Atmospheric Fate of HOHgO: the Hg(II) Product of OH-Initiated Oxidation of Hg(0)

Darshi Hewa Edirappulige (dthewaed@syr.edu), Camille K. Becket, Ilena J. Kirby, and Theodore S. Dibble (tsdibble@esf.edu)

State University of New York College of Environmental Science and Forestry

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Outline

1. Background
2. Formation and Fate of HOHgO•
3. Objectives
4. Computational Method
5. Results
6. Conclusions and Future Work
7. Acknowledgements

Background

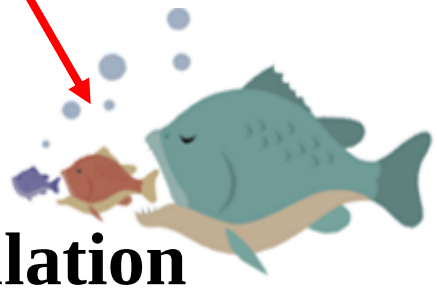
Hg- Global Pollutant

Anthropogenic

Natural

Hg(0) ⇌ Hg(II)

Hg(II) ⇌ CH_3Hg (Neurotoxin)



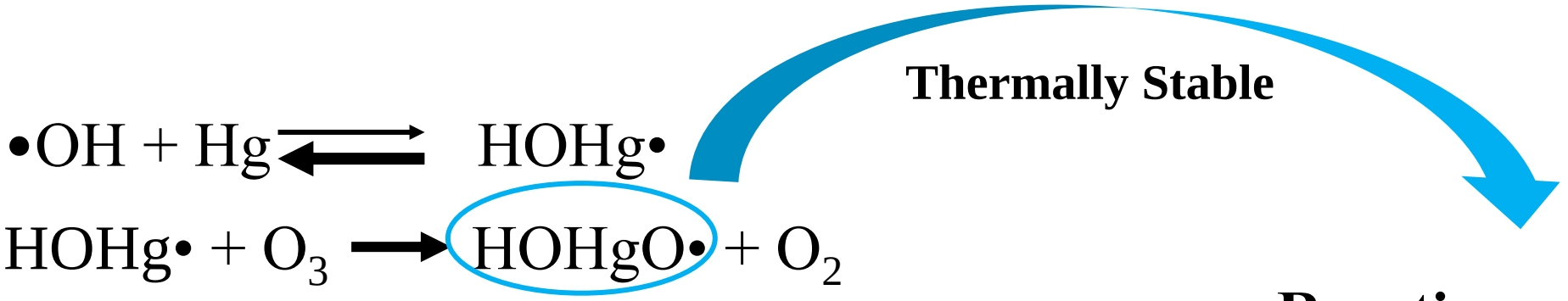
Bioaccumulation

Emissions

Depositions

Formation and Fate of HOHgO•

Formation in Two Steps



Reactions of HOHgO• ?

Stable Hg(II) ? or

Reduced to Hg(I) or Hg(0) ?

O_3 – Major HOHg• Oxidant

$[O_3]$ >> Σ[Radicals]

k($Hg^{(I)}$ + O_3) high and T-independent

Gomez Martin et al. *PCCP* **2022**

P. J. Castro et al. *submitted*. (see Dr. Dibble's talk in Atmospheric Hg cycling)

Objective

Determine the fate of HOHgO• in the atmosphere

Reactions with trace gases (NO, NO_2, CH_4, $CH_2{=}CH_2$, CH_2O, CO)

1. Determine thermodynamics and barriers to reaction
2. Determine (or recommend) rate constants

No experimental detection of HOHgO• (even in lab)

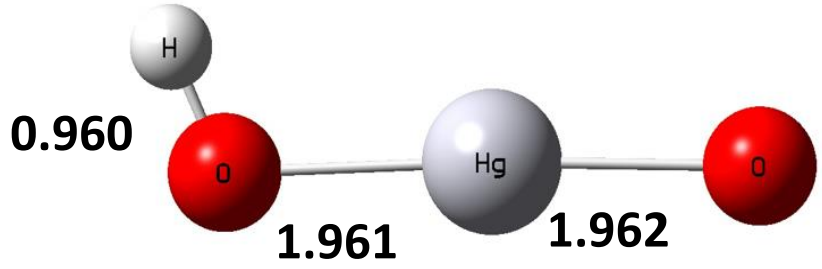
Computational Method

Graphical User Interface (Draw a molecule)

Gaussian 16 (Quantum Chem.)

Calculate Structure and Energy

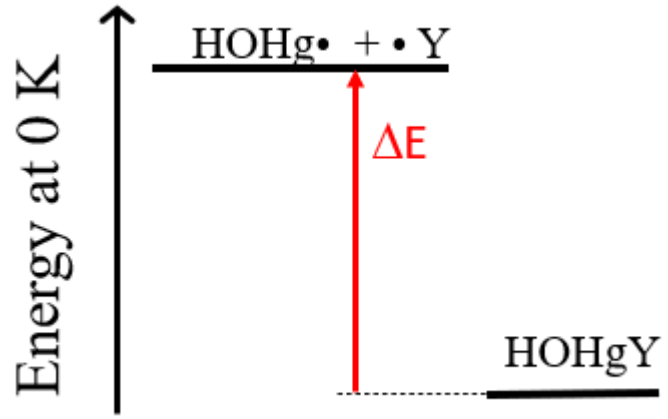
ΔE = E(products) – E(reactants)



Statistical Mechanics:

