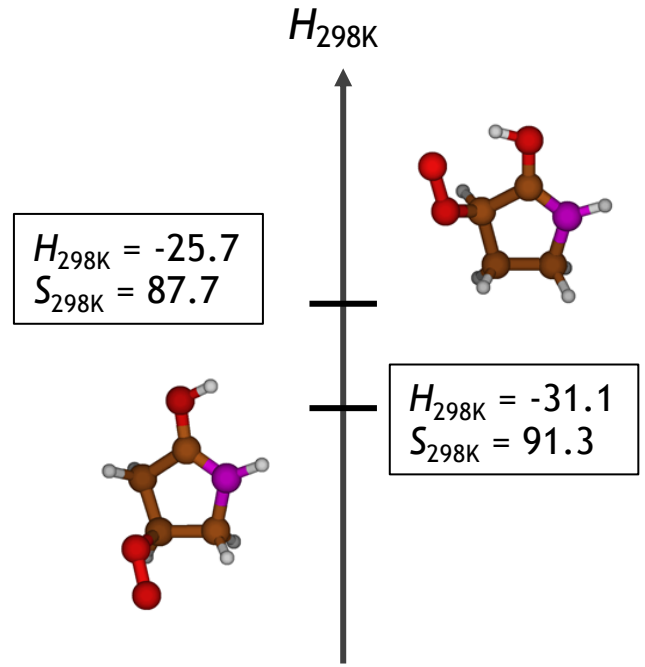
Acyclic radicals



Cyclic Ether

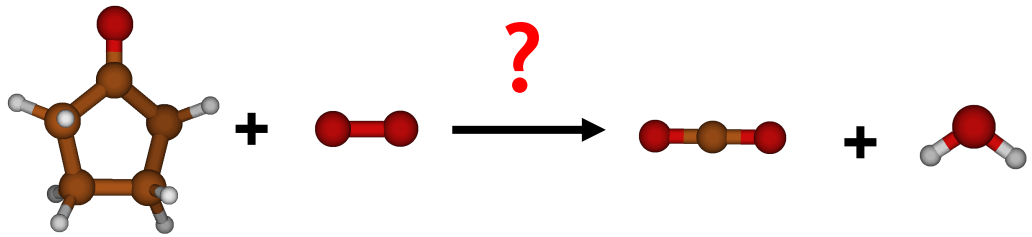


Enol



Outline of the talk

Combustion of CPO



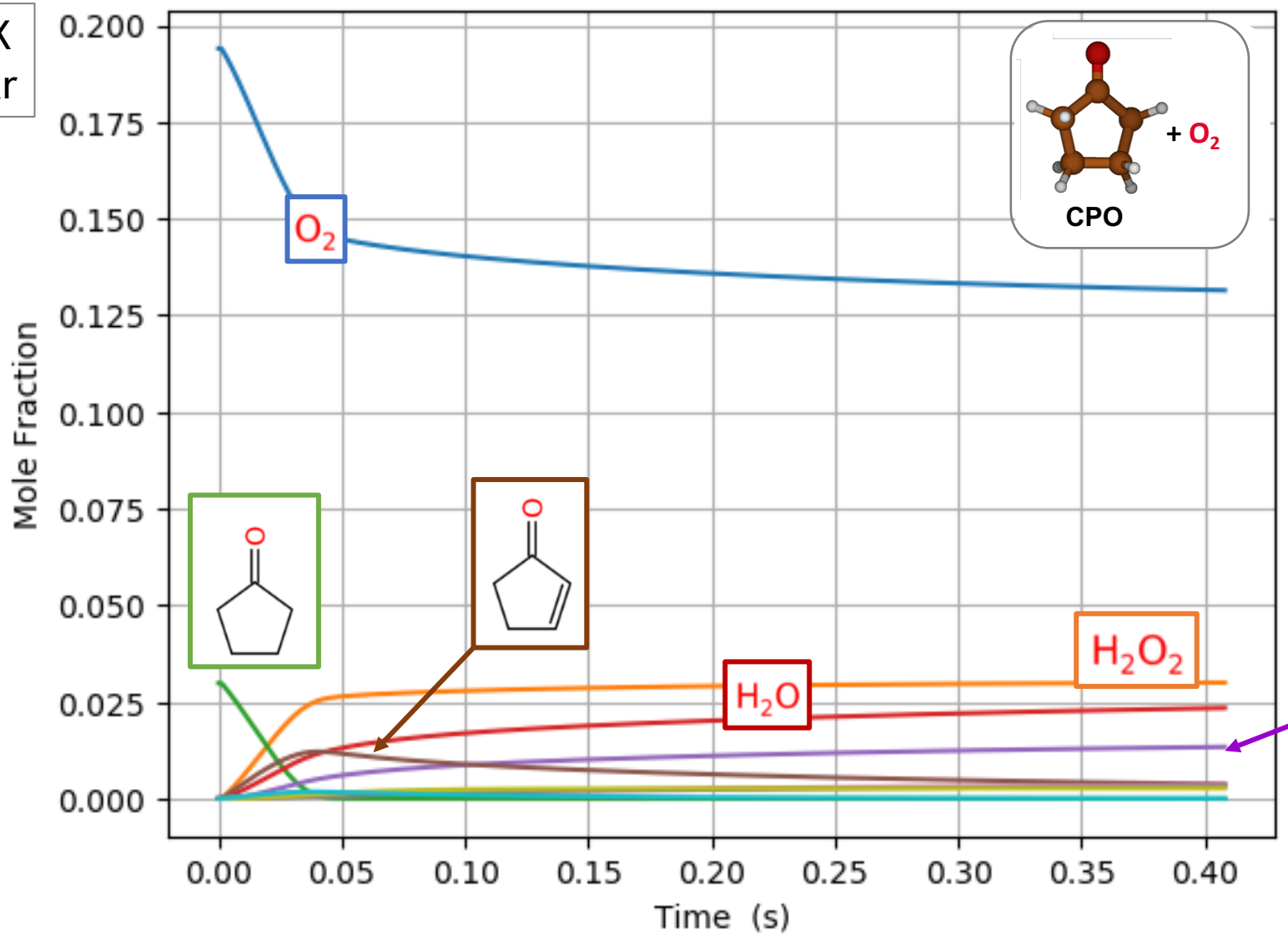
1. *Ab initio* **calculations**
   - QOO: H-migration *vs* HO_2 elimination
   - QOOH: Ring opening *vs* cycler ether formation

