Acids and Bases
Electrophiles and Nucleophiles
Organic Reaction Mechanisms

Chapters 2 & 6
Organic Chemistry, 8th Edition
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Brønsted-Lowry Acids and Bases

- Acids donate protons to an acceptor
  
  All Brønsted-Lowry acids contain a ionizable proton.

- Bases accept protons from a donor
  
  All Brønsted-Lowry bases contain a lone pair or a $\pi$ bond.

<table>
<thead>
<tr>
<th>Brønsted-Lowry acids</th>
<th>Brønsted-Lowry bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>B:</td>
</tr>
<tr>
<td>Inorganic</td>
<td>Inorganic</td>
</tr>
<tr>
<td>HCl</td>
<td>CH$_3$NH$_2$</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>CH$_3$O$^-$</td>
</tr>
<tr>
<td>HSO$_4^-$</td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td></td>
</tr>
<tr>
<td>H$_3$O$^+$</td>
<td></td>
</tr>
<tr>
<td>Organic</td>
<td>Organic</td>
</tr>
<tr>
<td>CH$_3$CO$_2$H</td>
<td>methyamine</td>
</tr>
<tr>
<td>acetic acid</td>
<td></td>
</tr>
<tr>
<td>citric acid</td>
<td>aceton</td>
</tr>
<tr>
<td></td>
<td>ethylene</td>
</tr>
</tbody>
</table>
Certain molecules can behave both as acids and bases.
Lewis Acids and Bases

- A Lewis acid accepts an electron pair from a donor. Lewis acids have a low energy empty orbital.
- A Lewis base donates an electron pair to an acceptor. Lewis bases have a high energy full orbital (lone pair or $\pi$ bonds).
Lewis Acids and Bases

- All Brønsted-Lowry acids are Lewis acids. Not all Lewis acids are Brønsted-Lowry acids.
- Only species with ionizable protons are Brønsted-Lowry acids. Any electron acceptor is a L.A.

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{CH}_3\text{OH} \\
\text{BF}_3 & \quad \text{AlCl}_3
\end{align*}
\]

- All Brønsted-Lowry bases are also Lewis bases. They must have either a lone pair or a π bond.

\[
\begin{align*}
\text{H} & \quad \text{CH}_3\text{O} & \quad \text{C} = \text{C} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]
Reactions Between Lewis Acids and Bases

- Organic reactions can in most cases be described as reactions between electron poor species (Lewis acids) and electron rich species (Lewis bases).
- The electron poor species (Lewis acid) is called electrophile.
- The electron rich species (Lewis base) is called nucleophile.
- The movement of electrons is indicated with curved arrows.

$$\text{Lewis acid} \quad \text{Lewis base}$$

**electrophile** **nucleophile**
Electrophiles and Nucleophiles

Electrophile + Nucleophile → New bond

Lewis acid + Lewis base → New bond
Electrophiles and Nucleophiles

- Nucleophiles and electrophiles may also contain polarized bonds

\[
\text{Nu} \quad \text{E} \\
\begin{array}{c}
\text{OH}^- \\
\delta^+ \\
\delta^- \\
\text{H}_3\text{C} \quad \text{Cl} \\
\delta^- \\
\delta^+ \\
\text{E} \\
\text{Nu} \\
\text{Li}^+ \\
\delta^- \\
\delta^+ \\
\text{O} \\
\delta^- \\
\delta^+ \\
\text{E} \\
\text{Nu} \\
\end{array} \\
\text{HO} \quad \text{CH}_3 \quad + \quad \text{Cl}^-
\]
How to Write an Organic Reaction

\[
\text{Cyclohexene} + \text{Br}_2 \rightarrow \text{Bromocyclohexane}
\]

\[
\text{Bromination of Cyclohexene}
\]

\[
\text{Bromination of Cyclohexene under UV or Heat, in CCl}_4
\]
How to Write an Organic Reaction

- In a sequence, the individual steps are numbered.

Inorganic byproducts are generally omitted.
Organic Reactions

• Type of reaction (bond breaking/bond formation):
  ➢ substitution
  ➢ addition
  ➢ elimination
  ➢ rearrangement/transposition

• Mechanism = movement of electrons:
  ➢ ionic (polar)
  ➢ radicalic
  ➢ pericyclic
In a general substitution reaction, an atom or group Y replaces an atom or group Z at carbon.