$\Delta H_r^\circ(T)$ & $\Delta G_r^\circ(T)$

$k(T)$ after optimizing structures of transition states

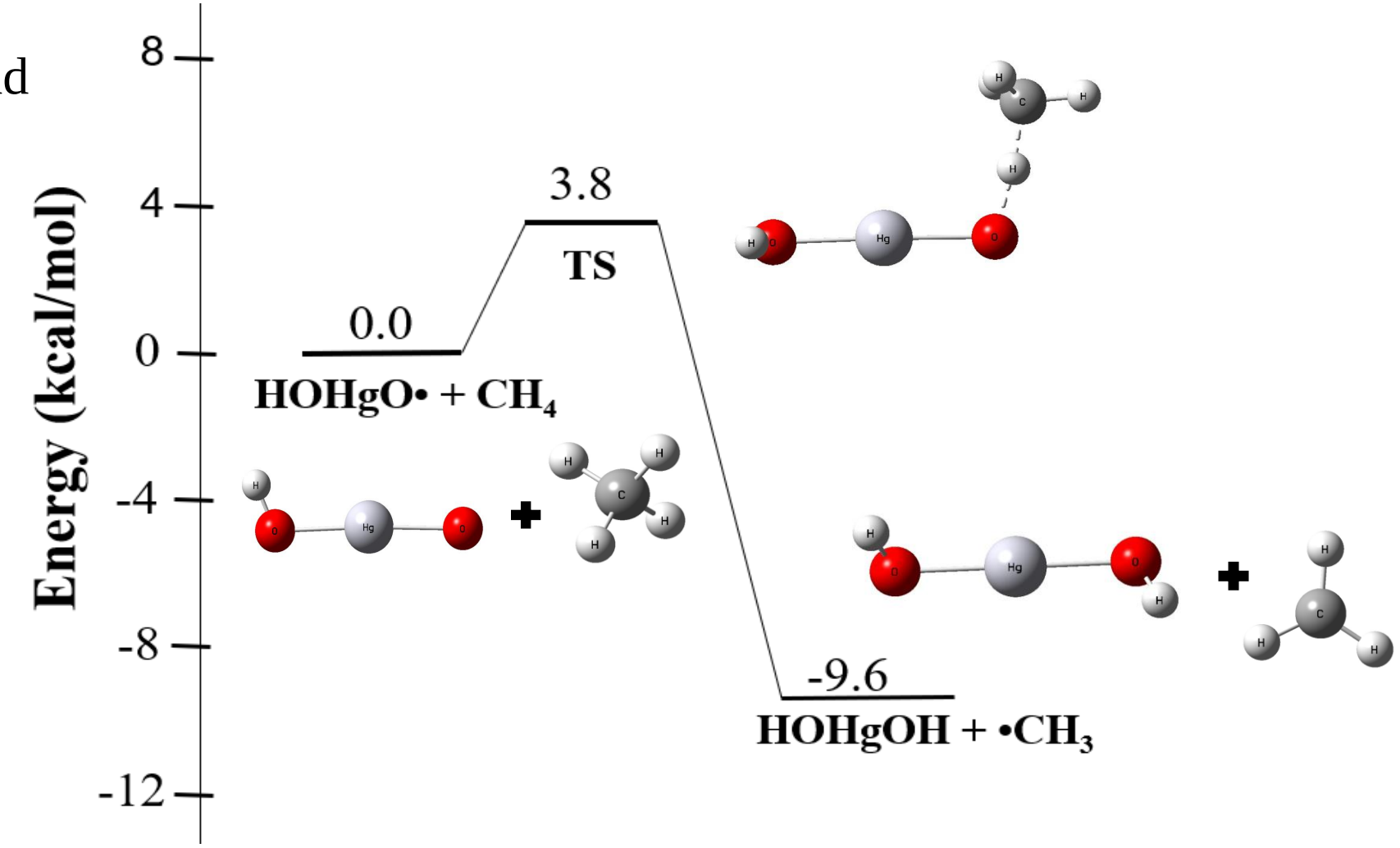


HOHgO• + (**RH**, $CH_2=CH_2$, NO, NO_2, CH_2O, CO)

H Abstraction

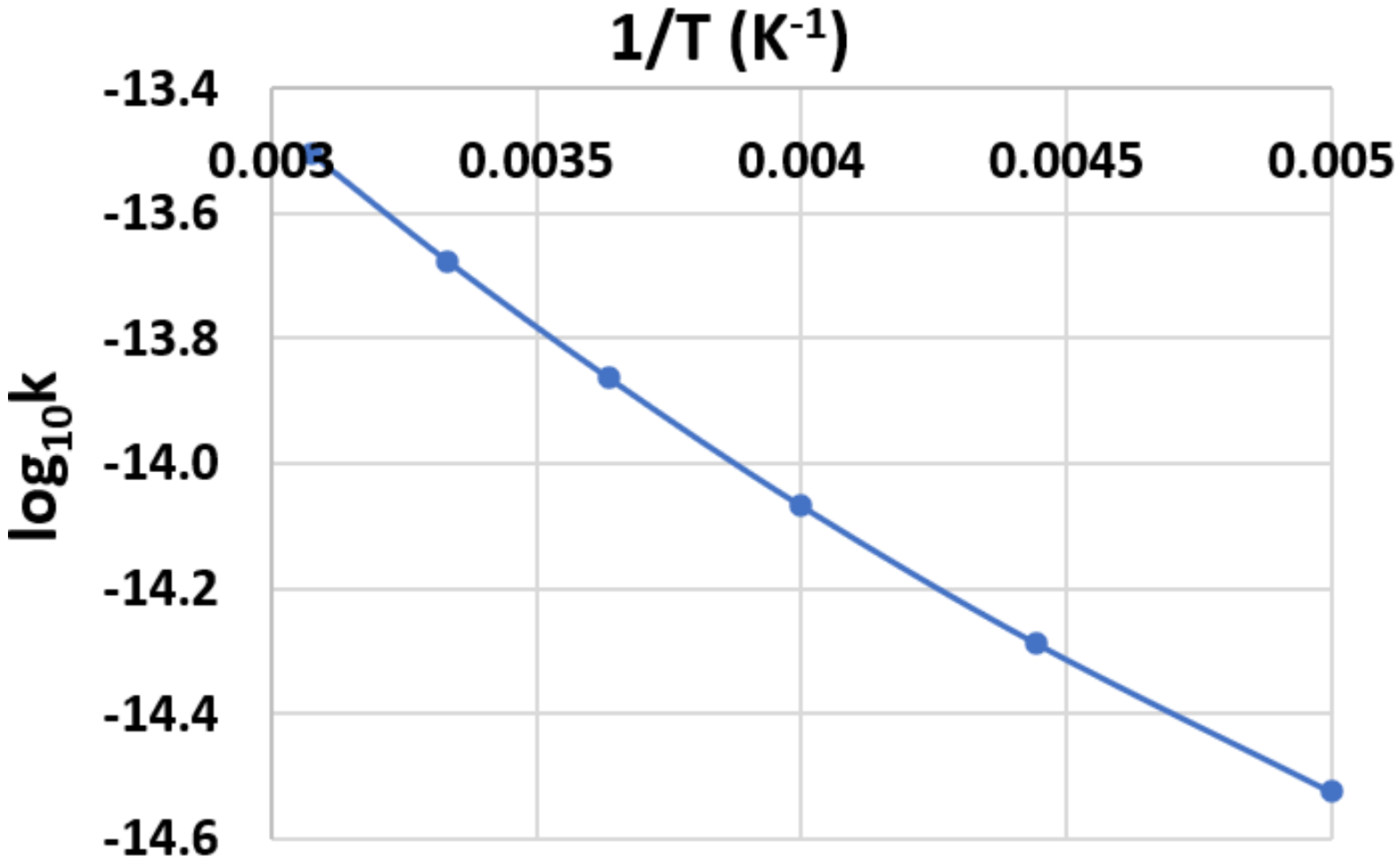
$HOHgO\bullet + CH_4 \longrightarrow Hg(OH)_2 + CH_3\bullet$

Model Compound



HOHgO• + (**RH**, $CH_2=CH_2$, NO, NO_2, CH_2O, CO)

- Rate constant 20 x higher than OH• + CH_4



200 K ≤ T ≥ 325 K

HOHgO• + (**RH**, $CH_2=CH_2$, NO, NO_2, CH_2O, CO)

H-abstraction from other organics should be faster (higher k)

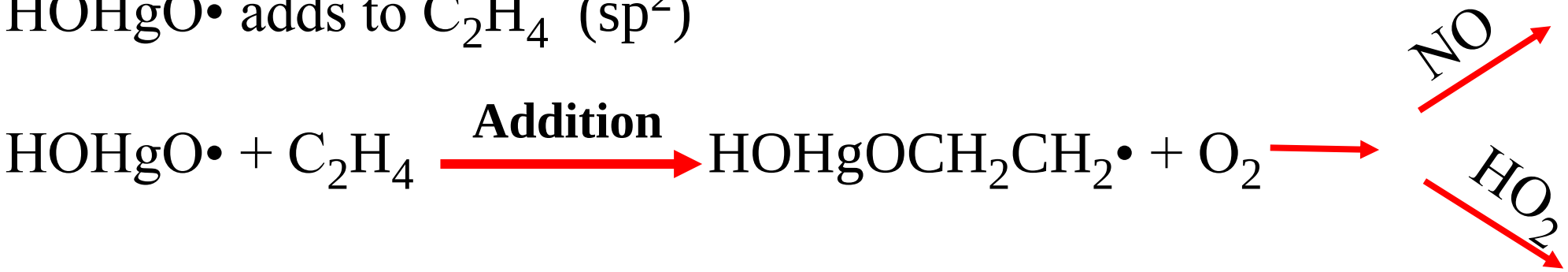
$HOHgO\bullet$ + Larger alkanes (R`H) → $Hg(OH)_2$ + R•

$HOHgO\bullet$ + Alcohols (RCH_2OH) → $Hg(OH)_2$ + $RC\bullet HOH$

$HOHgO\bullet$ + Larger Alkenes ($CH_3CH_2=CH_2$) → $Hg(OH)_2$ + $\bullet CH_2CH_2=CH_2$

HOHgO• + (RH, **CH_2=CH_2**, NO, NO_2, CH_2O, CO)

HOHgO• adds to C_2H_4 (sp^2)