2. **RMG simulations**
   - Evolution of the system with time
   - Sensitivity analysis

Oxidation of **CPO**

isothermal isobaric
batch reactor

T = 700 K
P = 10 bar

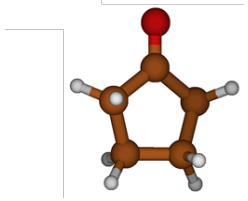


2.6% CPO, 19% O_2, 76% N_2

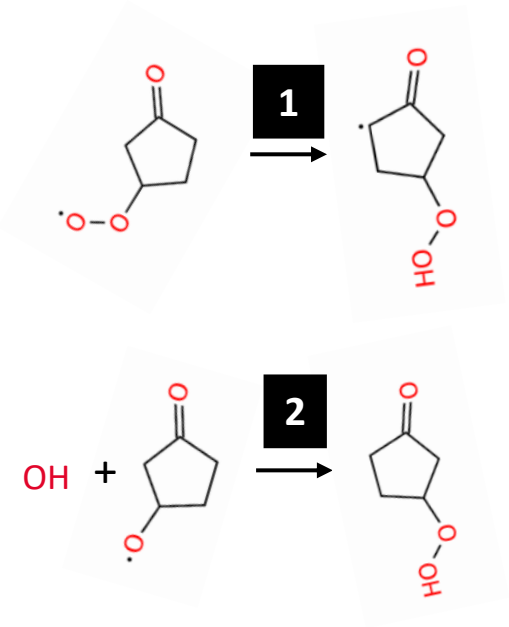