Substitutions involve breaking and forming σ bonds.

Substitution reactions examples:
- $\text{CH}_3\text{I} + \text{Cl}^- \rightarrow \text{CH}_3\text{Cl} + \text{I}^-$
- $\text{CH}_3\text{C} = \text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{COOH} + \text{Cl}^-$
Eliminations

- In an elimination reaction two $\sigma$ bonds are broken and one $\pi$ bond is formed.

\[
\text{C-C} + \text{reagent} \rightarrow \text{C=C} + \text{X-Y}
\]

- 2 $\sigma$ bonds are broken
- 1 $\pi$ bond is formed

\[
\text{H-H} + \text{H-C-C-H} + \text{OH} \rightarrow \text{C=C} + \text{H}_2\text{O} + \text{Br}^-
\]

\[
\text{H-OH} \stackrel{\text{H}_2\text{SO}_4}{\rightarrow} \text{H} + \text{H}_2\text{O}
\]
In an addition reaction a \( \pi \) bond is broken and two new \( \sigma \) bonds are formed.
Eliminations are the inverse of additions. A $\pi$ bond is formed in eliminations and a $\pi$ bond is broken in additions.
In a rearrangement or transposition the bonding pattern of a single reagent changes giving a constitutional isomer.

1-butene

2-butene
Bond Breaking and Forming

**Omolysis**

- Formed in radical (omolitic) reactions

**Heterolysis**

- Formed in polar (ionic) reactions

**Radical**

**Carbocation**

**Carbanion**
Bond Formation

- A new bond can be formed in two ways:
  - From two radicals each contributing a single electron.
    
    \[
    \text{A}^\cdot + \text{B}^\cdot \rightarrow \text{A}^-\text{B}^+ 
    \]
  - From a nucleophile contributing an electron pair and an electrophile accepting the electron pair. Nu and E may be ions or neutral molecules.

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

Energy is released in the formation of a bond.
Bond dissociation energy is the energy necessary to break a bond omolytically.

\[ \Delta H^\circ = \text{bond dissociation energy} \]
The bond dissociation energy is a measure of the strength of the bond.

The stronger the bond, the higher its dissociation energy.

In general, shorter bonds are stronger.

Bond dissociation energies decrease along a group.

![Diagram showing bond dissociation energies for CH₃-F, CH₃-Cl, CH₃-Br, and CH₃-I with corresponding bond strengths: ΔH° = 109 kcal/mole, 84 kcal/mole, 70 kcal/mole, and 56 kcal/mole respectively.](image)
A Reaction Mechanism......

- Accounts for all reagents and products and their ratios.

- Describes in which order bonds are broken and formed and the rates of individual steps.

- In a concerted reaction reagents are directly converted into products in a single step.

- A multistep reaction involves the formation of one or more reactive intermediates.
Carbocations, Carbanions, Radicals

- **empty p orbital**
- **Singly occupied p orbital**
- **lone pair sp³**

**C sp² planar**

**C sp³ tetrahedral**
Radicals and carbocations are **electrophiles** because the carbon atom does not have a full octet.

Carbanions are **nucleophiles** because the carbon atom has a lone pair.
Transition State Theory - Energy Diagrams

- The activation energy $\Delta G^*$ is the energy required for a reaction to take place.
- $\Delta G^* = \Delta H^* - T\Delta S^#$
- $\Delta G^*$ is correlated with the reaction’s rate constant.

Eyring equation:

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^*}{RT}}$$

- The transition state structure is intermediate between the structures of reagents and products. In the transition state there are partial bonds and partial charges (if the mechanism is ionic).
- Transition states are represented in brackets with the # symbol.
Energy Diagrams
Energy Diagrams

\[
\begin{align*}
\text{Br—H} & \quad + \quad \text{H}_2\text{C}≡\text{CH}_2 \\
\text{H}_3\text{C}—\text{CH}_2{}^+ & \quad \rightarrow \quad \text{H}_3\text{C}—\text{CH}_2\text{Br}
\end{align*}
\]
Complete energy diagram for the two-step reaction:

$$\text{Br} - \text{H} + \text{H}_2\text{C} = \text{CH}_2 \rightarrow \text{H}_3\text{C} - \text{CH}_2^+ \rightarrow \text{H}_3\text{C} - \text{CH}_2\text{Br}$$