If you scan any organic textbook you will encounter what appears to be a very large, often intimidating, number of reactions. These are the "tools" of a chemist, and to use these tools effectively, we must organize them in a sensible manner and look for patterns of reactivity that permit us make plausible predictions. Most of these reactions occur at special sites of reactivity known as functional groups, and these constitute one organizational scheme that helps us catalog and remember reactions. **Ultimately, the best way to achieve proficiency in organic chemistry is to understand how reactions take place, and to recognize the various factors that influence their course.** This is best accomplished by perceiving the reaction pathway or mechanism of a reaction.

### Introduction

Organic chemistry encompasses a very large number of compounds (many millions), and our previous discussion and illustrations have focused on their structural characteristics. Now that we can recognize these actors (compounds), we turn to the roles they are inclined to play in the scientific drama staged by the multitude of chemical reactions that define organic chemistry. We begin by defining some basic terms that will be used frequently as this subject is elaborated.

- **Chemical Reaction:** A transformation resulting in a change of composition, constitution and/or configuration of a compound (referred to as the reactant or substrate).
- **Reactant or Substrate:** The organic compound undergoing change in a chemical reaction. Other compounds may also be involved, and common reactive partners (reagents) may be identified. The reactant is often (but not always) the larger and more complex molecule in the reacting system. Most (or all) of the reactant molecule is normally incorporated as part of the product molecule.
- **Reagent:** A common partner of the reactant in many chemical reactions. It may be organic or inorganic; small or large; gas, liquid or solid. The portion of a reagent that ends up being incorporated in the product may range from all to very little or none.
- **Product(s):** The final form taken by the major reactant(s) of a reaction.
- **Reaction Conditions** The environmental conditions, such as temperature, pressure, catalysts & solvent, under which a reaction progresses optimally. Catalysts are substances that accelerate the rate (velocity) of a chemical reaction without themselves being consumed or appearing as part of the reaction product. Catalysts do not change equilibria positions.

Chemical reactions are commonly written as equations:

\[
\text{Reactant(s)} \xrightarrow{\text{Reaction Conditions}} \text{Product(s)}
\]

### Classification by Structural Change

First, we identify four broad classes of reactions based solely on the structural change occurring in the reactant molecules. This classification does not require knowledge or speculation concerning reaction paths or mechanisms. The letter R in the following illustrations is widely used as a symbol for a generic group. It may stand for simple substituents such as H– or CH₃–, or for complex groups composed of many atoms of carbon and other elements.

**Four General Reaction Classes**

In an addition reaction the number of σ-bonds in the substrate molecule increases, usually at the expense of one or more π-bonds. The reverse is true of elimination reactions, i.e. the number of σ-bonds in the substrate decreases, and new π-bonds are often formed. Substitution reactions, as the name implies, are characterized by replacement of an atom or group (Y) by another atom or group (Z). Aside from these groups, the number of bonds does not change. A rearrangement reaction generates an isomer, and again the number of bonds normally does not change.

The examples illustrated above involve simple alkyl and alkene systems, but these reaction types are general for most functional groups, including those incorporating carbon-oxygen double bonds and carbon-nitrogen double and triple bonds. Some common reactions may actually be a combination of reaction types. The reaction of an ester with ammonia to give an amide, as shown below, appears to be a substitution reaction (Y = CH₃O & Z = NH₂); however, it is actually two reactions, an addition followed by an elimination.

The addition of water to a nitrile does not seem to fit any of the above reaction types, but it is simply a slow addition reaction followed by a rapid rearrangement, as shown in the following equation. Rapid rearrangements of this kind are called tautomerizations.

Additional examples illustrating these classes of reaction may be examined by Clicking Here
Acidity and Basicity

It is useful to begin a discussion of organic chemical reactions with a review of acid-base chemistry and terminology for several reasons. First, acid-base reactions are among the simplest to recognize and understand. Second, some classes of organic compounds have distinctly acidic properties, and some other classes behave as bases, so we need to identify these aspects of their chemistry. Finally, many organic reactions are catalyzed by acids and/or bases, and although such transformations may seem complex, our understanding of how they occur often begins with the functioning of the catalyst. Organic chemists use two acid-base theories for interpreting and planning their work: the Brønsted theory and the Lewis theory.

