Alkenes - Reactions (sec 3.6) A reaction is defined by:

- Bonds Broken → lose full octet
- Bonds formed → restores full octet

Addition Reactions

Electrophilic addition to a double bond

Reaction Mechanisms - "Arrow pushing" mechanism

Two 'Players'
1) Nucleophile $\text{Nu}^-$ high $\epsilon^-$ density, $\Theta$ charge or $S^-$
2) Electrophile $E^+$ low $\epsilon^-$ density, $\Theta$ or $S^+$

Famous nucleophiles: $\text{Cl}^-, \text{Br}^-, \text{H}_2\text{O}^-, \text{CN}^-, \text{CH}_3\text{CH}_2\text{O}^-, \text{S}^-, \text{C}^-$

Famous Electrophiles: $\text{H}^+$, $\text{H}-\text{Br}$

Mechanism of H-Br addition to an alkene/Electrophilic addition was the bond

- Bouncing

- Both $\epsilon^-$ to bromine

- Carboxylation (High energy)

- Intermediates

- New bonds

- Old bonds lost $\pi$ bond

$C-\text{H} = 108^\circ > 1$}\n
$C-\text{H} = 72^\circ$
**Thermodynamics**

Thermodynamic:

- Reactants → Products

**Kinetics**

Kinetics:

- How fast will the products be formed?

**Energy**

- Activation energy

**Gibbs Free Energy (ΔG)**

- ΔG: Gibbs Free Energy
  - ΔG^+ = ΔG_{AB}
  - ΔG = ΔG^+ + RT ln K

**Equilibrium Constant (Keq)**

- K_{eq} = \frac{[C][D]}{[A][B]}

**Exothermic-Release Heat**

ΔG is "-" → Favorable / Spontaneous

- ΔG is large → Product

**Rate of Reaction**

- Rate = k[A][B]

**Speed**

- Rate constant → ΔG^+

- ΔG^+ is large → K is small
What can you say about these reaction coordinate diagrams?

1. \( \Delta G^+ \) 
2. \( \Delta G^+ \) 
3. \( \Delta G^+ \) 
4. \( \Delta G^+ \)

- \( \Delta G \rightarrow -\Delta G \) 
- \( \Delta G^+ \) large, \( \Delta G^- \) small 
- Rate \( k \) small, rate \( k \) large 
- Fast reaction, slow reaction

\( \Delta G = 0 \) 
\( K = 1 \)

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Reaction Coordinate Diagram for the Electrophilic addition to an alkene (Carbocation)

- **Step 1**: 
  - \( CH_3 \) 
  - \( \text{C} = \text{C} \) 
  - \( \text{Br} \) 
  - \( \text{H} \) 

- **Step 2**: 
  - \( CH_3 \) 
  - \( \text{C} = \text{C} \) 
  - \( \text{Br} \) 
  - \( \text{H} \)

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High energy intermediate 
\( \Delta G \) 
\( \Delta H \) 

Normal molecule 
\( A + B \) 
\( \Delta G \)

- **Step 1**: Carbocation 
- **Step 2**: Rate determining step
Closer look at $\Delta G$

$\Delta G$ is made up of Bonds formed vs Bonds lost and Entropy changes

$$\Delta G = \Delta H - T \Delta S$$

Randomness / disorder

Our rxn: $\text{CH}_3\text{CH} = \text{CHCH}_3 + \text{H-Br}$  $\text{CH}_3\text{CH} = \text{CHCH}_3$  $\Delta S^\circ = -$ 

Bonds Made: C-H, C-Br

Bonds Lost: C=C, H-Br

$\Delta H =$ Energy Bonds lost - Energy Bonds gained (Table 3.2)

$$\left(62 \text{ KJ} + 87 \text{ KJ}\right) - \left(149 \text{ KJ} \right) = -24 \text{ Kcal}$$

$\Delta G^\circ = E_q$

$\Delta S$ Value? More freedom? Less freedom of motion

$\text{A} + \text{B} \rightarrow \text{C}$  Less freedom of motion  $\Delta S^\circ =$ -

$\text{A} + \text{B} \rightarrow \text{D} + \text{E}$  $\Delta S = 0$

solid + solid $\rightarrow$ liquid + gas  $\Delta S = +$

Review: Thermodynamics:

$\rightarrow$ all $\Delta G = \Delta H - T \Delta S \rightarrow \text{Keg}$

Good Bonds Good Products

Is the reaction worth the journey? Nothing to do with the rate or $\Delta G^\circ$

Thermodynamic stability: $\rightarrow$ stable product/bonds

Kinetics: $\rightarrow$ rate/speed of reaction  $\Delta G^\circ$, Ea

Mean mechanistic pathway

Kinetic stability: $\rightarrow$ high barrier  Large $\Delta G^\circ$ - no rxn
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\[ \text{CH}_3 - \text{C} = \text{C} - \text{CH}_3 + \text{H} - \text{Br} \rightarrow \text{H} - \text{C} - \text{C} - \text{CH}_3 + \text{H} - \text{C} - \text{C} - \text{CH}_3 \]

1. \( \text{CH}_3 \)
2. \( \text{CH}_3 \)
3. \( \text{CH}_3 \)
4. \( \text{CH}_3 \)

Regioselectivity - H will attach at 1 more than 2

Carbocation stability:

- Lowest Energy: \( \text{SP}^2 \)
- Highest Energy: Methyl

Geometry of the Carbocation: \( \text{SP}^2 \), trigonal planar, flat, no electrons

Hyperconjugation:

\[ \text{R} - \text{C} = \text{R} \]
The rate of the reaction is determined by carbocation stability. The most stable cation is 3°, followed by 2° and 1°, which is the least stable cation.

ΔG° is the energy difference between the reactant and the transition state (‡). The transition state is the highest energy point.

Are we forgetting something?

Acid pKa conjugate base

H-Br -9 → Br⁻
H-Cl -7
\( \text{H}_3\text{O}^+ \) -1.3
R-\( \text{O}^- \) 5
H₂O 15.7
CH₃OH 16