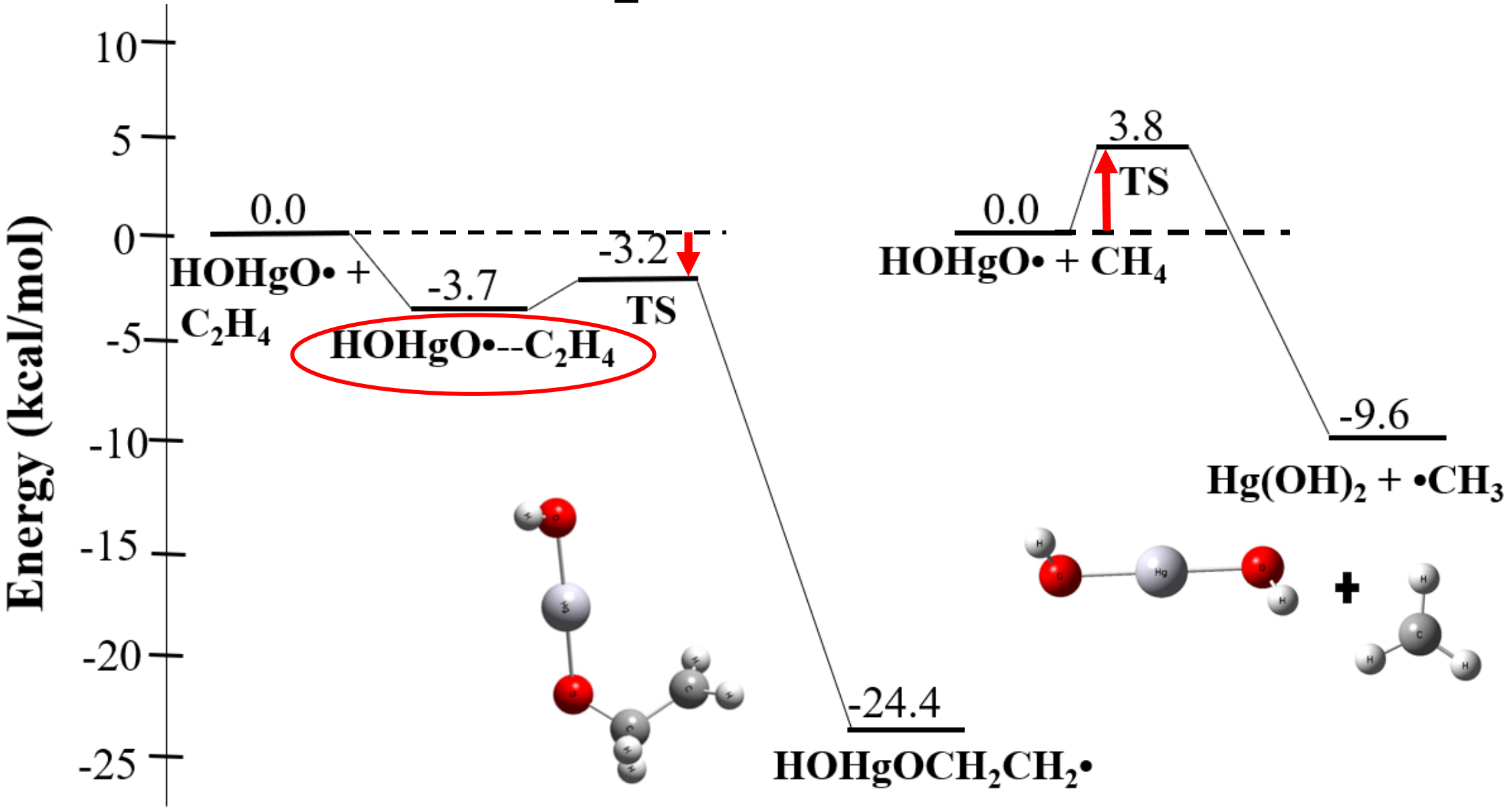


Rate constant (analogy to BrHgO•) ~ 4 x slower than OH• + C_2H_4

Differences from HOHgO• + CH_4

- van der Waals complex of reactants (HOHgO•--C_2H_4)
- Barrier from complex to products lies below reactants

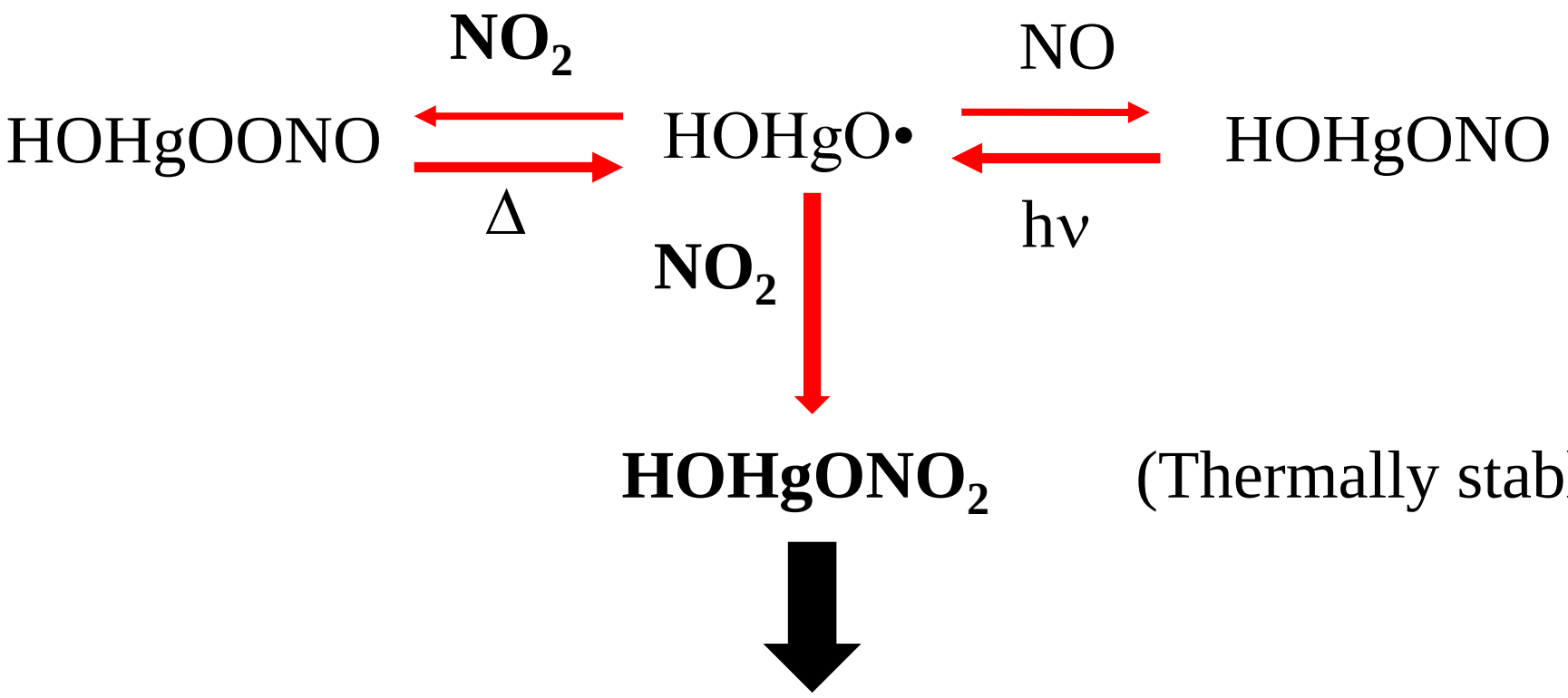
HOHgO• Adds to CH_2=CH_2



HOHgO• + (RH, CH_2=CH_2, **NO, NO_2,** CH_2O, CO)

Form bonds with no energy barrier ⇒ high-rate constants

2-3 × 10^{-11} analogous to CH_3O• + NO_x



HOHgO• + (RH, CH_2=CH_2, NO, NO_2, **CH_2O**, CO)

✓ $HOHgO• + CH_2O$ —**Abstraction**→ $Hg(OH)_2 + HCO•$
$HOHgO• + CH_2O$ —Addition→ $HOHgOCH_2O•$
} 2 Channels