Brønsted Theory

According to the Brønsted theory, an acid is a proton donor, and a base is a proton acceptor. In an acid-base reaction, each side of the equilibrium has an acid and a base reactant or product, and these may be neutral species or ions.

\[
\text{H-A + B}^{-} \rightleftharpoons \text{A}^{-} + \text{B-H} \\
\text{(acid}^1\text{)} \ (\text{base}^1) \rightleftharpoons \text{(base}^2\text{)} \ (\text{acid}^2)
\]

Structurally related acid-base pairs, such as \{H-A and A^{-}\} or \{B^{-} and B-H\} are called conjugate pairs. Substances that can serve as both acids and bases, such as water, are termed amphoteric.

\[
\text{H-Cl + H}_2\text{O} \rightleftharpoons \text{Cl}^{-} + \text{H}_3\text{O}^{(+)} \\
\text{(acid)} \ (\text{base}) \rightleftharpoons \text{(base)} \ (\text{acid})
\]

\[
\text{H}_3\text{N: + H}_2\text{O} \rightleftharpoons \text{NH}_4^{(+)} + \text{HO}^{-} \\
\text{(base)} \ (\text{acid}) \rightleftharpoons \text{(acid)} \ (\text{base})
\]

The relative strength of a group of acids (or bases) may be evaluated by measuring the extent of reaction that each group member undergoes with a common base (or acid). Water serves nicely as the common base or acid for such determinations. Thus, for an acid H-A, its strength is proportional to the extent of its reaction with the base water, which is given by the equilibrium constant \(K_{eq}\).

\[
\text{H-A + H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{(+)} + \text{A}^{-} \\
K_{eq} = \frac{\text{[H}_3\text{O}^{+}]\ [\text{A}^{-}]}{[\text{H-A}][\text{H}_2\text{O}]}
\]

Since these studies are generally extrapolated to high dilution, the molar concentration of water (55.5) is constant and may be eliminated from the denominator. The resulting \(K\) value is called the acidity constant, \(K_a\). Clearly, strong acids have larger \(K_a\)'s than do weaker acids. Because of the very large range of acid strengths (greater than \(10^{40}\)), a logarithmic
scale of acidity ($pK_a$) is normally employed. Stronger acids have smaller or more negative $pK_a$ values than do weaker acids.

**Some useful principles of acid-base reactions are:**

- Strong acids have weak conjugate bases, and weak acids have strong conjugate bases.
- Acid-base equilibria always favor the weakest acid and the weakest base.

### Examples of Brønsted Acid-Base Equilibria

<table>
<thead>
<tr>
<th>Acid-Base Reaction</th>
<th>Conjugate Acids</th>
<th>Conjugate Bases</th>
<th>$K_a$</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{HBr} + \text{H}_2\text{O}$</td>
<td>$\text{H}_3\text{O}^{(+)} + \text{Br}^{(-)}$</td>
<td>$\text{HBr}$ $\text{H}_3\text{O}^{(+)}$</td>
<td>$\text{Br}^{(-)}$ $\text{H}_2\text{O}$</td>
<td>$10^5$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O}$</td>
<td>$\text{H}_3\text{O}^{(+)} + \text{CH}_3\text{CO}_2^{(-)}$</td>
<td>$\text{CH}_3\text{CO}_2\text{H}$ $\text{H}_3\text{O}^{(+)}$</td>
<td>$\text{CH}_3\text{CO}_2^{(-)}$ $\text{H}_2\text{O}$</td>
<td>$1.77 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$</td>
<td>$\text{H}_3\text{O}^{(+)} + \text{C}_2\text{H}_5\text{O}^{(-)}$</td>
<td>$\text{C}_2\text{H}_5\text{OH}$ $\text{H}_3\text{O}^{(+)}$</td>
<td>$\text{C}_2\text{H}_5\text{O}^{(-)}$ $\text{H}_2\text{O}$</td>
<td>$10^{-16}$</td>
</tr>
<tr>
<td>$\text{NH}_3 + \text{H}_2\text{O}$</td>
<td>$\text{H}_3\text{O}^{(+)} + \text{NH}_2^{(-)}$</td>
<td>$\text{NH}_3$ $\text{H}_3\text{O}^{(+)}$</td>
<td>$\text{NH}_2^{(-)}$ $\text{H}_2\text{O}$</td>
<td>$10^{-34}$</td>
</tr>
</tbody>
</table>

In all the above examples water acts as a common base. The last example ($\text{NH}_3$) cannot be measured directly in water, since the strongest base that can exist in this solvent is hydroxide ion. Consequently, the value reported here is extrapolated from measurements in much less acidic solvents, such as acetonitrile.

