Topics to be covered today:
- Stability of conjugated dienes
- Electrophilic Addition Reactions
- Kinetic vs. Thermodynamic Control.

Stability of Conjugated Dienes:

- By heats of stabilization:
  
  \[
  \begin{align*}
  &\text{Equation} & \text{Delta F} & \text{Aff. Value (kJ/mol)} \\
  &\text{H}_{2} + \text{H}_{2} & -127 & \\
  &\text{H}_{2} + \text{H}_{2} & -126 & \\
  &\text{H}_{2} + 2\text{H}_{2} & -254 & \text{(twice the energy of a single alkene)} \\
  &\text{H}_{2} + 2\text{H}_{2} & -239 & \\
  \\
  \end{align*}
  \]

In the last case, we would expect -254 kJ/mol as well. But it is stabilized by 15 kJ/mol.
• Using a molecular orbital picture.

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\[ \text{HOMO} \quad \vdots \quad \text{LUMO} \]
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This has a large gap than corresponding HOMO/LUMO for the 3 double bond system.

For lower energy HOMO-LUMO transitions, able to use UV/Visible light spectroscopy (300-800 nm)

able to calculate energy of transition using 

\[ E = h \nu \]

\[ E = h \frac{\nu}{\lambda} \]

For the above compounds:

\[ \text{B-catenin} \]

\[ \text{217 nm wavelength} \]

\[ \text{absorbed} \]

\[ \text{highest} \]

\[ \text{energy HOMO-LUMO} \]

\[ \text{lower} \]

\[ \text{energy HOMO-LUMO} \]

\[ \text{(in visible range)} \]
Consider: HCl addition to conjugated diene.

\[
\overset{-}{\overset{\text{HCl (1 equivalent)}}{\underset{25^\circ}{\rightarrow}}} \overset{?}{\rightarrow}\overset{?}{\rightarrow}
\]

Consider: Mechanism

\[
\overset{+}{\overset{\text{H}^+}{\underset{\text{H}^+}{\rightarrow}}} \overset{\text{but allyl cation resonates}}{\underset{\text{but allyl cation resonates}}{\rightarrow}} \overset{\text{Cl}}{\underset{\text{Cl}}{\rightarrow}} \overset{\text{Cl}}{\underset{\text{Cl}}{\rightarrow}}
\]

(\text{1,2 addition})

(\text{major product})

Now consider: Bromine addition

\[
\overset{\text{Br}_2}{\overset{\text{eq.}}{\underset{?}{\rightarrow}}} \overset{?}{\rightarrow}
\]

what would you expect based on the above mechanism...?
True reactions are very temperature dependent.

Consider HBr addition:

\[
\text{\begin{align*}
\text{HBr} \quad \rightarrow & \quad \text{\text{Br}} \\
& \quad \text{80\%} \quad \text{80\%}
\end{align*}}
\]

\[
\text{HBr} \quad \rightarrow \quad 20\% \quad 80\%
\]

Why the difference?

Mechanism:

\[
\text{\begin{align*}
\text{HBr} \quad \rightarrow & \quad \text{\text{\text{Br}}} \\
& \quad \text{formed fastest}
\end{align*}}
\]

\[
\text{equilibrium} \quad \rightarrow \quad \text{Br}
\]

At low temperatures, the product formed fastest dominates. …

"Kinetic product"

"Thermodynamic product"
Using an Energy Diagram

1,4 transition state
1,2 transition state

1,2 product
1,4 product

At low temperatures, you only have enough energy to follow the easier path (1,2 addition) ... that is the transition state energy is at lower energy.