Lecture 20: Mechanistic Experiments

Announcements:
• PS 5 returned today.
• Midterm 2 on Thurs.

Today:
• More mechanistic experiments

Hammett Correlation:
\[ \log \left( \frac{k_\text{f}}{k_\text{h}} \right) \rightarrow \text{slope} = \rho \]

Other LFER:
Sigman ACIE 2008, 47, 771. Stereo bulk vs ee?

\[ \text{PhCHO} + \text{Br} \rightarrow \text{H0}^{14} \]

10% CrO3
10% L
TMSCl, Mn0
then TBAF

Substituent of interest
Chauvin values
$\log(\text{er})$ vs. charton value

$\log(\text{kr})$ vs. $\Theta$

V-shape $\Rightarrow$ change in mechanism.
Change in rols or total in mech.
Isotope Effects

\[ C-H \quad \text{vs} \quad C-D \]

→ KIE related to change in mass \( \rightarrow H \) vs. \( D \)

(1) Detect if \( X-H/X-D \) bond is broken in or before rds.

(2) Detect changes in hybridization @ \( X-H/D \) in rds.

\[ A \quad \text{and} \quad B \]

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{ke}{\mu}} \]

- \( \nu \): frequency of vibration
- \( k \): spring force constant
- \( e \): electron

\( \mu = \text{reduced mass} = \frac{m_A m_B}{m_A + m_B} \)

- Heavier mass \( \Rightarrow \) Lower frequency

\( C-H \quad \text{vs} \quad C-D \)

- \( C \) lower frequency
- More stable/stronger bond
\[ \frac{k_H}{k_D} = K_{IE} = e^{-\Delta E/k_B T} \]

Max \( K_{IE} \approx 0.5 \)

for "normal" organic reaction.

**Equilibrium Isotope Effects**

\[
A-H/D + B^\Theta \rightleftharpoons A^\Theta + B-H/D \rightarrow P
\]
Kinetic Isotope Effects (KIE)

When C-H/D is not fully cleaved.

Consider linear TS:

\[ \text{A-H + B} \rightarrow \text{A} + \text{H-B} \]

\[ \rightarrow [\text{A - H - B}]^+ \]

Vibrational Frequencies:

1) Asymmetric Stretch = rxn coord
   \[ \text{A<-->H<-->B} \]
   \[ \text{no frequency in TS} \]

2) Bending
   \[ \text{A-H-B} \]

3) Wag
   \[ \text{A-H-B} \]

4) Symmetric Stretch
   \[ \text{A<-->H-->B} \]
   \[ \text{New to TS} \]
   \[ \text{Not in A-H or B-H} \]
   \[ \text{Can be affected by isotopes.} \]

\[ . \quad 1 \]
Case 1: Early TS / Exothermic

Case 2: Late TS / Endothermic

If $H \rightarrow B \approx H \rightarrow A$, then small KIE.
If $H \rightarrow B \neq H \rightarrow A$, then you will probably see KIE.

$\Delta G_H^+ < \Delta G_D^+$ \Rightarrow$ faster for A-H than A-D.
Case 3: Thermoneutral

\[
\Delta G_D^\neq < \Delta G_H^\neq
\]

Symm. stretch holds H in place

\[A \leftrightarrow H \rightarrow B\]

\[\text{Typical for Primary KIE's}\]

\[\uparrow 1^0\]

\[\text{Expect KIE 2 \rightarrow 7}\]

\[KIE = \frac{k_H}{k_D}\]