Since many organic reactions either take place in aqueous environments (living cells), or are quenched or worked-up in water, it is important to consider how a conjugate acid-base equilibrium mixture changes with pH. A simple relationship known as the [Henderson-Hasselbach equation](#) provides this information.

**Henderson-Hasselbach Equation:**

$$pK_a = \text{pH} + \log \frac{[\text{HA}]}{[\text{A}^-]}$$

When the pH of an aqueous solution or mixture is equal to the $pK_a$ of an acidic component, the concentrations of the acid and base conjugate forms must be equal (the log of 1 is 0). If the pH is lowered by two or more units relative to the $pK_a$, the acid concentration will be greater than 99%. On the other hand, if the pH (relative to $pK_a$) is raised by two or more units the conjugate base concentration will be over 99%. Consequently, mixtures of acidic and non-acidic compounds are easily separated by adjusting the pH of the water component in a two phase solvent extraction.

For example, if a solution of benzoic acid ($pK_a = 4.2$) in benzyl alcohol ($pK_a = 15$) is dissolved in ether and shaken with an excess of 0.1 N sodium hydroxide (pH = 13), the acid is completely converted to its water soluble (ether insoluble) sodium salt, while the alcohol is unaffected. The ether solution of the alcohol may then be separated from the water layer, and pure alcohol recovered by distillation of the volatile ether solvent. The pH of the water solution of sodium benzoate...
may then be lowered to 1.0 by addition of hydrochloric acid, at which point pure benzoic acid crystallizes, and may be isolated by filtration.

For a discussion of how acidity is influenced by molecular structure, Click Here.

Basicity

The basicity of oxygen, nitrogen, sulfur and phosphorus compounds or ions may be treated in an analogous fashion. Thus, we may write base-acid equilibria, which define a $K_b$ and a corresponding $pK_b$. However, a more common procedure is to report the acidities of the conjugate acids of the bases (these conjugate acids are often "onium" cations). The $pK_a$'s reported for bases in this system are proportional to the base strength of the base. A useful rule here is: $pK_a + pK_b = 14.$

We see this relationship in the following two equilibria:

<table>
<thead>
<tr>
<th>Acid-Base Reaction</th>
<th>Conjugate Acids</th>
<th>Conjugate Bases</th>
<th>$K$</th>
<th>$pK$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_3 + \text{H}_2\text{O}$</td>
<td>$\text{NH}_4^{(+)} + \text{OH}^{(-)}$</td>
<td>$\text{NH}_3^{(+)}$ $\text{H}_2\text{O}$</td>
<td>$\text{NH}_3$ $\text{OH}^{(-)}$</td>
<td>$K_b = 1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\text{NH}_4^{(+)} + \text{H}_2\text{O}$</td>
<td>$\text{H}_3\text{O}^{(+)} + \text{NH}_3$</td>
<td>$\text{NH}_4^{(+)}$ $\text{H}_2\text{O}$</td>
<td>$\text{NH}_3$ $\text{H}_2\text{O}$</td>
<td>$K_a = 5.5 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Tables of $pK_a$ values for inorganic and organic acids (and bases) are available in many reference books, and may be examined here by clicking on the appropriate link:

- Inorganic Acidity Constants
- Organic Acidity Constants
- Basicity Constants

Although it is convenient and informative to express $pK_a$ values for a common solvent system (usually water), there are serious limitations for very strong and very weak acids. Thus acids that are stronger than the hydronium cation, $\text{H}_3\text{O}^{(+)}$, and weak acids having conjugate bases stronger than hydroxide anion, $\text{OH}^{(-)}$, cannot be measured directly in water solution. Solvents such as acetic acid, acetonitrile and nitromethane are often used for studying very strong acids. Relative acidity measurements in these solvents may be extrapolated to water. Likewise, very weakly acidic solvents such as DMSO, acetonitrile, toluene, amines and ammonia may be used to study the acidities of very weak acids. For both these groups, the reported $pK_a$ values extrapolated to water are approximate, and many have large uncertainties. A useful table of $pK_a$ values in DMSO solution has been compiled from the work of F.G. Bordwell, and may be reached by clicking here.

