Lecture 17: Kinetics (continued)

Announcements:
• Seminar: Prof. Nate Szymczak (University of Michigan)
  Catalytic Hydrogen Transfer Reactions Enabled by Ligand Design
  Wed, 4pm, 219 BRL
• Problem Set 4 due Thurs, 11/3

Today:
• Arrow-pushing for radical reactions
• Catalysis (in general terms)
• Kinetics of Catalytic Reactions

Practice Problem: Mechanism?

Tips for Radical Mechanisms
1) Count S (especially helpful for H-abstractions)
2) Anything that stabilizes a cation or anion stabilizes a radical.
3) Use (not \( \overrightarrow{\text{pushing 1e-}} \) pushing 2 e-s.
   (need 2 of these to make a bond)
Catalysis

Important in:
- Pharmaceuticals
- Biological systems (enzymes)
- Energy research

What is it?

![Diagram of reaction Gibbs free energy (ΔG) changes with catalyst (Cat) involvement.]

Linus Pauling:
Differential binding of catalyst to substrate & transition state.
Catalyst binds TS more strongly.

\[
K_{cat} = \frac{[\text{sub}][\text{cat}]}{[\text{sub}][\text{cat}]} \\
1 < \frac{k_{cat}}{k_{uncat}} = \frac{K_{cat}^{-}}{K_{cat}^{+}}
\]

Turnover of catalyst: catalyst can & does repeat catalytic cycle.

Practical outcome: Substoichiometric amounts of catalyst used.
Catalyst doesn't change.
Kinetics of Catalytic Cycle

\[
\text{rate} = k_{\text{obs}} [\text{cat}]
\]

Possibility #1: All steps = irreversible

rate = \( k_{\text{obs}} [\text{cat}][A][B] \)

*atypical*
Possibility #2: Reversible steps (more likely)

- Rate-determining step or turnover-limiting step (Funnel for cat. cycle)

\[ G \]

\[ \text{rxn coord} \]

- \[ \text{cat} + A + B \]
- \[ \text{step 1} \]
- \[ \text{cat} \cdot A \cdot B \]
- \[ \text{step 2} \]
- \[ \text{cat} \cdot A \cdot B \]
- \[ \text{step 3} \]
- \[ \text{cat} \cdot P \]
- \[ \text{step 4} \]
- \[ \text{cat} + P \]

Rate:

\[ \text{rate} = k_2 [\text{cat} \cdot A] [B] \]

Equilibrium Approx:

\[ K_1 = \frac{k_1}{k_1} = \frac{[\text{cat} \cdot A]}{[\text{cat}][A]} \]

\[ [\text{cat} \cdot A] = \frac{k_1 [\text{cat}][A]}{-k_1} \]

\[ \text{rate} = \frac{-k_1 - k_2 [\text{cat}][A][B]}{-k_1} \]

Steady State:

\[ \text{rate} = \frac{-k_1 - k_2 [\text{cat}][A][B]}{-k_1 + k_2} \]

But...

1. Changes \([A], [B], [Pdt]\) over rxn course ➔ change in rds
2. May not have clearly defined rds
3. Catalyst “resting state” may not be naked catalyst ➔ catalyst may change over rxn course.
rate = \frac{-k_1k_2 [cat] [A] [B]}{-k_1 + -k_2}

[cat]_{total} = [cat]_T = [cat] + [cat \cdot A]

[cat] = [cat]_t - [cat \cdot A]

rate = -k_2 [cat \cdot A] \frac{[B]}{[A][B]} = \frac{k_1k_2 [A][B] ([cat]_T - [cat \cdot A])}{-k_1 + -k_2}

Solve for [cat \cdot A]:

- k_2 [cat \cdot A]

... to be continued...