451 species & 18188 reactions
ε = 0.01

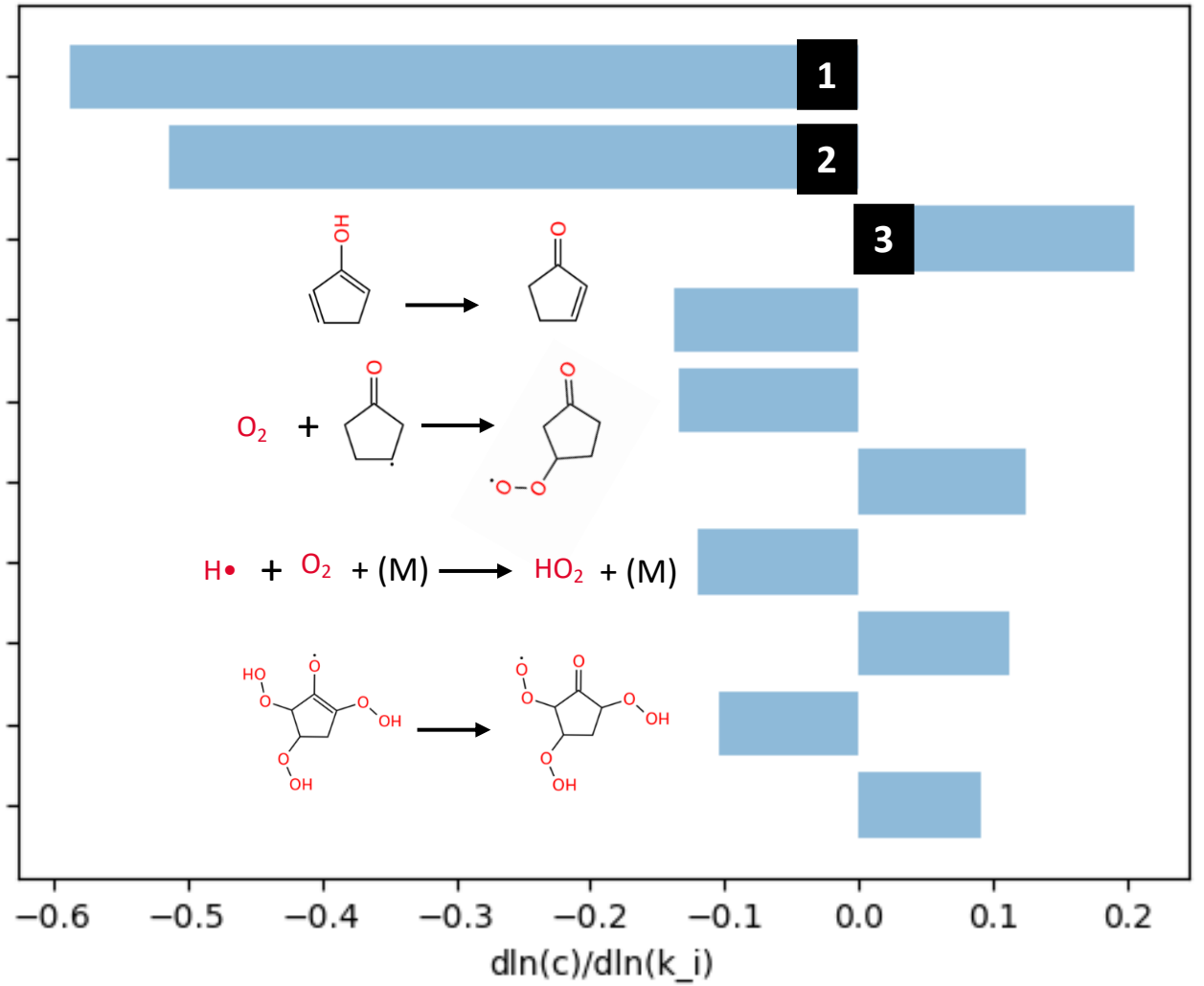
Sensitivity Analysis

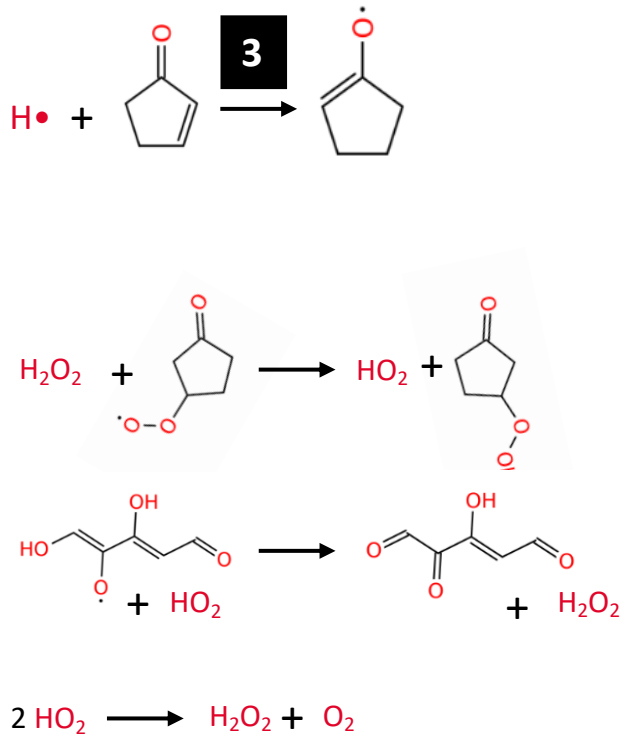
T = 700 K
P = 10 bar



Sensitivity of the concentration of CPO (c) to the kinetics (k_i)
of the RMG-generated model