Lewis Theory

According to the Lewis theory, an acid is an electron pair acceptor, and a base is an electron pair donor. Lewis bases
are also Brønsted bases; however, many Lewis acids, such as BF$_3$, AlCl$_3$ and Mg$^{2+}$, are not Brønsted acids. The product of a Lewis acid-base reaction, is a neutral, dipolar or charged complex, which may be a stable covalent molecule. Two examples of Lewis acid-base equilibria are shown in equations 1 & 2 below.

In the first example, an electron deficient aluminum atom bonds to a covalent chlorine atom by sharing one of its non-bonding valence electron pairs, and thus achieves an argon-like valence shell octet. Because this sharing is unilateral (chlorine contributes both electrons), both the aluminum and the chlorine have formal charges, as shown. If the carbon-chlorine bond in this complex breaks with both the bonding electrons remaining with the more electronegative atom (chlorine), the carbon assumes a positive charge. We refer to such carbon species as 

**Carbocations**. Carbocations are also Lewis acids, as the reverse reaction demonstrates.

Many carbocations (but not all) may also function as Brønsted acids. Equation 3 illustrates this dual behavior; the Lewis acidic site is colored red and three of the nine acidic hydrogen atoms are colored orange. In its Brønsted acid role the carbocation donates a proton to the base (hydroxide anion), and is converted to a stable neutral molecule having a carbon-carbon double bond.

A terminology related to the Lewis acid-base nomenclature is often used by organic chemists. Here the term **electrophile** corresponds to a Lewis acid, and **nucleophile** corresponds to a Lewis base.

**Electrophile**: An electron deficient atom, ion or molecule that has an affinity for an electron pair, and will bond to a base or nucleophile.

**Nucleophile**: An atom, ion or molecule that has an electron pair that may be donated in bonding to an electrophile (or Lewis acid).

To learn more about the relationship of basicity and nucleophilicity, and for examples of acid/base catalysis of organic reactions Click Here.

**Oxidation and Reduction Reactions**

A parallel and independent method of characterizing organic reactions is by **oxidation-reduction** terminology. Carbon
Atoms may have any oxidation state from $-4$ (e.g. $\text{CH}_4$) to $+4$ (e.g. $\text{CO}_2$), depending upon their substituents. Fortunately, we need not determine the absolute oxidation state of each carbon atom in a molecule, but only the **change in oxidation state** of those carbons involved in a chemical transformation. To determine whether a carbon atom has undergone a redox change during a reaction we simply note any changes in the number of bonds to hydrogen and the number of bonds to more electronegative atoms such as O, N, F, Cl, Br, I, & S that has occurred. Bonds to other carbon atoms are ignored. This count should be conducted for each carbon atom undergoing any change during a reaction.

1. If the number of hydrogen atoms bonded to a carbon increases, and/or if the number of bonds to more electronegative atoms decreases, the carbon in question has been **reduced** (i.e. it is in a lower oxidation state).

2. If the number of hydrogen atoms bonded to a carbon decreases, and/or if the number of bonds to more electronegative atoms increases, the carbon in question has been **oxidized** (i.e. it is in a higher oxidation state).

3. If there has been no change in the number of such bonds, then the carbon in question has not changed its oxidation state. In the hydrolysis reaction of a nitrile shown above, the blue colored carbon has not changed its oxidation state.

These rules are illustrated by the following four addition reactions involving the same starting material, cyclohexene. Carbon atoms colored blue are reduced, and those colored red are oxidized. In the addition of hydrogen both carbon atoms are reduced, and the overall reaction is termed a reduction. Peracid epoxidation and addition of bromine oxidize both carbon atoms, so these are termed oxidation reactions. Addition of HBr reduces one of the double bond carbon atoms and oxidizes the other; consequently, there is no overall redox change in the substrate molecule.

![Reaction Diagram]

For a discussion of how oxidation state numbers may be assigned to carbon atoms Click Here.

Since metals such as lithium and magnesium are less electronegative than hydrogen, their covalent bonds to carbon are polarized so that the carbon is negative (reduced) and the metal is positive (oxidized). Thus, Grignard reagent formation from an alkyl halide reduces the substituted carbon atom. In the following equation and half-reactions the carbon atom (blue) is reduced and the magnesium (magenta) is oxidized.

