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CHEMISTRY II

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ORGANIC CHEMISTRY: INTRODUCTION



1. INTRODUCTION

1.1. What is Organic Chemistry?

Chemistry involves investigating the arrangement of molecules and the principles that regulate their behavior. Organic chemistry, a specific branch of chemistry, delves into compounds primarily composed of carbon and hydrogen, occasionally incorporating other elements such as oxygen, nitrogen, sulfur, and phosphorus. Consequently, it shares connections with the disciplines of biology, physics, and mathematics.

Organic chemistry is the chemistry of carbon and its compounds.

These compounds are called *organic molecules*.

1.2. Where can organic molecules be found?

Only a few compounds containing C atoms are classified as inorganic: CO, CO₂, carbonates such as H₂CO₃ and Na₂CO₃, such as NaHCO₃, and cyanides such as HCN and NaCN bicarbonates.

Organic molecules serve as the fundamental building blocks of life. Substances like fats, sugars, proteins, and nucleic acids are primarily composed of carbon atoms. These carbon molecules are also prevalent in numerous everyday items we often take for granted. From natural materials like cotton and silk used in clothing to synthetic materials like polyester, organic compounds play a key role. They're present in dental hygiene products, toiletries, fragrances, furniture, carpets, plastic products, artwork, food, and a myriad of other everyday objects. Furthermore, organic substances, including gasoline, medicines, pesticides, and polymers, have significantly enhanced our quality of life.

2. FUNCTIONAL GROUPS

An objective within the realm of organic chemistry is to establish a connection between a molecule's structure and the reactions it can partake in. This endeavor allows us to dissect the mechanisms behind each type of reaction and acquire the skills to synthesize novel molecules through these processes.

Indeed, it is logical to categorize organic molecules based on the constituent subunits and bonds that dictate their chemical reactivity. These defining components are referred to as functional groups.

A *Functional Group* is a cluster of atoms primarily responsible for shaping the chemical behavior of the parent molecule. Molecules featuring identical types of functional groups tend to undergo analogous reactions.

2.1. Hydrocarbons

They present the general empirical formula C_xH_y .

ALKANES	<ul style="list-style-type: none"> • Present the general empirical formula C_nH_{2n+2}. • Contain only SIMPLE BONDS. • Carbon atoms have sp^3 hybridization. • Molecules whose carbons form a ring, are called <i>cycloalkanes</i>. • They are relatively nonpolar and unreactive.
ALKENES	<ul style="list-style-type: none"> • Present the general empirical formula C_nH_{2n}. • The functional group is the DOUBLE BOND. • Carbon atoms in the double bond are sp^2 hybridized and the double bond is made up of a σ bond and a π bond.
ALKYNES	<ul style="list-style-type: none"> • Present the general empirical formula C_nH_{2n-2}. • The functional group is the TRIPLE BOND. • Carbon atoms in the double bond are sp hybridized and the double bond is made up of a σ bond and two π bonds.
ARENES	<ul style="list-style-type: none"> • Aromatic compounds. • Double bonds are incorporated into a six-membered ring.

2.2. Functional groups with polar bonds

The behavior of numerous classes of molecules is influenced by polar bonds. It's important to remember that polarity arises from variations in electronegativity between two atoms that are chemically bonded to each other.

Table 1: Classification of functional groups with polar bonds and structure of the different functional groups.

	FUNCTIONAL GROUP	STRUCTURE*
Carbon singly bonded to an electronegative atom	Haloalkane	
	Alcohol	
	Thiol	

	Ether	
Carbon singly bonded to an electronegative atom	Amine	
Carbon-oxygen double bond	Aldehyde	
	Ketone	
	Carboxylic acid	
	Ester	
	Amide	

*Structures were made by authors.

3. STRUCTURE AND REACTIVITY

In the upcoming discussions, we will explore various methods employed by chemists to describe and explain chemical reactivity. This will serve as the groundwork for comprehending the particular reactions that will be discussed in subsequent sections. Notably, concepts such as bond polarity, the acid-base properties of molecules, and hydrogen bonding play a crucial role in establishing this foundation.

