Reaction Energetics Lab
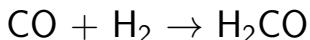
Thermodynamics and Kinetics of $CO + H_2 \rightarrow H_2CO$

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What You'll Learn:

- Running ORCA calculations
- Geometry optimization
- Frequency calculations
- Zero-point energy corrections
- Thermodynamics vs. Kinetics
- Transition state theory

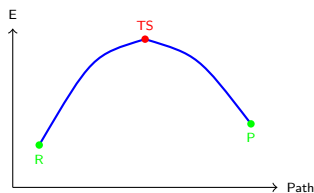**The Reaction:**

$$CO + H_2 \rightarrow H_2CO$$
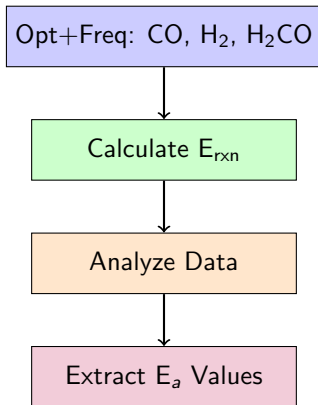
Your Tasks:

1. Calculate energies of CO, H_2, H_2CO
2. Determine E_{rxn} (thermodynamics)
3. Analyze provided IRC data
4. Extract activation barriers (kinetics)

Workflow Summary

Zero-Point Energy (ZPE)

What is ZPE?

- Molecules vibrate even at 0 K
- Quantum mechanical effect
- Must include for accurate energies

Formula:

$$E_{\text{total}} = E_{\text{SCF}} + \text{ZPE}$$

Example:

- E(SCF) = -113.876543 Eh
- ZPE = 0.012345 Eh
- E(total) = -113.864198 Eh

From ORCA output:

```
Zero point energy:  0.012345 Eh
```

Why it matters:

- Typically 5-20 kJ/mol
- Different for each molecule
- Changes reaction energies
- Always include!

ORCA Input: Opt + Freq in One Job

Single job does both optimization and frequency:

```
1 # Optimize then calculate frequencies
2 ! RHF STO-3G TightSCF Opt NumFreq
3
4 * xyzfile 0 1 molecule.xyz
```

What ORCA does:

1. Optimizes geometry (finds minimum)
2. Calculates frequencies on optimized structure
3. Outputs: E(SCF), ZPE, vibrational modes

Keywords:

- RHF STO-3G: Method/basis (fast, small)
- Opt: Optimize geometry
- NumFreq: Calculate frequencies
- 0 1: Charge 0, singlet

Step 1: Build Molecules in Avogadro

Build three molecules:

CO: C triple-bonded to O

1. Draw Tool → Click for C
2. Click and drag to create bond
3. Change second atom to O
4. Change bond to triple
5. Extensions → Optimize Geometry
6. Save As → CO.xyz

H$_2$: Two H atoms bonded → Save as H2.xyz

H$_2$CO: C with C=O double bond and two C-H bonds → Save as H2CO.xyz

Transfer to cluster:

```
1  scp *.xyz $USER@c1cluster:~/Reaction_Lab/
```

Step 2: Create ORCA Input Files

For each molecule, create .inp file:

```
1  nano CO.inp
```

```
1  # CO calculation
2  ! RHF STO-3G TightSCF Opt NumFreq
3
4  * xyzfile 0 1 CO.xyz
```

Repeat for H2.inp and H2CO.inp

Create submission script:

```
1 nano CO.sh
```

```
1 #!/bin/bash
2 #SBATCH --job-name=CO
3 #SBATCH --time=01:00:00
4 #SBATCH --mem-per-cpu=4000
5
6 module load orca/6.0.0
7 orca CO.inp
```

Submit all three:

```
1 sbatch CO.sh
2 sbatch H2.sh
3 sbatch H2CO.sh
```

Monitor: squeue -u $USER

Step 4: Extract Energies and ZPE

After jobs complete, extract values:

```
1 grep "FINAL SINGLE POINT ENERGY" *.out
2 grep "Zero point energy" *.out
```

Record in table:

Molecule	E(SCF) (Eh)	ZPE (Eh)	E(total) (Eh)
CO	_____	_____	_____
H_2	_____	_____	_____
H_2CO	_____	_____	_____

Calculate: E(total) = E(SCF) + ZPE for each

Step 5: Calculate Reaction Energy

Combine your results:

$$E_{\text{reactants}} = E_{\text{CO}} + E_{\text{H}_2}$$

$$E_{\text{product}} = E_{\text{H}_2\text{CO}}$$

$$\Delta E_{\text{rxn}} = E_{\text{product}} - E_{\text{reactants}}$$

Convert to kJ/mol:

$$\Delta E_{\text{kJ/mol}} = \Delta E_{\text{Hartree}} \times 2625.5$$

Interpretation:

- Negative = exothermic (releases energy)
- Positive = endothermic (requires energy)

Where is the Transition State?

Locating the TS on Your Plot: Since we cannot compare absolute energies directly, use the **relative barrier height** from the literature.

The Magic Number:

- The literature states the TS is **105.3 kcal/mol** higher in energy than H_2CO (at the HF level).
- **Action:** Take your calculated Energy(H_2CO) and add 105.3 kcal/mol.
- Plot the TS at this level.

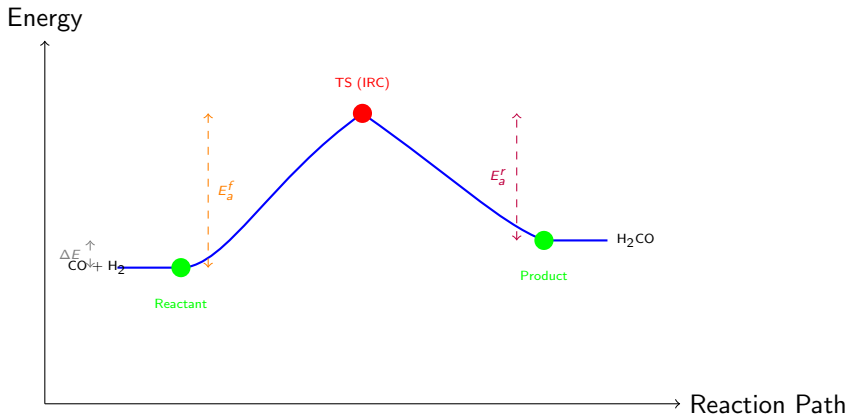*Source: HF Barrier from Martins et al., J. Phys. Chem. A 1998, 102, 10805 [Table 3]*

Context: Is this "High"?

Yes. A barrier of >80 kcal/mol is extremely high.

- This explains why Formaldehyde is stable at room temperature.
- It does not spontaneously decompose back to CO + H_2 without high heat or a catalyst.

Understanding Your Results

Green: Your calculations (endpoints)
Red: TS from IRC
Blue: Complete minimum energy path

Important Concepts

1. **Thermodynamics tells you "where"**
   - E determines equilibrium position
   - Negative E favors products
   - Doesn't tell you about rate

2. **Kinetics tells you "how fast"**
   - E_a determines reaction rate
   - $k = Ae^{-E_a/RT}$
   - High E_a = slow, even if favorable

3. **ZPE matters**
   - Quantum effect, always present
   - Include for accurate E
   - Typically 20- 80 kJ/mol

Done early?

Try calculating the IRC on your own!

Ask your TA for guidance.