---

**Classification by Functional Group**

**Functional groups** are atoms or small groups of atoms (usually two to four) that exhibit a characteristic reactivity when treated with certain reagents. To view a table of the common functional groups and their class names Click Here.
Here. A particular functional group will almost always display its characteristic chemical behavior when it is present in a compound. Because of this, the discussion of organic reactions is often organized according to functional groups. The following table summarizes the general chemical behavior of the common functional groups. For reference, the alkanes provide a background of behavior in the absence of more localized functional groups.

<table>
<thead>
<tr>
<th>Functional Class</th>
<th>Formula</th>
<th>Characteristic Reactions</th>
</tr>
</thead>
</table>
| Alkanes            | C–C, C–H                | Substitution (of H, commonly by Cl or Br)  
Combustion (conversion to CO$_2$ & H$_2$O)                                              |
| Alkenes            | C=C–C–H                 | Addition  
Substitution (of H)                                                              |
| Alkynes            | C≡C–H                   | Addition  
Substitution (of H)                                                              |
| Alkyl Halides      | H–C–C–X                 | Substitution (of X)  
Elimination (of HX)                                                              |
| Alcohols           | H–C–C–O–H               | Substitution (of H);  
Substitution (of OH);  
Elimination (of HOH);  
Oxidation (elimination of 2H)                                                      |
| Ethers             | (α)C–O–R                | Substitution (of OR);  
Substitution (of α–H)                                                               |
| Amines             | C–NRH                   | Substitution (of H);  
Addition (to N);  
Oxidation (of N)                                                                  |
| Benzene Ring       | C$_6$H$_6$              | Substitution (of H)                                                                  |
| Aldehydes          | (α)C–CH=O               | Addition  
Substitution (of H or α–H)                                                        |
| Ketones            | (α)C–CR=O               | Addition  
Substitution (of α–H)                                                            |
| Carboxylic Acids   | (α)C–CO$_2$H             | Substitution (of H);  
Substitution (of OH);  
Substitution (of α–H);  
Addition (to C=O)                                                               |
| Carboxylic Derivatives | (α)C–CZ=O (Z = OR, Cl, NHR, etc.) | Substitution (of Z);  
Substitution (of α–H);  
Addition (to C=O)               |
This table does not include any reference to rearrangement, due to the fact that such reactions are found in all functional classes, and are highly dependent on the structure of the reactant. Furthermore, a review of the overall reaction patterns presented in this table discloses only a broad and rather non-specific set of reactivity trends. This is not surprising, since the three remaining categories provide only a coarse discrimination (comparable to identifying an object as animal, vegetable or mineral). Consequently, apparent similarities may fail to reflect important differences. For example, addition reactions to C=C are significantly different from additions to C=O, and substitution reactions of C-X proceed in very different ways, depending on the hybridization state of carbon.

The Variables of Organic Reactions

In an effort to understand how and why reactions of functional groups take place in the way they do, chemists try to discover just how different molecules and ions interact with each other as they come together. To this end, it is important to consider the various properties and characteristics of a reaction that may be observed and/or measured as the reaction proceeds. The most common and useful of these are listed below:

1. Reactants and Reagents

   A. Reactant Structure: Variations in the structure of the reactant may have a marked influence on the course of a reaction, even though the functional group is unchanged. Thus, reaction of 1-bromopropane with sodium cyanide proceeds smoothly to yield butanenitrile, whereas 1-bromo-2,2-dimethylpropane fails to give any product and is recovered unchanged. In contrast, both alkyl bromides form Grignard reagents (RMgBr) on reaction with magnesium.

   \[
   \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{CN}^- \xrightarrow{\text{alcohol}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} + \text{Br}^-
   \]

   \[
   (\text{CH}_3)_2\text{CCH}_2\text{Br} + \text{CN}^- \xrightarrow{\text{alcohol}} \text{Nu Reaction}
   \]

   B. Reagent Characteristics: Apparently minor changes in a reagent may lead to a significant change in the course of a reaction. For example, 2-bromopropane gives a substitution reaction with sodium methylthiolate but undergoes predominant elimination on treatment with sodium methoxide.

2. Product Selectivity

   A. Regioselectivity: It is often the case that addition and elimination reactions may, in principle, proceed to more than one product. Thus 1-butene might add HBr to give either 1-bromobutane or 2-bromobutane, depending on which carbon of the double bond receives the hydrogen and which the bromine. If one possible product out of two or more is formed preferentially, the reaction is said to be regioselective.
Simple substitution reactions are not normally considered regioselective, since by definition only one constitutional product is possible. However, rearrangements are known to occur during some reactions.