3.1. Bond Polarity

Bond polarity is due to the difference in electronegativity. Molecular charge distributions can be visually represented using *electrostatic potential maps*, which employ color to illustrate areas that are electron-rich (typically shown in red, denoting a partial negative charge, or δ^-) and electron-poor (usually depicted in blue, indicating a partial positive charge, or δ^+). These electrostatic potential maps, shown in Figure 1, offer a convenient means of quickly identifying the electron-rich and electron-poor regions within molecules.



Source: Organic Chemistry. A tenth Edition. John McMurry, Cornell University (Emeritus), CC BY-SA 4.0, <https://openstax.org/details/books/organic-chemistry>.

Figure 1. Electrostatic potential maps.

When discussing an atom's ability to induce polarity in a bond, we frequently refer to the *inductive effect*. It describes the electron shift within a sigma (σ) bond due to the electronegativity of neighboring atoms. Metals like lithium and magnesium tend to inductively donate electrons, while reactive nonmetals like oxygen and nitrogen tend to inductively withdraw electrons. Understanding inductive effects is crucial for comprehending chemical reactivity.

3.2. Kinetic and Thermodynamic of Chemical Processes

The simplest chemical reactions may be described as equilibration between two distinct species. Such processes are governed by two fundamental considerations:

1. *Chemical thermodynamic* is concerned with studying the changes in energy that happen during processes like chemical reactions. It governs how far a reaction proceeds to completion.
2. *Chemical kinetics* deals with the speed or rate at which the concentrations of reactants and products change over time. In other words, kinetics explains how quickly a reaction reaches completion.

When a transformation leads to the formation of the most stable products, it is said to be under thermodynamic control. This outcome is determined by the overall favorable change in energy as the system transitions from initial substances to final products. Conversely, a reaction where the product is determined by its fastest formation rate is considered to be under kinetic control. In such cases, the resulting product may not necessarily be the one with the highest thermodynamic stability.

So, what do we mean by a "favorable change in energy"? A favorable energy change indicates that the system's energy content has decreased. In nature, energy tends to flow from systems with higher energy content to those with lower energy content.

3.3. Acids and Bases

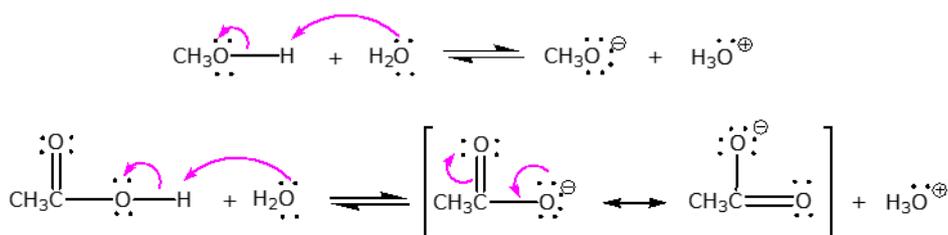
Brønsted and Lowry have provided us with a straightforward definition of acids and bases: An acid is a substance that donates protons (H^+ ions), while a base is a substance that accepts protons. The concepts of acidity and basicity are often discussed in the context of water. When an acid reacts with water, it donates a proton to water, forming hydronium ions (H_3O^+). Conversely, a base interacts with water by removing a proton from water, producing hydroxide ions (OH^-). The resulting species after deprotonation

of an acid is referred to as its conjugate base, and the product of protonation of a base is known as its conjugate acid.

The connection between the structure of molecules and their acidity or basicity is readily apparent in acid-base chemistry. In fact, specific structural characteristics allow us to make qualitative assessments of the relative strength of an acid, denoted as HA. The guiding principle is as follows: The stronger the conjugate base's stability (i.e., the weaker its basicity), the stronger the corresponding acid will be. There are several key structural factors that influence the strength of the conjugate base A^- , and we will discuss these effects as they become relevant in subsequent discussions.

