10/21/11  Single versus electron pair mechanisms
stepwise versus concerted; anionic vs. cationic
stereochemical and regiochemical consequences

Electron Pair Mechanisms

**Heterolysis** - Uneven breaking of a bond
\[ \text{H}^+ + \text{O}^- \rightarrow \text{H} \text{O}^- + \text{O}^- \]
\[ + \text{H}^+ \rightarrow + \text{O}^- + \text{H} \]

**Heterogenesis** - Uneven formation of a bond
\[ \text{H} \rightarrow \text{H}^+ \]
\[ + \text{O}^- \rightarrow + \text{O}^- + \text{H} \]

Protonation - add H\text{+}^+ to a molecule.

**Single Electron Mechanisms**

**Homolysis** - Even breaking of a bond
\[ \text{O}^- + \text{O}^- \rightarrow 2 \text{O}^- \text{.} \text{ (uncharged)} \]

**Homogenesis** - Even formation of a bond
\[ \text{O}^- \text{CH}_3 \rightarrow + \text{CH}_3 \text{.} \]

Disproportionation
\[ \text{H}_3\text{C}^- \rightarrow \text{H}_3\text{C}-\text{H} \text{.} \text{CH}_3 \]
Types of mechanisms

Cationic — often involve acids and/or the formation of a carbocation as a key reaction step

Examples: $S\text{N}1$

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

\[ \rightarrow \text{+} \]

Dehydration

\[ \text{OH} \rightarrow \text{+} \rightarrow \text{H}^+ \]

Stepwise — mechanisms that contain multiple elementary steps

Anionic — usually involve strong bases and occur in a small number of steps

Examples: $S\text{N}2$

\[ \text{H}^+ \rightarrow \text{+} \rightarrow \text{H}^+ \]

Grignard

\[ \text{+} \rightarrow \text{H}^+ \]

Concerted — mechanism with simultaneous steps
Work-up - A secondary rxn or sequence of rxns used to isolate a product.

These numbers indicate reaction order. The reagents for step 2 are not introduced until the reaction in step 1 is fully completed.

Radical -

Stereochemical consequences -

Retention of configuration -
configuration remains unchanged

Inversion of configuration
loss of configuration

H₂O → HO⁻ + H⁺

or

or

Regiochemical consequences

regioisomers - isomers that are structurally very similar except for the position of a key functional group

specific - happens often in anionic rxns

non-specific - cationic mechanisms

carbocation rearrangement hydride shift