**B. Stereoselectivity:** If the reaction products are such that stereoisomers may be formed, a reaction that yields one stereoisomer preferentially is said to be stereoselective. In the addition of bromine to cyclohexene, for example, cis and trans-1,2-dibromocyclohexane are both possible products of the addition. Since the trans-isomer is the only isolated product, this reaction is stereoselective.

**C. Stereospecificity:** This term is applied to cases in which stereoisomeric reactants behave differently in a given reaction. Examples include:

Here, the (R)-reactant gives the configurationally inverted (S)-product, and (S)-reactant produces (R)-product. The (R) and (S) notations for configuration are described in a later section of this text.

(ii) Different rates of reaction, as in the base-induced elimination of cis & trans-4-tert-butylcyclohexyl bromide (equation 1 below).

(iii) Different reaction paths leading to different products, as in the base-induced elimination of cis & trans-2-methylcyclohexyl bromide (equation 2 below).
The mechanisms of these substitution and elimination reactions are discussed in the alkyl halide section of this text.

1. (i) Formation of different stereoisomeric products, as in the reaction of enantiomeric 2-bromobutane isomers with sodium methylthiolate, shown in the following diagram.

---

3. Reaction Characteristics

1. **Reaction Rates**: Some reactions proceed very rapidly, and some so slowly that they are not normally observed. Among the variables that influence reaction rates are temperature (reactions are usually faster at a higher temperature), solvent, and reactant / reagent concentrations. Useful information about reaction mechanisms may be obtained by studying the manner in which the rate of a reaction changes as the concentrations of the reactant and reagents are varied. This field of study is called **kinetics**.

2. **Intermediates**: Many reactions proceed in a stepwise fashion. This can be convincingly demonstrated if an intermediate species can be isolated and shown to proceed to the same products under the reaction conditions. Some intermediates are stable compounds in their own right; however, some are so reactive that isolation is not possible. Nevertheless, evidence for their existence may be obtained by other means, including spectroscopic observation or inference from kinetic results.

---

4. Factors that Influence Reactions

It is helpful to identify some general features of a reaction that have a significant influence on its facility. Some of the most important of these are:

1. **Energetics**: The potential energy of a reacting system changes as the reaction progresses. The overall change may be **exothermic** (energy is released) or **endothermic** (energy must be added), and there is usually an **activation energy** requirement as well. Tables of Standard Bond Energies are widely used by chemists for estimating the energy change in a proposed reaction. As a rule, compounds constructed of strong covalent bonds are more stable than compounds incorporating one or more relatively weak bonds.

2. **Electronic Effects**: The distribution of electrons at sites of reaction (functional groups) is a particularly important factor. Electron deficient species or groups, which may or may not be positively charged, are attracted to electron rich species or groups, which may or may not be negatively charged. We refer to these species as **electrophiles & nucleophiles** respectively. In general, **opposites attract and like repel**. The charge distribution in a molecule is usually discussed with respect to two interacting effects: An **inductive effect**, which is a function of the electronegativity differences that exist between atoms (and groups); and a **resonance effect**, in which electrons move in a discontinuous fashion between parts of a molecule.

3. **Steric Effects**: Atoms occupy space. When they are crowded together, van der Waals repulsions produce an
unfavorable steric hindrance. Steric hindrance may influence conformational equilibria, as well as destabilizing transition states of reactions.

4. **Stereoelectronic Effects:** In many reactions atomic or molecular orbitals interact in a manner that has an optimal configurational or geometrical alignment. Departure from this alignment inhibits the reaction.

5. **Solvent Effects:** Most reactions are conducted in solution, not in a gaseous state. The solvent selected for a given reaction may exert a strong influence on its course. Remember, solvents are chemicals, and most undergo chemical reaction under the right conditions.

---

**Mechanisms of Organic Reactions**

A detailed description of the changes in structure and bonding that take place in the course of a reaction, and the sequence of such events is called the *reaction mechanism*. A reaction mechanism should include a representation of plausible electron reorganization, as well as the identification of any intermediate species that may be formed as the reaction progresses. These features are elaborated in the following sections.