Evaluating the acidity of **HA** involves considering the following factors:

- *Electronegativity*: As we move from left to right across a period in the periodic table, the increasing electronegativity of atom A is associated with greater acidity. When the acidic proton is attached to a more electronegative atom, the bond becomes more polar, making the proton more acidic. For example, the trend of increasing acidity in the series $H_4C < H_3N < H_2O < HF$ mirrors the rising electronegativity of atom A.
- *Hybridization*: The electronegativity of atom A depends on its hybridization. When the s character of the orbital on atom A involved in bonding with the acidic proton increases (as in the transition from sp^3 to sp^2 to sp hybridization), atom A becomes more electronegative, leading to increased acidity of the C-H bond.
- *Inductive Effect*: The proximity of atom A to other electronegative atoms also enhances the stability of A^- and increases the acidity of the proton bonded to A. This effect, known as the inductive effect, arises from the electron-attracting influence of the additional electronegative atom(s) transmitted through the molecule's bonds.
- *Atomic Size*: Moving down a group in the periodic table, the acid strength of hydrogen halides increases ($HF < HCl < HBr < HI$). This trend is attributed to the larger size of atom A as you move down the group. With increasing size, atom A becomes less electronegative, resulting in reduced polarity of the H-A bond. This leads to weaker coulombic attraction between H and A and a weaker bond. Additionally, the larger outer-shell orbitals allow electrons to occupy a larger space, reducing electron-electron repulsion in the resulting anion.
- *Resonance*: The presence of resonance in A^- , which allows charge delocalization over several atoms, can affect acidity. This effect is often augmented by additional electronegative atoms in A^- . For instance, acetic acid is more acidic than methanol (Figure 2). In both cases, an O-H bond dissociates into ions. The methoxide ion, the conjugate base of methanol, carries a localized negative charge on oxygen. In contrast, the acetate ion has two resonance forms, enabling charge delocalization onto a second oxygen atom. Consequently, the acetate ion can better accommodate the negative charge, stabilizing it and rendering it a weaker base.



Source: Image made by the authors.

Figure 2. Comparative acidity of methanol and acetic acid.

3.4. Intermolecular Forces

Intermolecular forces affect chemical reactivity. *Dipole-dipole forces* are interactions that occur between polar molecules due to electrostatic interactions among their dipoles. These forces can be either attractive or repulsive, depending on how the molecules are oriented. They are attractive when unlike charges are close together and repulsive when like charges are in proximity. The attractive orientation is lower in energy and is more prevalent.

Dispersion forces, on the other hand, exist between all neighboring molecules and arise because the distribution of electrons within molecules is constantly changing. Even in nonpolar molecules, the electron distribution is likely to be temporarily nonuniform at any given instant. This causes a molecule to develop a temporary dipole, with one side having a slight excess of electrons relative to the other. The nearby molecules then respond by developing a temporary, opposite dipole, resulting in a weak attraction between them. Although these temporary molecular dipoles have a fleeting existence and are continuously changing, their cumulative effect is often strong enough to keep molecules close together, causing a substance to exist in the liquid or solid phase rather than as a gas.

Hydrogen bonds are a particularly strong type of dipole-dipole interaction. They occur when a hydrogen atom is bonded to an electronegative oxygen (O) or nitrogen (N) atom and interacts with an unshared electron pair on another O or N atom. In essence, a hydrogen bond involves polarized O-H or N-H bonds. Hydrogen bonding has profound implications in biology, as it causes water to remain a liquid at ordinary temperatures, helps maintain the shapes of enzymes necessary for biological reactions, and is responsible for the pairing and coiling of DNA strands into the double helix structure that stores genetic information. As curiosity, in biochemistry, the terms "hydrophilic" and "hydrophobic" are frequently used to describe substances' affinity for water. Hydrophilic substances, like table sugar, have ionic charges or polar -OH groups in their structure, enabling them to form hydrogen bonds with water. In contrast, hydrophobic substances, such as vegetable oil, lack groups that can form hydrogen bonds, so their attraction to water is limited to weak dispersion forces.

4. ORGANIC REACTIONS

4.1. Kinds of Organic Reactions

Organic chemical reactions can be broadly categorized in two ways: by the type of reactions that occur and by the mechanisms through which these reactions take place. Let's start by examining the different types of organic reactions, which can be classified into four general categories:

- a. *Addition Reactions.* These reactions occur when two reactants combine to form a single product, and no atoms are left unaccounted for in the process. For instance, the reaction of an alkene like ethylene with hydrogen bromide (HBr) results in the formation of an alkyl bromide.
- b. *Elimination Reactions.* In contrast to addition reactions, elimination reactions involve a single reactant splitting into two products. Often, a small molecule like water or HBr is generated during the process. An example is the acid-catalyzed reaction of an alcohol, which produces water and an alkene.
- c. *Substitution Reactions.* Substitution reactions occur when two reactants exchange parts to create two new products. For instance, the reaction of an ester, such as methyl acetate, with water leads to the formation of a carboxylic acid and an alcohol. Similar substitution reactions play a significant role in various biological pathways, including the metabolism of dietary fats.
- d. *Condensation and Rearrangement Reactions.* Apart from additions, eliminations, and substitutions, organic reactions also encompass condensation reactions and rearrangement reactions. Condensation reactions involve the combination of two molecules, often with the elimination of a small molecule like water. Rearrangement reactions involve the reorganization of atoms or functional groups within a molecule to form a different structural isomer. An example is the conversion of dihydroxyacetone phosphate into its constitutional isomer glyceraldehyde 3-phosphate, a step in the glycolysis pathway by which carbohydrates are metabolized.

Understanding these general categories of organic reactions is fundamental in the study of organic chemistry, as they provide a framework for describing and predicting chemical transformations in organic compounds.

4.2. Mechanisms of Organic Reactions

Reaction mechanisms provide a detailed account of the movement of electrons when chemical bonds are formed or broken. In these mechanisms, curved arrows are used to illustrate the flow of electrons. A reaction mechanism offers a comprehensive description of how a chemical reaction unfolds, detailing the sequence of events, including which bonds are broken and formed, their order, and the

relative rates of each step. A complete mechanism must also account for all reactants consumed and all products generated.

All chemical reactions involve the breaking of existing bonds and the formation of new ones. When two molecules come together and react to produce products, specific bonds in the reactant molecules are broken and specific bonds in the product molecules are created. Essentially, there are two ways in which a covalent two-electron bond can be broken. A bond can break symmetrically, resulting in one electron remaining with each product fragment, or it can break asymmetrically, with both bonding electrons staying with one product fragment, leaving the other with an empty orbital. The symmetric cleavage is termed "homolytic," while the asymmetric cleavage is termed "heterolytic" (Figure 3). Processes involving symmetric bond-breaking and bond-making are known as *radical reactions* and those involving asymmetric bond-breaking and bond-making are called *polar reactions*.

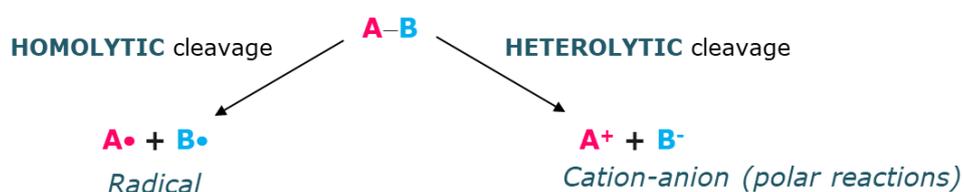


Figure 3. Mechanisms of organic reactions; Radical and Polar reactions.

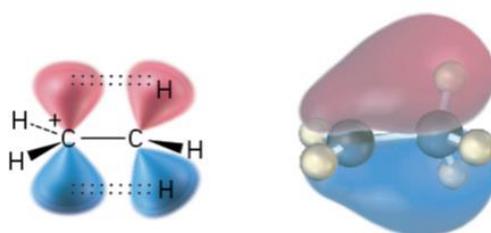
A radical, often referred to as a "free radical," is a neutral chemical species that contains an odd number of electrons, thereby possessing a single, unpaired electron in one of its orbitals. On the other hand, polar reactions involve species with an even number of electrons, and they have only electron pairs in their orbitals. In heterolytic cleavage, chemists use the terms "nucleophile" and "electrophile" to refer to the electron-rich and electron-poor species involved in polar reactions. A nucleophile is a substance that is attracted to the nucleus (positively charged) and possesses a negatively polarized, electron-rich atom. It forms a bond by donating a pair of electrons to a positively polarized, electron-poor atom. Nucleophiles can be either neutral or negatively charged, and examples include ammonia, water, hydroxide ions, and chloride ions. In contrast, an electrophile is electron-seeking and features a positively polarized, electron-poor atom. It forms a bond by accepting a pair of electrons from a nucleophile. Electrophiles can also be either neutral or positively charged, and examples include acids (donors of H^+ ions), alkyl halides, and carbonyl compounds. Radicals and ions are *reaction intermediates* that are formed by the action of reactants.