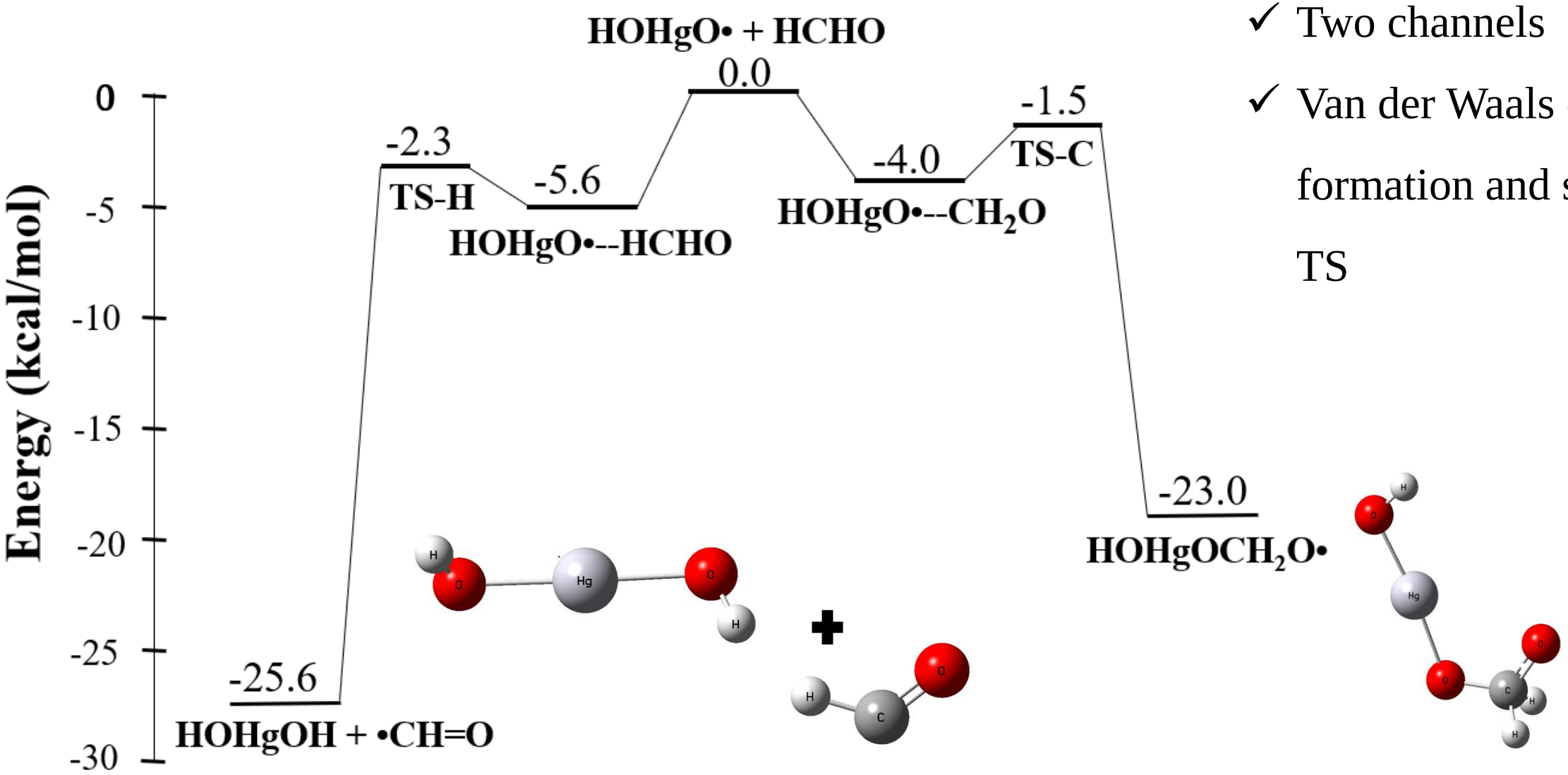
- ✓ **Abstraction** favors over Addition (~10 x faster)
- ✓ $OH• + CH_2O$ system shows only **Abstraction**
- ✓ Rate constants adapted from analogous $BrHgO• + CH_2O$ system,

I. **Abstraction** ~ 5-6 x 10^{-11} cm^3/molecule sec
II. Addition ~ 4-6 x 10^{-12} cm^3/molecule sec
} 200 K ≤ T ≥ 333 K

Reaction of HOHgO• with CH_2=O

HOHgO• + CH_2=O,

- ✓ Two channels
- ✓ Van der Waals complex formation and submerged TS



HOHgO• + (RH, CH_2=CH_2, NO, NO_2, CH_2O, **CO**)

- HOHgO• reacts with CO w/o energy barrier (high-rate constants)
- Reduce Hg(II) to Hg(I)
- Large uncertainties in rate constant ;

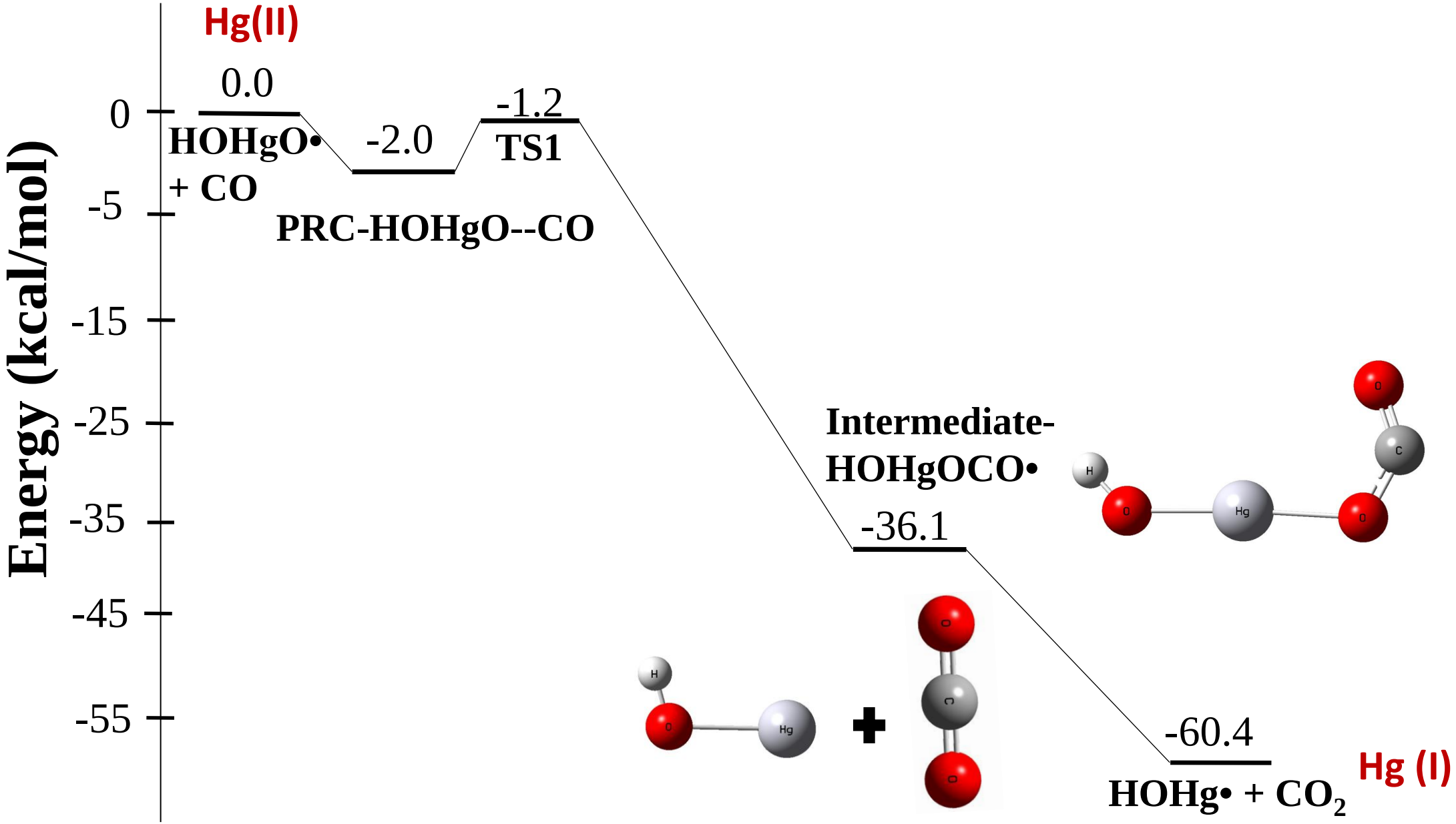
($5.2 \times 10^{-11} - 9.4 \times 10^{-12}$ cm^3/molecule sec) – huge uncertainty kinetics of this reaction