---

**The Arrow Notation in Mechanisms**

Since chemical reactions involve the breaking and making of bonds, a consideration of the movement of bonding (and non-bonding) valence shell electrons is essential to this understanding. It is now common practice to show the movement of electrons with curved arrows, and a sequence of equations depicting the consequences of such electron shifts is termed a *mechanism*. In general, two kinds of curved arrows are used in drawing mechanisms:

- A full head on the arrow indicates the movement or shift of an electron pair:
  
  \[
  \text{A full head on the arrow indicates the movement or shift of an electron pair:}
  \]

- A partial head (fishhook) on the arrow indicates the shift of a single electron:
  
  \[
  \text{A partial head (fishhook) on the arrow indicates the shift of a single electron:}
  \]

The use of these symbols in bond-breaking and bond-making reactions is illustrated below. If a covalent single bond is broken so that one electron of the shared pair remains with each fragment, as in the first example, this bond-breaking is called *homolysis*. If the bond breaks with both electrons of the shared pair remaining with one fragment, as in the second and third examples, this is called *heterolysis*.

**Bond-Breaking**

**Bond-Making**
Other Arrow Symbols

Chemists also use arrow symbols for other purposes, and it is essential to use them correctly.

<table>
<thead>
<tr>
<th>The Reaction Arrow</th>
<th>The Equilibrium Arrow</th>
<th>The Resonance Arrow</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Reaction Arrow" /></td>
<td><img src="image2.png" alt="Equilibrium Arrow" /></td>
<td><img src="image3.png" alt="Resonance Arrow" /></td>
</tr>
</tbody>
</table>

The following equations illustrate the proper use of these symbols:

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{Energy}
\]

\[
\text{H}_3\text{C}===\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{C}===\text{O} + \text{H}_3\text{O}^+
\]

\[
\text{H}_2\text{C}==\text{C}==\text{H} \leftrightarrow \text{H}_2\text{C}==\text{C}==\text{H}_2
\]

For further information about the use of curved arrows in reaction mechanisms Click Here.
Reactive Intermediates

The products of bond breaking, shown above, are not stable in the usual sense, and cannot be isolated for prolonged study. Such species are referred to as reactive intermediates, and are believed to be transient intermediates in many reactions. The general structures and names of four such intermediates are given below.

A pair of widely used terms, related to the Lewis acid-base notation, should also be introduced here.

**Electrophile:** An electron deficient atom, ion or molecule that has an affinity for an electron pair, and will bond to a base or nucleophile.

**Nucleophile:** An atom, ion or molecule that has an electron pair that may be donated in bonding to an electrophile (or Lewis acid).

Using these definitions, it is clear that carbocations (called carbonium ions in the older literature) are electrophiles and carbanions are nucleophiles. Carbenes have only a valence shell sextet of electrons and are therefore electron deficient. In this sense they are electrophiles, but the non-bonding electron pair also gives carbenes nucleophilic character. As a rule, the electrophilic character dominates carbene reactivity. Carbon radicals have only seven valence electrons, and may be considered electron deficient; however, they do not in general bond to nucleophilic electron pairs, so their chemistry exhibits unique differences from that of conventional electrophiles. Radical intermediates are often called free radicals.

The importance of electrophile / nucleophile terminology comes from the fact that many organic reactions involve at some stage the bonding of a nucleophile to an electrophile, a process that generally leads to a stable intermediate or product. Reactions of this kind are sometimes called ionic reactions, since ionic reactants or products are often involved. Some common examples of ionic reactions and their mechanisms may be examined by Clicking Here.

The shapes ideally assumed by these intermediates becomes important when considering the stereochemistry of reactions in which they play a role. A simple tetravalent compound like methane, CH$_4$, has a tetrahedral configuration. Carbocations have only three bonds to the charge bearing carbon, so it adopts a planar trigonal configuration. Carbanions are pyramidal in shape (tetrahedral if the electron pair is viewed as a substituent), but these species invert rapidly at room temperature, passing through a higher energy planar form in which the electron pair occupies a p-orbital. Radicals are intermediate in configuration, the energy difference between pyramidal and planar forms being very small. Since three points determine a plane, the shape of carbenes must be planar; however, the valence electron distribution varies.

Practice Problems

The following problems include acid base relationships, recognition of different functional groups, recognition of nucleophiles and electrophiles, classification of reactions by structural change and oxidation/reduction change, and the use of curved arrow notation.

Choose a Problem
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