4.2.1. Carbocation Stability

The increased stability of substituted carbocations can be attributed to various effects, including inductive effects and hyperconjugation, particularly involving methyl groups or aliphatic chains attached to the carbocationic center. Carbocations exhibit sp^2 hybridization, resulting in a flat structure with bond angles of 120 degrees. The trivalent carbon in a carbocation is sp^2 -hybridized, and its three substituents are arranged in an equilateral triangle configuration. The p orbital extending above and below the plane of the molecule is unoccupied due to the utilization of all six valence electrons in the three sigma bonds.

In accordance with the laws of electrostatics, stability in a charged system increases as the charge is dispersed. For example, when 2-methylpropene reacts with H^+ to form a carbocation, the resulting product is a tertiary carbocation (3°) with three alkyl substituents, rather than a primary carbocation (1°) with only one alkyl substituent. Thermodynamic measurements confirm that the stability of carbocations follows the order: tertiary > secondary > primary > methyl. Carbocations can be stabilized through various effects:

- *Inductive Effect.* Aliphatic chains exhibit an inductive effect where they donate electron density from sigma bonds to the cationic center. This donation of electron density helps stabilize the system by reducing the electron deficiency of the sp^2 carbon. Alkyl groups can shift electrons more easily towards a neighboring positive charge compared to hydrogen. Thus, the more alkyl groups attached to the positively charged carbon, the greater the inductive stabilization of the carbocation.
- *Resonance Effect.* When positive charge in a carbocation is distributed among several atoms due to the presence of a double bond, atoms with adjacent pairs of electrons, or aromatic rings, the load is stabilized. This effect involves the delocalization of π electrons.
- *Hyperconjugation Effect.* This effect arises from the partial overlap of filled orbitals with empty orbitals. A sigma bond adjacent to the positively charged carbon shares its electrons with the empty orbital of the carbocation, thereby stabilizing it. Hyperconjugation involves the interaction between the C-H bond of the methyl group and the partially empty p orbital with a positive charge (Figure 4). This interaction allows the pair of electrons in the sigma orbital to delocalize into the partially empty p orbital, stabilizing the carbocation. When alkyl substituents are present, one of the sp^3 orbitals, parallel to the empty p orbital, extends to stabilize the electron-deficient carbon atom. The more alkyl groups present on the carbocation, the greater the potential for hyperconjugation, resulting in increased stability.



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Figure 4. Hyperconjugation (dashed line) due to donation of electrons in filled sp^3 hybrids to the partly filled p orbital.

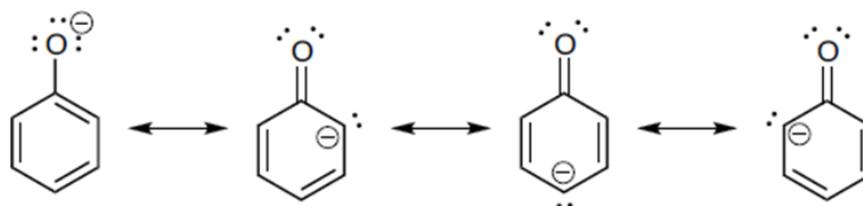
Carbocations are electrophilic, meaning they are electron-deficient species that are attracted to electron-rich areas. They participate in chemical reactions by accepting a pair of electrons, forming a bond with a nucleophile.

4.2.2. Carbanion Stability

In contrast to radicals and carbocations, carbanions are electron-rich species, not deficient in electrons but rather having an abundance of them. The stability order of carbanions decreases as we progress from primary to tertiary carbanions because the presence of methyl groups, with their +I (inductive) effect, intensifies the negative charge on the central carbon of tertiary carbanions, rendering them less stable.

Alkyl groups, like the methyl group, influence the electron density through both the *inductive effect* and *hyperconjugation*. These substituents and other electron-donating groups increase the instability of carbanions by causing a higher concentration of electron density on the carbon atom carrying the negative charge. Consequently, the stability order of carbanions is the reverse of that for carbocations and radicals. Alkyl groups exhibit a +I (positive inductive) effect. When an alkyl group is attached to the carbon atom bearing the negative charge of the carbanion, it tends to release electrons towards the carbon. This intensifies the negative charge on the carbon atom, leading to the destabilization of the carbanion. The more alkyl groups attached to the carbon atom carrying the negative charge, the greater the intensity of the negative charge on that carbon atom, resulting in reduced stability of the carbanion.