HOHgO• + CO → HOHg• + CO_2

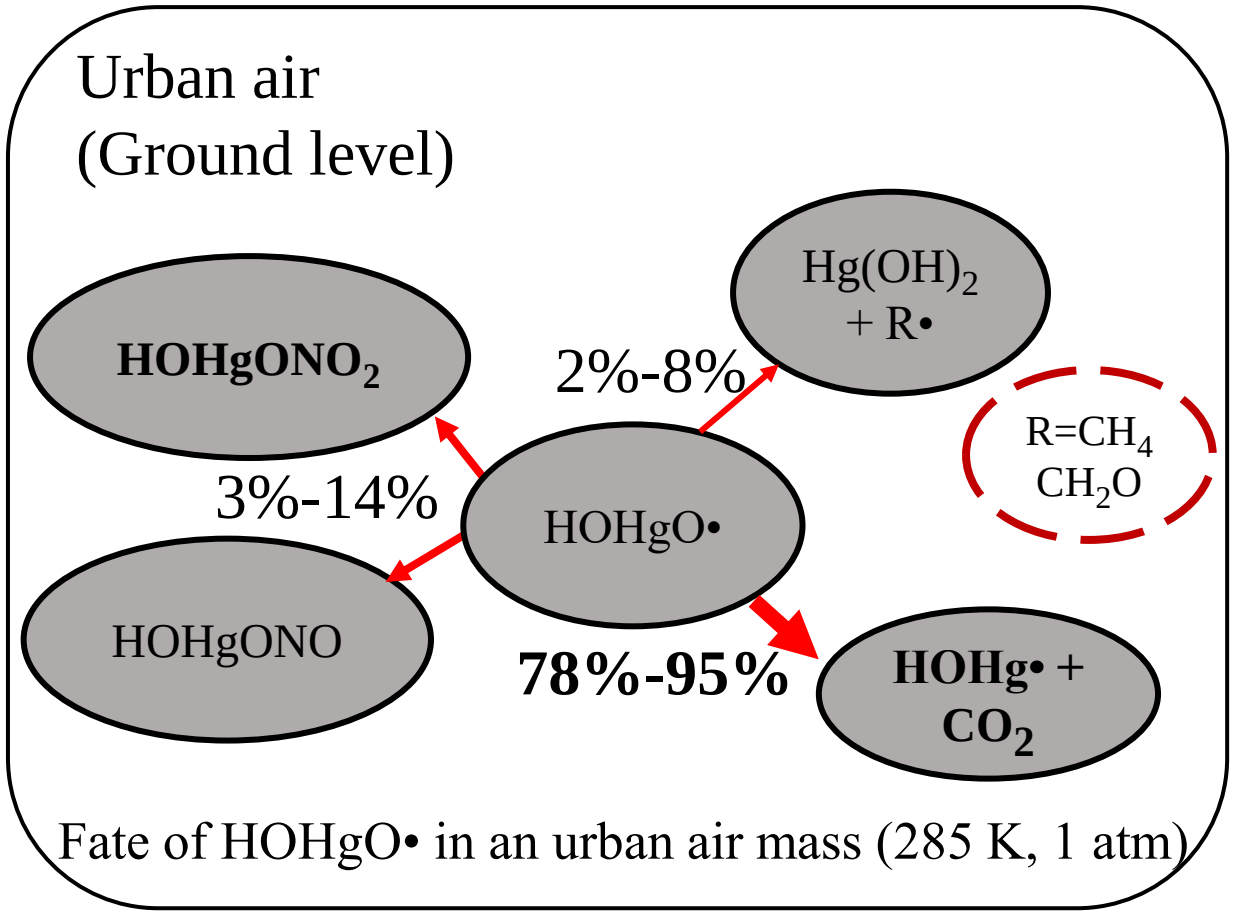
↓

Dissociate back to Hg(0) or react with O_3

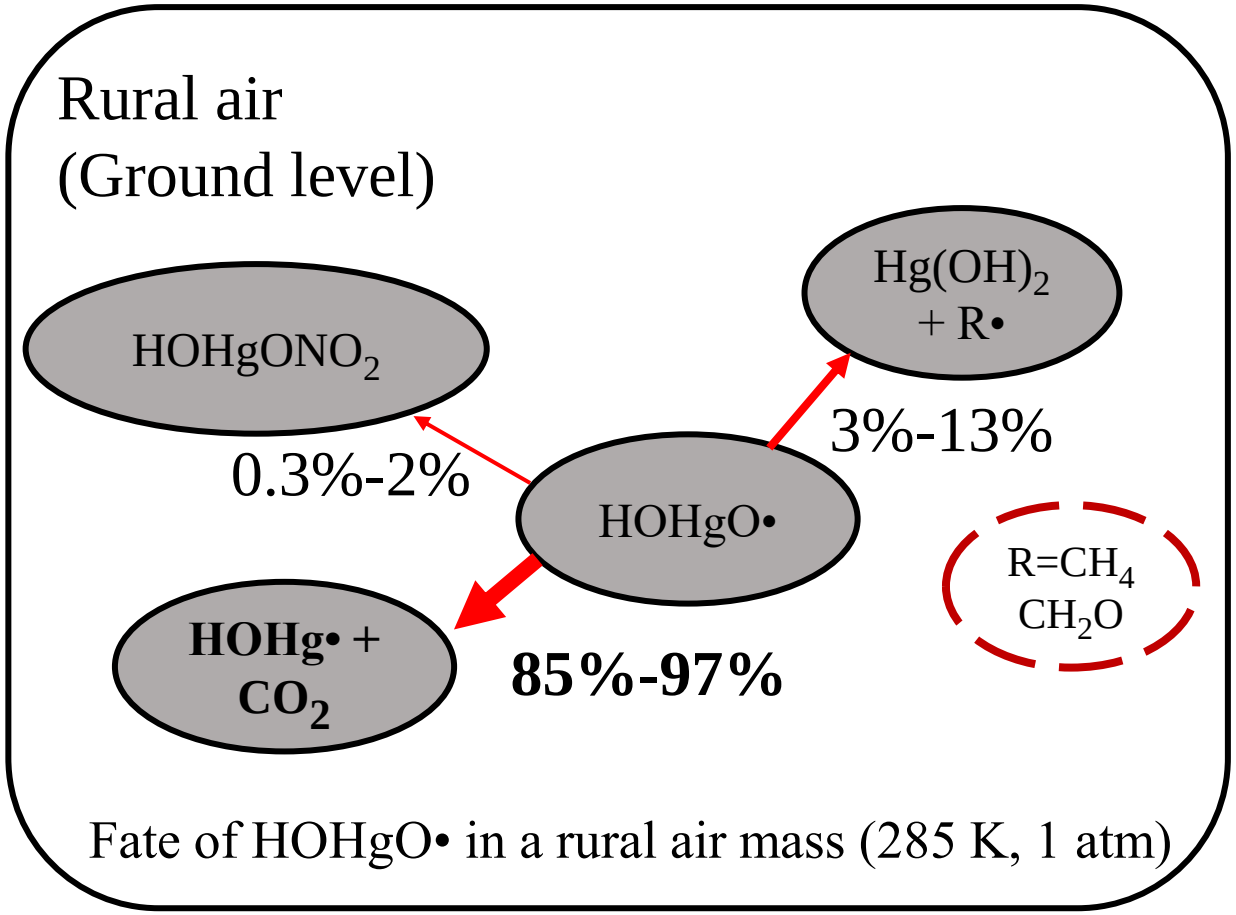
Reaction of HOHgO• with CO



Analysis



Fate of HOHgO• in an urban air mass (285 K, 1 atm)