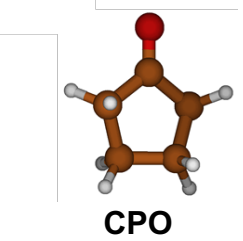




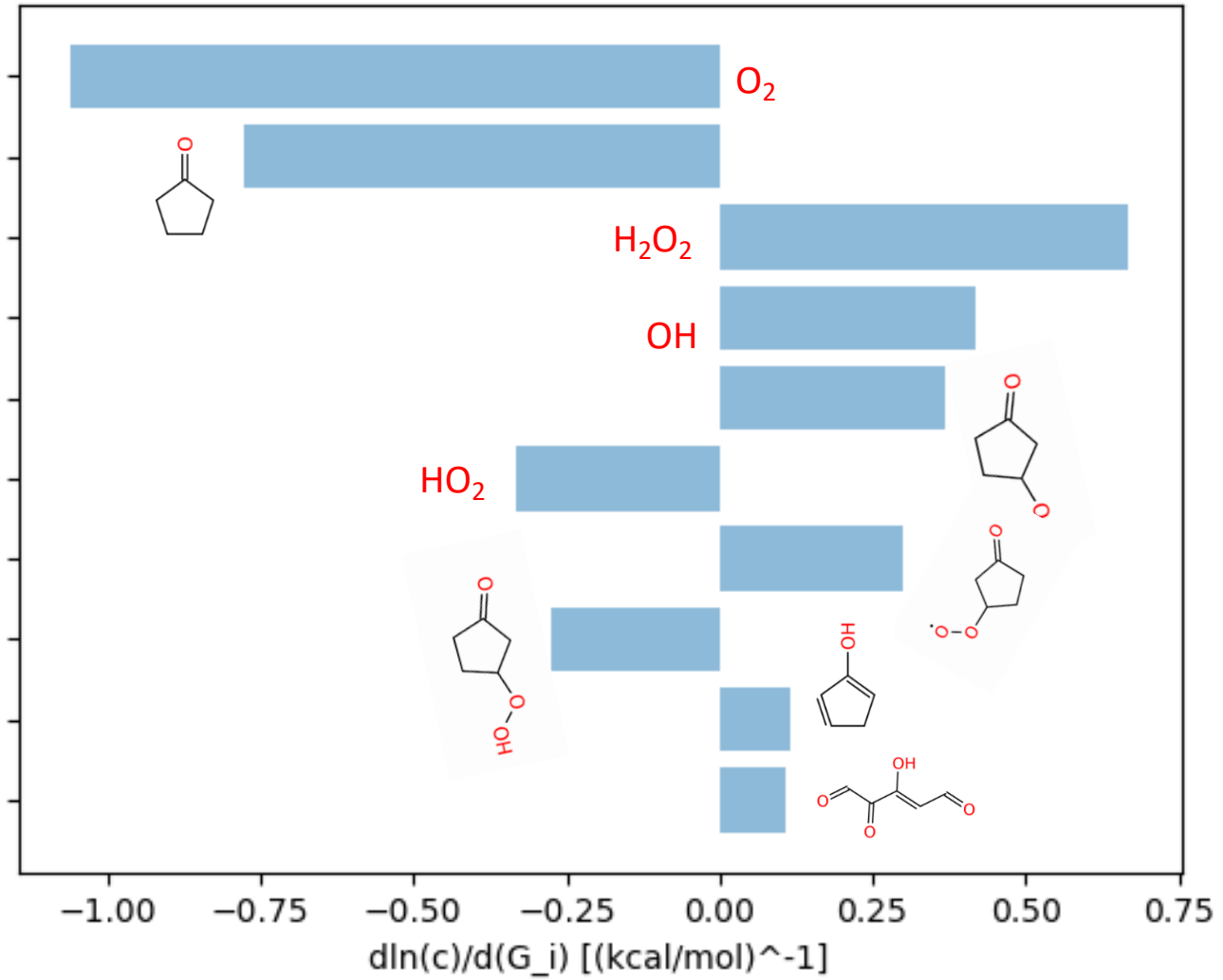


T = 700 K
P = 10 bar

Sensitivity Analysis



Sensitivity of the concentration of CPO (c) to the thermo (G_i)
of the RMG-generated model



Conclusions and Perspectives

1. *Ab initio* calculations

- PES for αR• + O_2 and βR• + O_2 @ CBS-QB3 level of theory
  - QOO species: Competition between HO_2 elimination (termination) and α'-Habs (propagation)
  - QOOH species: enol formation for αQOOHα', cyclic ether formation (3-membered rings)

Mechanism of 20 species, 21 rate constants and 15 thermodynamic data

2. RMG simulations

- Mechanism of 450 species and 18800 reactions
  - Olefin obtained from HO_2 elimination

- Compute thermo and kinetics for the species/reactions of the sensitivity analysis
- Ignition delay = f(*T*)

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Green Group members
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