Benzyl carbanions are an exception and are stabilized by *resonance*. In these cases, the negative charge can be distributed among several atoms through resonance, reducing the concentration of negative charge on any single carbon atom and stabilizing the carbanion (Figure 5).



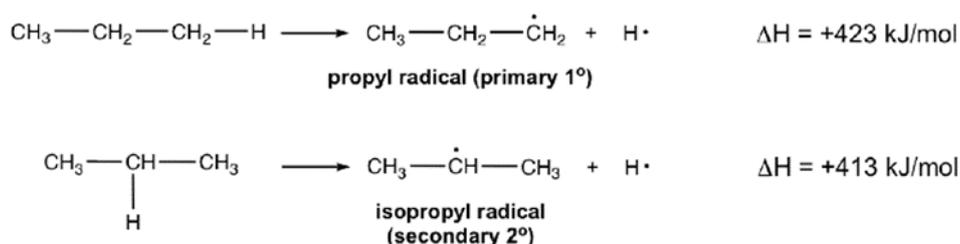
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Figure 5. Resonance stabilization of phenoxide ion.

4.2.3. Radical Stability

Homolytic cleavage of a covalent bond results in each species retaining one of the electrons that initially formed the bond. These species are known as radicals, and they are highly unstable, energetically excited, and electrically neutral particles. The process of homolytic bond cleavage typically requires the presence of heat or ultraviolet light ($h\nu$).

It's important to note that tertiary radicals are more stable than secondary radicals, and secondary radicals are more stable than primary radicals. This stability trend arises from the fact that as the bond strength decreases, the stability of the corresponding radical increases. This relationship is illustrated in Figure 6.

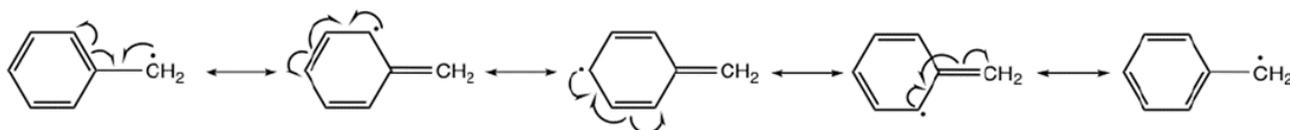


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Figure 6. Comparative radical stability.

The planar structures of alkyl radicals play a crucial role in explaining their relative stabilities. Spectroscopic measurements have demonstrated that the methyl radical, and potentially other alkyl radicals, adopt a nearly planar configuration, best described by sp^2 hybridization. The unpaired electron occupies the remaining p orbital, which is perpendicular to the molecular plane. In the ethyl radical, there exists a conformer in which a C-H bond of the CH_3 group aligns with and overlaps one of the lobes of the singly occupied p orbital on the radical center. This arrangement allows the bonding pair of electrons in the σ orbital to delocalize into the partly empty p orbital, a phenomenon known as *hyperconjugation*. The interaction between a filled orbital and a singly occupied orbital has a net stabilizing effect.

Radicals can be also stabilized by *resonance* through delocalization of π electrons (Figure 7). Both, hyperconjugation and resonance, involve electron delocalization, with hyperconjugation being associated with overlap with σ bond orbitals, while resonance typically refers to π -type overlap of p orbitals.



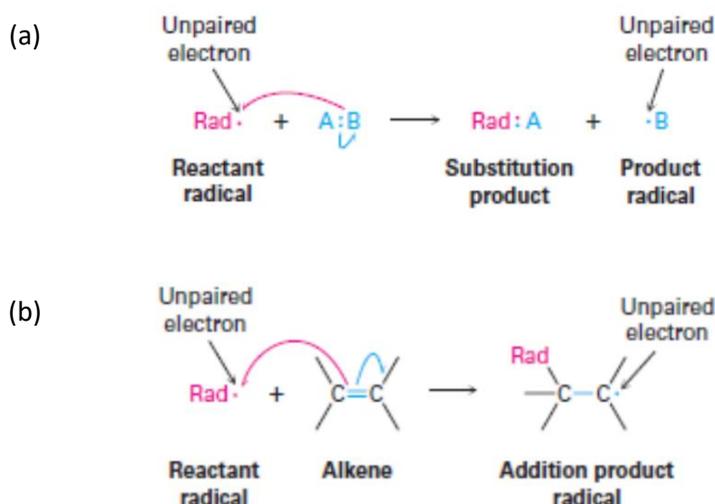
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Figure 7. Resonance stabilization of benzyl radical.