Fate of HOHgO• in a rural air mass (285 K, 1 atm)

Conclusions

- $HOHgO\bullet + NO_X$ or RH ($CH_2=CH_2$, CH_2O ?) $\Rightarrow$ stable Hg(II)
- $HOHgO\bullet + CO \Rightarrow$ Hg(II) reduction to Hg(I)
- Main fate: reaction with RH and CO

Future Work

- Rate constant for $HOHgO\bullet + CO$
- $HOHgO\bullet + O_3 \longrightarrow HOHg\bullet + 2O_2$

Acknowledgements

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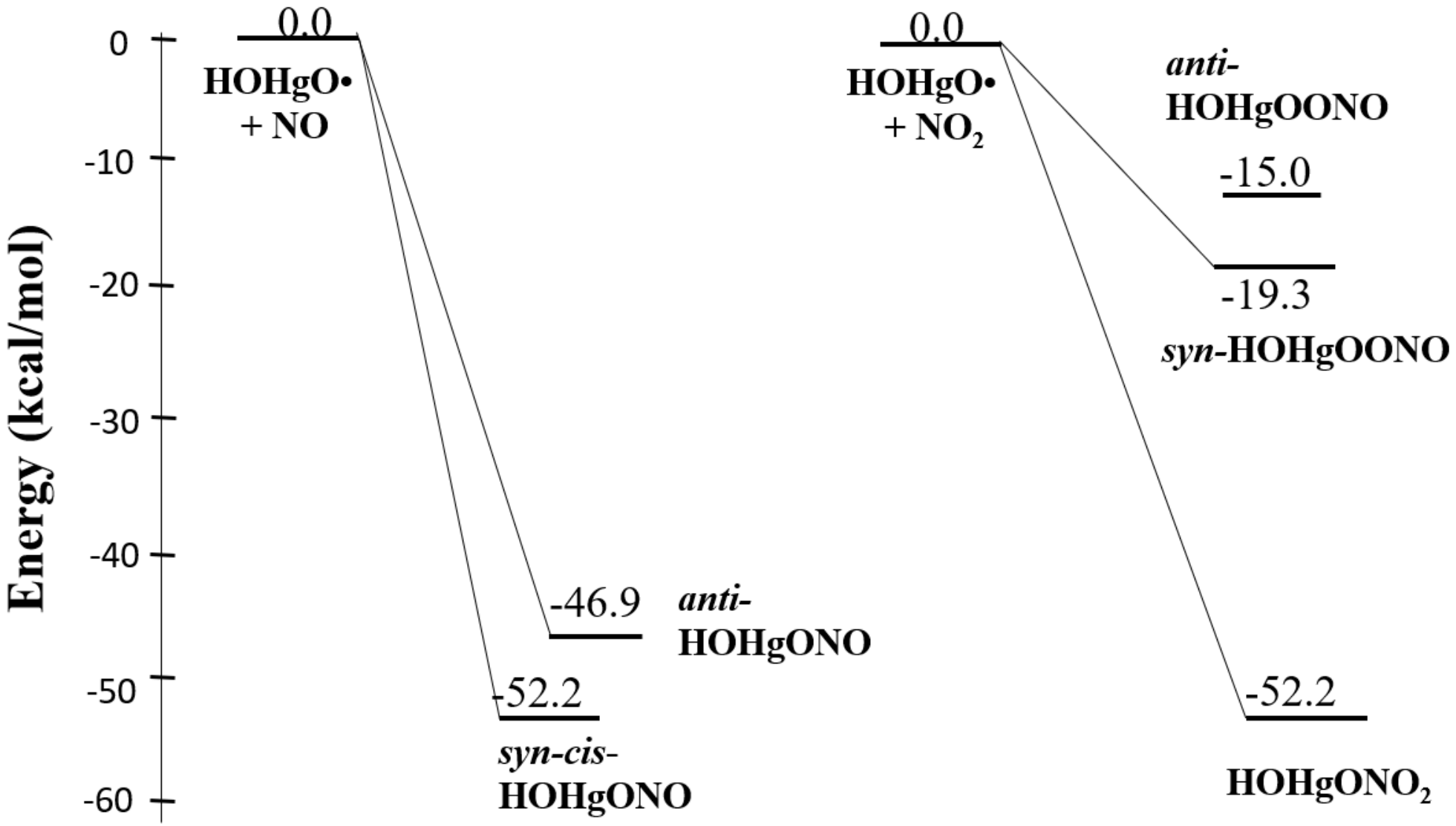
Thank you!

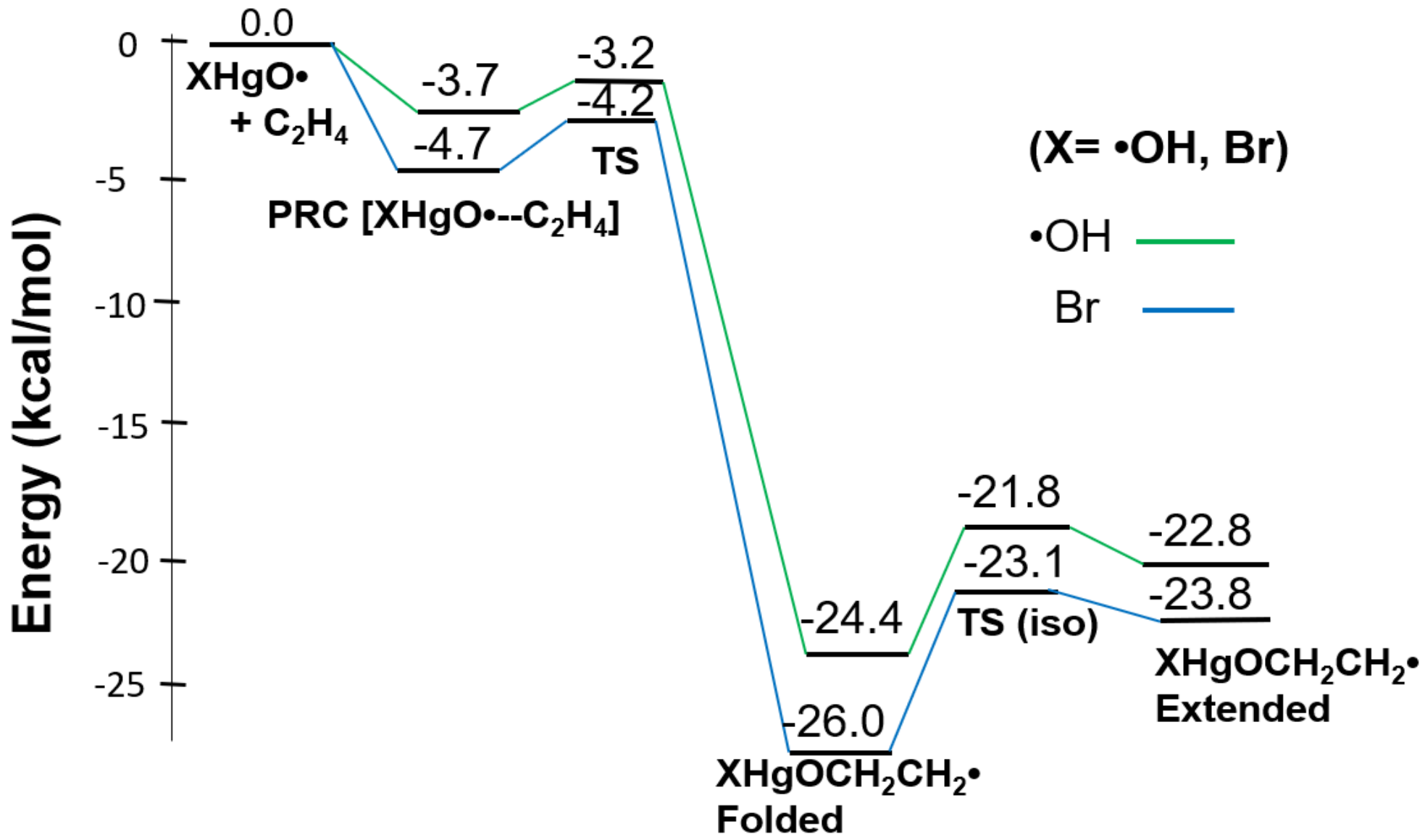
Send me questions at **dthewaed@syr.edu**
Or via the *ICMGP website*

