WELCOME TO MODERN ORGANIC CHEMISTRY
Chapter 4
The Study of Chemical Reactions
WHAT IS A REACTION MECHANISM

A DESCRIPTION OF STRUCTURES AND ENERGIES OF STARTING MATERIALS AND PRODUCTS OF A REACTION AS WELL AS ANY REACTION INTERMEDIATES.

IN ADDITION, ALL OF THE TRANSITION STATES (ENERGY MAXIMA) SEPARATING THE REACTANTS FROM THE PRODUCTS (ENERGY MINIMA) MUST BE DETERMINED.
PRODUCT DETERMINATION

1. ISOLATE THEM

2. TAKE THEIR SPECTRA
   a. IR - FUNCTIONAL GROUPS
   b. NMR - environment of hydrogen and carbon atoms
   c. MS - actual MW
   d. X-RAY
ORTEP
STRUCTURE OF TRANSITION STATE?

CAN'T MEASUREMENT DIRECTLY MEASURE THE RATE LAW TELLS NUMBER AND KIND OF MOLECULES INVOLVED IN TS

CERTAIN ENZYMES RECOGNIZE TS - THAT IS THEY BOND WITH IT!!
HOW FAR DOES A REACTION GO?

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 = -2.3 \times R \times T \times \log K_{eq} \]

HOW FAST DOES A REACTION GO? KINETICS

RATE IS INVERSELY PROPORTIONAL TO ACTIVATION ENERGY (E_A)
Chlorination of Methane

\[
\begin{align*}
\text{H} & \quad \text{C} & \quad \text{H} & + & \quad \text{Cl}_2 & \quad \xrightarrow{\text{heat or light}} & \quad \text{H} & \quad \text{C} & \quad \text{Cl} & \quad + & \quad \text{HCl} \\
\text{H} & & & & & & \text{H} & & & & \\
\end{align*}
\]

- Requires heat or light for initiation.
- The most effective wavelength is blue, which is absorbed by chlorine gas.
- Lots of product formed from absorption of only one photon of light (chain reaction).
Free-Radical Chain Reaction

- Initiation generates a reactive intermediate.
- Propagation: the intermediate reacts with a stable molecule to produce another reactive intermediate (and a product molecule).
- Termination: side reactions that destroy the reactive intermediate.

=>
Initiation Step

A chlorine molecule splits homolytically into chlorine atoms (free radicals)

\[
\begin{align*}
:Cl :Cl & + \text{ photon (} h\nu \text{)} \rightarrow :Cl^\cdot + :Cl^\cdot 
\end{align*}
\]
Propagating Step (1)

The chlorine atom collides with a methane molecule and abstracts (removes) a H, forming another free radical and one of the products (HCl).

\[ \text{H}_3\text{C}-\text{H} + :\text{Cl}^* \rightarrow \text{H}_3\text{C}^* + \text{H}-\text{Cl} \]
Propagation Step (2)

The methyl free radical collides with another chlorine molecule, producing the other product (methyl chloride) and regenerating the chlorine radical.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} \cdot \\
\text{H} & \quad \text{Cl} \quad \text{Cl} \\
\text{H} & \quad \text{C} \quad \text{Cl} \\
\text{H} & \quad \text{Cl} \cdot \\
\end{align*}
\]

\[=\]
Overall Reaction

\[ \text{Overall Reaction} \]

\[ \text{Overall Reaction} \]

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\[ \text{Overall Reaction} \]
Termination Steps

• Collision of any two free radicals
• Combination of free radical with contaminant or collision with wall.

\[
\begin{align*}
\text{H}_2\text{C}^\cdot + \text{Cl}^\cdot & \rightarrow \text{H}_2\text{C} = \text{Cl} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Can you suggest others?
Equilibrium constant

- \( K_{\text{eq}} = \frac{[\text{products}]}{[\text{reactants}]} \)
- For chlorination \( K_{\text{eq}} = 1.1 \times 10^{19} \)
- Large value indicates reaction “goes to completion.”
Free Energy Change

• $\Delta G = \text{free energy of (products - reactants), amount of energy available to do work.}$
• Negative values indicate spontaneity.
• $\Delta G^o = -RT \ln K_{eq}$
  where $R = 1.987 \text{ cal/K-mol}$
  and $T = \text{temperature in kelvins}$
• Since chlorination has a large $K_{eq}$, the free energy change is large and negative.

=>
Factors Determining $\Delta G^\circ$

- Free energy change depends on
  - enthalpy
  - entropy
- $\Delta H^\circ = (\text{enthalpy of products}) - (\text{enthalpy of reactants})$
- $\Delta S^\circ = (\text{entropy of products}) - (\text{entropy of reactants})$
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ =>
Enthalpy

- $\Delta H^\circ$ = heat released or absorbed during a chemical reaction at standard conditions.
- Exothermic, (-$\Delta H$), heat is released.
- Endothermic, (+$\Delta H$), heat is absorbed.
- Reactions favor products with lowest enthalpy (strongest bonds).

$\Rightarrow$
PROBLEMS

Which entropy value shown below is correct?

\[ C_4H_{10} \rightarrow C_2H_6 + C_2H_4 \]

POSSIBLE ANSWERS

A. 0  B. -35  c. +35

\[ C_4H_6 + C_2H_4 \rightarrow C_6H_{10} \]

A. 0  B. -18  c. +18
Entropy

- $\Delta S^o = \text{change in randomness, disorder, freedom of movement.}$
- Increasing heat, volume, or number of particles increases entropy.
- Spontaneous reactions maximize disorder and minimize enthalpy.
- In the equation $\Delta G^o = \Delta H^o - T \Delta S^o$ the entropy value is often small.

$\Rightarrow$
Bond Dissociation Energy

• Bond breaking requires energy (+BDE)
• Bond formation releases energy (-BDE)
• Table 4.2 gives BDE for homolytic cleavage of bonds in a gaseous molecule.

\[ \text{A : B} \rightarrow \text{A}^\cdot + \text{B}^\cdot \]

We can use BDE to estimate $\Delta H$ for a reaction.
Which is more likely?

Estimate $\Delta H$ for each step using BDE.

$$\begin{align*}
\text{CH}_4 & + \text{Cl}^\cdot & \rightarrow & \cdot \text{CH}_3 & + \text{HCl} \\
& 104 & & & 103 \\
\cdot \text{CH}_3 & + \text{Cl}_2 & \rightarrow & \text{CH}_3\text{Cl} & + \text{Cl}^\cdot \\
& 58 & & & 84 \\
\text{or} \\
\text{CH}_4 & + \text{Cl}^\cdot & \rightarrow & \text{CH}_3\text{Cl} & + \text{H}^\cdot \\
& 104 & & & 84 \\
\text{H}^\cdot & + \text{Cl}_2 & \rightarrow & \text{HCl} & + \text{Cl}^\cdot \\
& 58 & & & 103 \\
\Rightarrow & & & & &
\end{align*}$$
Kinetics

• Answers question, “How fast?”
• Rate is proportional to the concentration of reactants raised to a power.
• Rate law is experimentally determined.
Reaction Order

• For A + B \[\rightarrow\] C + D, \( \text{rate} = k[A]^a[B]^b \)
  – a is the order with respect to A
  – a + b is the overall order
• Order is the number of molecules of that reactant which is present in the rate-determining step of the mechanism.
• The value of \( k \) depends on temperature as given by Arrhenius: \( \ln k = -\frac{E_a}{RT} + \ln A \)

\[
RT \rightarrow
\]

=>
Activation Energy

• Minimum energy required to reach the transition state.

• At higher temperatures, more molecules have the required energy.