4.2.4. Radical Reactions

Radical reactions, while less common than polar reactions, play a significant role in certain industrial processes and biological pathways. Radicals are characterized by their high reactivity, derived from the presence of an atom with an odd number of electrons (typically seven) in their valence shell, in contrast to the stable noble-gas octet.

Radicals can attain a valence-shell octet through various mechanisms (Figure 8). For instance, they may abstract an atom and one bonding electron from another reactant, thereby generating a new radical. This process is referred to as a radical substitution reaction. Alternatively, a reactant radical can undergo addition to a double bond, taking one electron from the double bond and producing a new radical. This leads to a radical addition reaction.



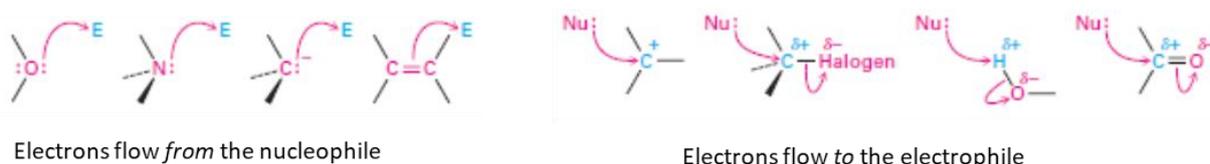
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Figure 8. (a) Radical substitution reaction and (b) Radical addition reaction.

4.2.5. Polar Reactions

Polar reactions arise from the electrostatic attraction between positively and negatively charged or polarized centers within functional groups in molecules. Mechanism in polar reactions follows a few rules and a few common patterns:

- **Rule 1:** Electrons flow from a nucleophilic source (Nu: or Nu:-) to an electrophilic sink (E or E+). The nucleophilic source typically possesses an available electron pair, which can be in the form of a lone pair or within a multiple bond.



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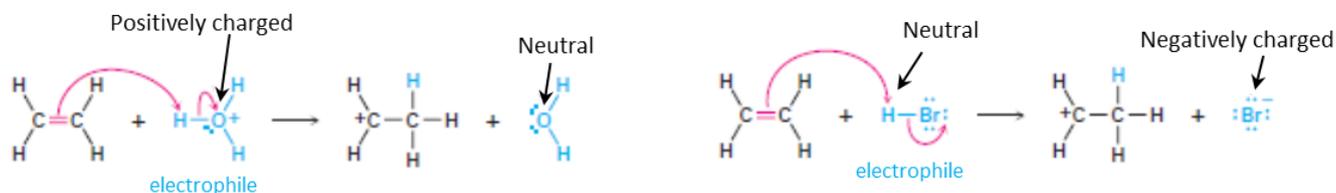
- **Rule 2:** The nucleophile can either be negatively charged or neutral. If the nucleophile is negatively charged, the atom donating the electron pair becomes neutral. If the nucleophile is neutral, the atom donating the electron pair gains a positive charge.



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- **Rule 3:** The electrophile can also be either positively charged or neutral. When the electrophile is positively charged, the atom carrying that charge becomes neutral after accepting the electron pair.

If the electrophile is neutral, the atom receiving the electron pair acquires a negative charge. To achieve this, the negative charge must be stabilized, typically by being located on an electronegative atom like oxygen, nitrogen, or a halogen. Carbon and hydrogen generally do not stabilize a negative charge.



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- Rule 4:** The octet rule must be adhered to. In other words, no second-row atom should exceed ten electrons (or four for hydrogen). If an electron pair moves to an atom that already has an octet (or two for hydrogen), another electron pair must simultaneously leave that atom to maintain the octet. For instance, when two electrons move from the C=C bond in ethylene to the hydrogen atom of H_3O^+ , two electrons must depart from that hydrogen. This necessitates the breaking of the H-O bond, and the electrons remain with the oxygen, ultimately forming neutral water.