Details of the Chemistry in the last few slides and 4 minutes

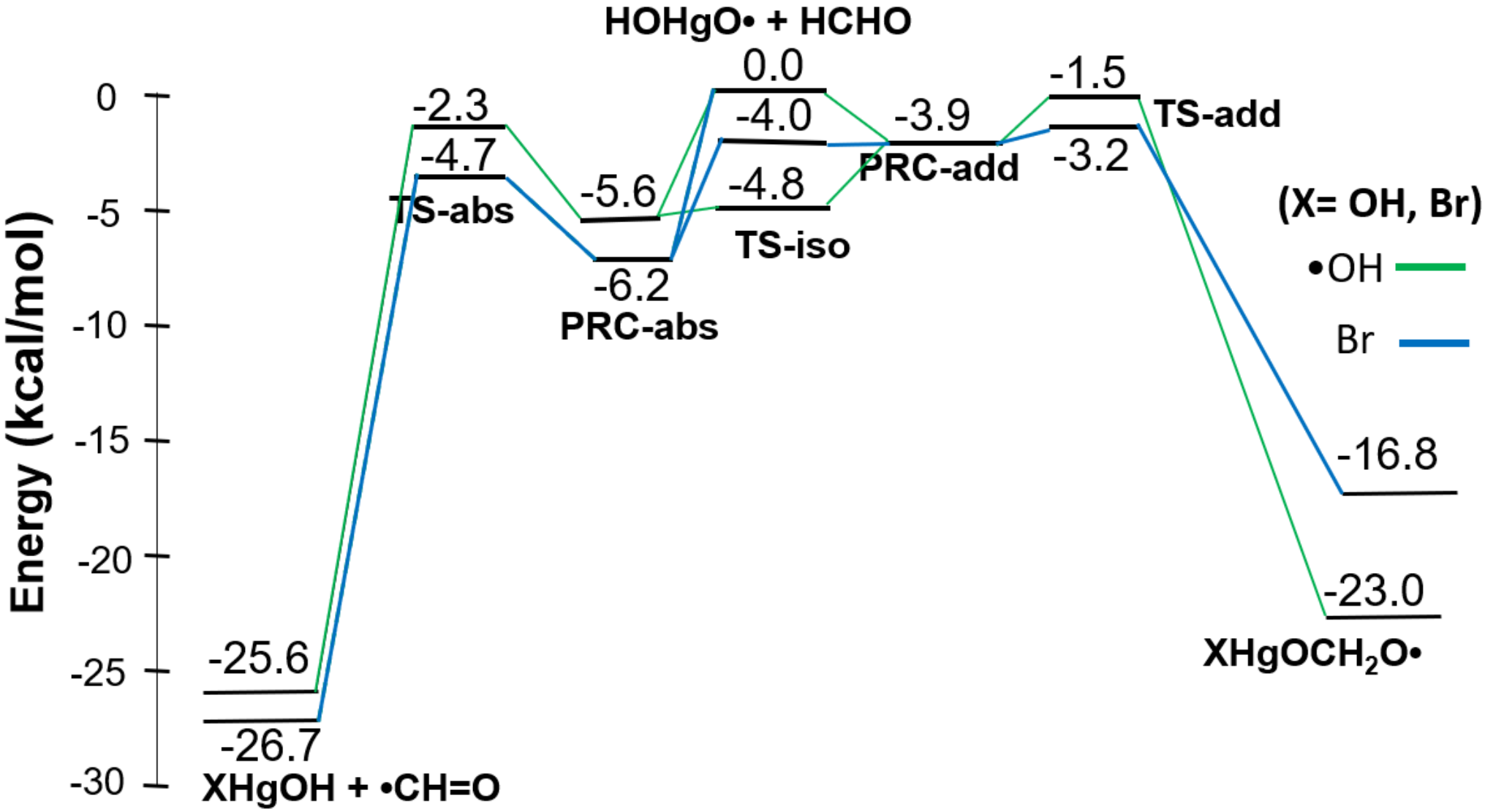
HOHgO• Adds to NOx w/o a Barrier



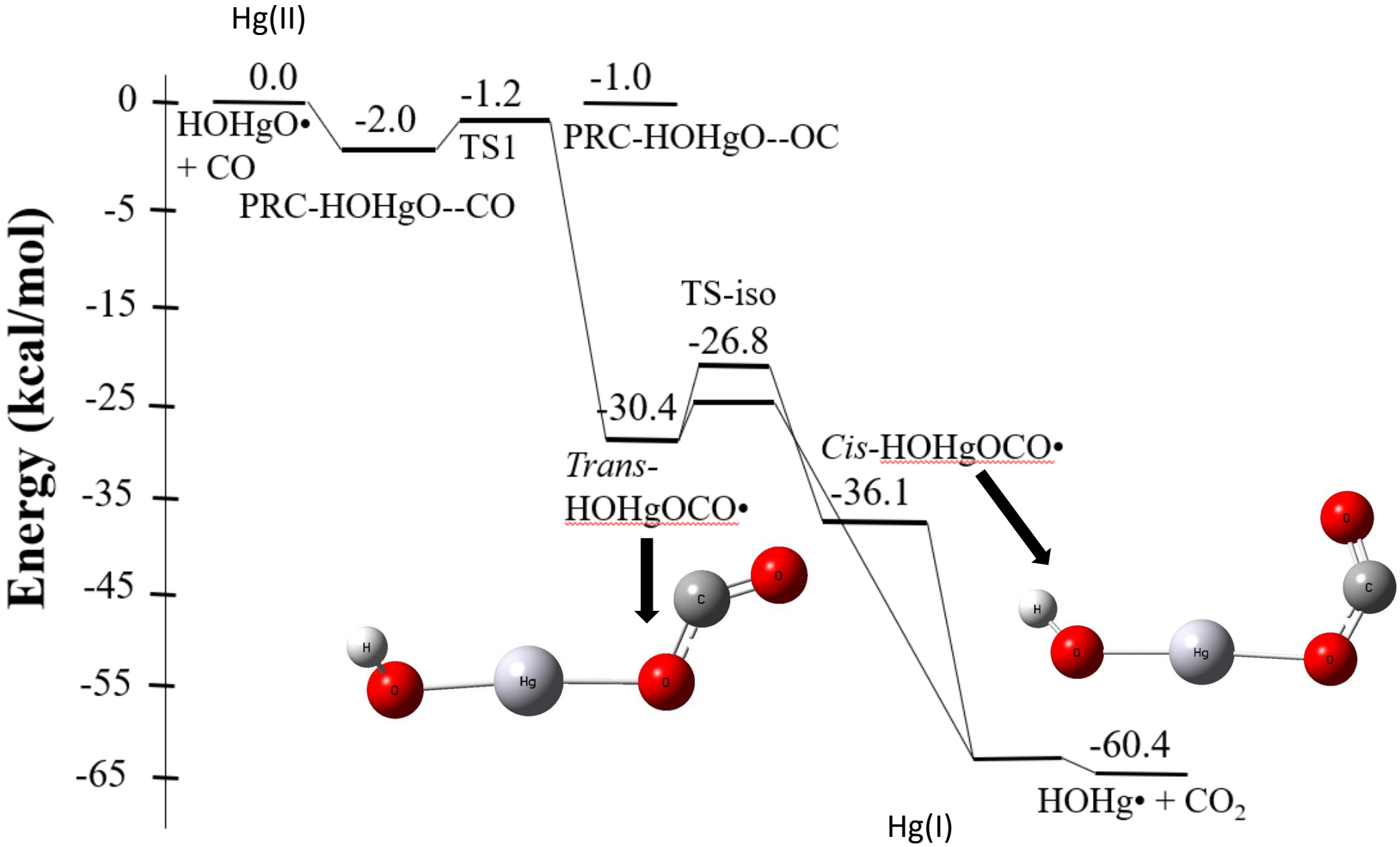
HOHgO• Adds to C_2H_4



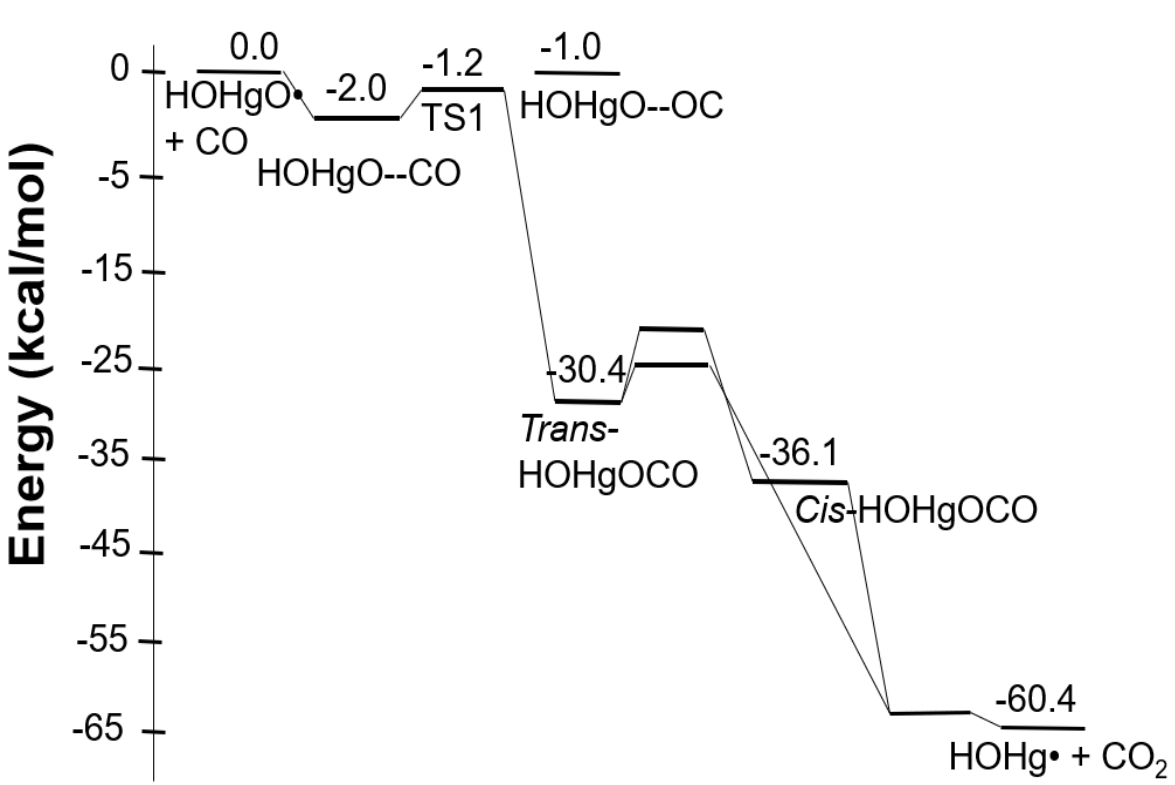
$HOHgO\bullet + CH_2=O$ – Addition and Abstraction

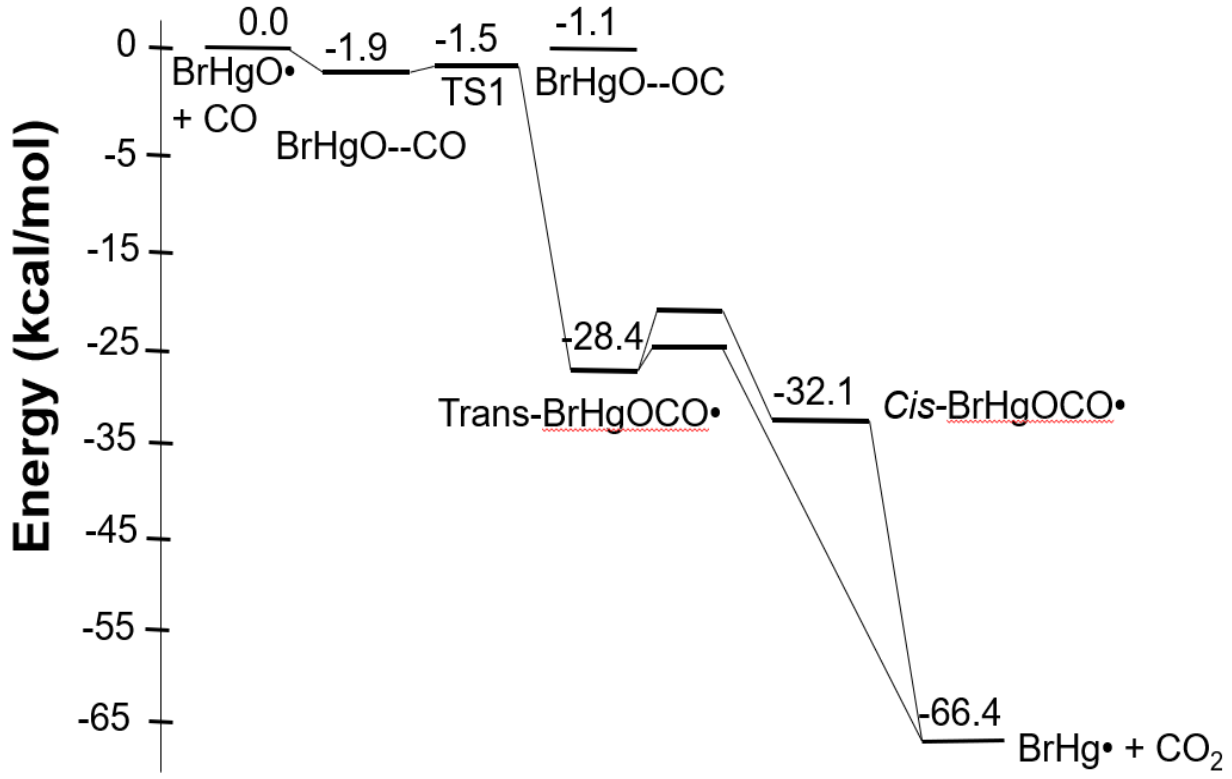


Reaction of HOHgO• with CO



HOHgO• adds to CO





Calculation of k ($HOHgO\bullet + CH_4$)

Free energies (G) were calculated from 200K to 325K at 25K intervals

Transition State Theory (TST) with maximum $\Delta G^{\ddagger}$ was used to compute k,

$$k(TST) = \frac{k_B T}{hC_0} e^{-\frac{\Delta G^{\ddagger}(T)}{RT}}$$

$\Delta G^{\ddagger}(T)$ is the maximum free energy along the path

$k_B = 1.3807 \times 10^{-23}$ J/K (Boltzmann's constant)

$h = 6.6262 \times 10^{-34}$ J·s (Planck's constant)

$R = 1.987\text{E}{-3}$ kcal·mol^{-1}K^{-1} (Ideal gas constant)

$T =$ temperature in K

C_0 = Number Density (molecules cm^{-3})

Where, $C_0 = 2.46 \text{ X } 10^{19} * (298/T)$ molecules cm^{-3}