Lecture 13: Kinetics (continued)

Announcements:
• Midterm 1 is still not graded (in progress, though!)
• Problem Set 3 will be posted tomorrow. Due next Thurs.

Today:
• 1 correction from last time
• Transition State Theory
• Hammond Postulate
• Kinetic rate laws
Transition State Theory

How do we get information about TS's (and intermediates) that are not observable?

Simplest Case:

\[ A \rightarrow B \]

![Diagram of free energy profile with TS indicated]

Recall: \( \text{rate} = -\frac{d[CA]}{dt} = \frac{d[CB]}{dt} = \frac{k}{[A]} = k^+ [TS] \)

\[ k^+ \approx \frac{k_B}{h} \frac{T}{k} \]

- Boltzmann constant
- Planck's constant
- Fastest possible reaction rate (no barrier)

\( k_B = 2.083 \times 10^{10} \text{ s}^{-1} \text{ K}^{-1} \)

\( k = 6 \times 10^{12} \text{ s}^{-1} \approx 10^{13} \text{ s}^{-1} \)

Equilibrium between A & TS.

\[ k^+ = \frac{[TS]}{[A]} \]

\[ [TS] = k^+ [A] \]

\[ [TS] = e^{-\Delta G^+/RT} [A] \]

\[ [TS] = \frac{k[CA]}{k^+} \]

Recall:

\[ \Delta G = -RT \ln K_{eq} \]

\[ K_{eq} = e^{-\Delta G/RT} \]
\[ \frac{k[A]^0}{k^+} = e^{-\frac{\Delta G^*}{RT}} [A] \cdot k^+ \]

\[ k = \frac{k_B}{h} T \exp \left( -\frac{\Delta G^*}{RT} \right) \]

\[ k^+ = \frac{k_B}{h} T \exp \left( \frac{\Delta G^*}{RT} \right) \]

\[ \ln \left( \frac{k}{k^+} \right) = -\frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R} \]

\[ R \ln \left( \frac{k}{k^+} \right) = -\Delta H^* \]

\[ y = mx + b \]

Eyring Equation
Warning: For multistep reactions, you are measuring composites of $\Delta H^\pm$ and $\Delta S^\pm$.

Enthalpy Control: $\Delta H^+$ is major contributor to $\Delta G^+$.

Entropy Control: $T \Delta S^\pm$ is major contributor to $\Delta G^\pm$.

$\Delta G$ changes with Temperature.
Interpretation of $\Delta S^\pm$

If $\Delta S^\pm < 0 \rightarrow$ TS is more ordered than ground state.

**Ex:** $\text{S}_2 \text{N}_2$ $\text{NC}^\Theta \rightarrow \text{CH}_3^- \text{I}^+ \rightarrow \text{NC-CH}_3 \text{I}^\Theta$

\[
\begin{array}{c}
\text{H} \\
\text{NC} \\
\text{I} \\
\text{H} \\
\text{H}
\end{array}
\quad \Rightarrow \quad \text{highly ordered TS.}
\]

$\Delta S^\pm = -30 \text{ eu}$

\[
\begin{array}{c}
\text{Nu}^\Theta \\
\text{C}^\Theta \\
\rightarrow \\
\text{Nu} \sim \text{O}^\Theta \\
\end{array}
\quad \Rightarrow \quad \Delta S^\pm = -8 \text{ eu}
\]

$\rightarrow$ Entropy not as negative b/c epoxide opening (more degrees of freedom).

If $\Delta S^\pm > 0$ : TS more disordered than GS

**Ex:** $\text{R-OR}$ $\rightarrow 2 \text{ RO}^- \quad \Delta S^\pm = +10 \text{ eu}$

In general:

$-30 \text{ eu} \leq \Delta S^\pm \leq +10 \text{ eu}$

(exceptions for trimolecular TS)
Arrhenius Equation

\[ k = A e^{(-E_a/RT)} \]

\[ \text{related to } \Delta H^\ddagger \]

\[ \text{related to } \Delta S^\ddagger \]

<table>
<thead>
<tr>
<th>( \Delta G^\ddagger ) (kcal/mol)</th>
<th>rate ( (s^{-1}) )</th>
<th>( t_{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>( 4.2 \times 10^{10} )</td>
<td>( 1.6 \times 10^{-11} )</td>
</tr>
<tr>
<td>10</td>
<td>( 3.6 \times 10^5 )</td>
<td>( 2 \times 10^{-6} )</td>
</tr>
<tr>
<td>20</td>
<td>0.02</td>
<td>33</td>
</tr>
<tr>
<td>30</td>
<td>( 1.2 \times 10^{-9} )</td>
<td>( 6 \times 10^8 ) ( (18 \text{ years}) )</td>
</tr>
</tbody>
</table>
Hammond Postulate

Endothermic
"product-like TS"

"Starting material like TS"

Exothermic

Ex: Electrophilic Aromatic Substitution

\[
\begin{array}{c}
\text{Ar} \quad \text{X} \\
\uparrow \\
\text{El}^+ \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{Ar} \\
\text{El} \\
\text{X} \\
\end{array}
\]

Why do EDG accelerate EAS?