

General Organic Chemistry (GOC) for JEE

Important GOC Topics

The primary topics that fall under general organic chemistry include:

- Electrophiles and Nucleophiles
- Inductive Effect (+I and -I Effects)
- Electromeric Effect (+E and -E Effects)
- Hyperconjugation
- Mesomeric Effect
- Resonance and the Resonance Effect
- Isomerism - Structural Isomerism and Stereoisomerism

GOC Basics

General Components of an Organic Reaction

A typical reaction mechanism proceeds in the following manner:

Reactants + Catalyst or Energy → Intermediate (Transition State) → Product

Adequate reaction conditions facilitate the formation of an intermediate from the chemical reaction between the reactants. These intermediates are generally unstable and quickly react further to yield a product.

The reactants of an organic reaction can be classified as:

- **Reagents** - reactive chemical species that trigger the reaction by attacking another species.
- **Substrate** - the species that is attacked by a reagent in an organic reaction.

The site of reagent attack can vary based on the nature of the reagent (electrophilic or nucleophilic):

Electrophiles - They are electron-deficient species that attack the substrate at a region where the electron density is high.

Nucleophiles - They are electron-rich species that tend to donate their electrons. [Nucleophiles](#) generally attack the reagent at a region where the electron density is low.

Cleavage of Bonds & Reaction Intermediates

Chemical reactions generally involve the breakage of existing chemical bonds and the formation of new ones. A [covalent bond](#) can break in two different ways:

Homolytic Fission - the covalent bond is cleaved in such a manner that each participating atom leaves with one unpaired electron. The chemical species that are created as a result of homolytic fission are called free radicals. They are highly reactive (due to their unstable electron configurations).

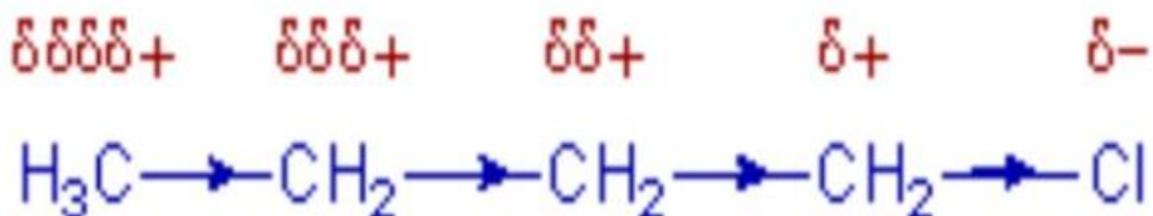
Heterolytic Fission - the covalent bond is cleaved in such a manner that one atom retains both the electrons and the other retains none. Heterolytic fissions feature the formation of an ion pair - a positively charged cation and a negatively charged anion.

Inductive Effect

(Main Article: [Inductive Effect](#))

The introduction of an electron-rich or electron-deficient species to a carbon chain results in the formation of a permanent dipole. This effect is called the inductive effect (since the dipole is induced by the difference in the electronegativities of the atoms in the molecule).

The direction of the [dipole moment](#) depends on the electronegativity of the attacking species (relative to the carbon atom it bonds with). Note that the partial charge (positive or negative) gained by the carbon atom is relayed through the carbon chain, as illustrated below.



- In this example, the electronegativity of chlorine is higher than that of carbon, causing the bond pair of electrons to shift closer to the chlorine atom.
- This results in the formation of a permanent dipole where the chlorine has a partial negative charge (since the electron density around it is high) and the carbon atom has a partial positive charge (since the electron density around it is low).
- Since the alkyl group is an electron-donating group, the partial positive charge on the chlorine-bonded carbon is stabilized by the rest of the chain. Therefore, the inductive effect propagates through sigma bonds.
- Eventually, the partial charge propagates through the entire carbon chain.

Important Note: The magnitude of the partial charge decreases down the carbon chain. Its magnitude can be neglected from the 4th carbon atom in the chain.

Salient Features of the Inductive Effect

1. It is a permanent effect.
2. It is dependent on distance (its magnitude decreases as the distance between the atoms increases).
3. It is relayed through sigma bonds.

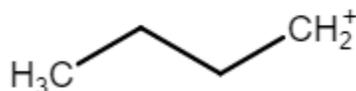
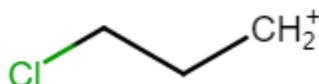
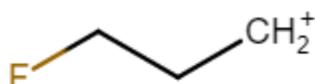
Types of Inductive Effects

+I effect: The positive inductive effect (abbreviated to +I effect) involves the transmission of a negative charge through the chain. It occurs when an electron-donating group is introduced to a chain of atoms. **Example of +I species:** Alkyl group.

-I effect: The -I effect, also known as the negative inductive effect, occurs when an electron-withdrawing group is introduced to a chain of atoms. This results in the transmission of a positive charge through the chain. **Example of -I species:** Halogens (such as fluorine and chlorine).

Gauging the Stability of Molecules with the Inductive Effect (Solved Example)

Question: Which of the Following Compounds is the most stable?

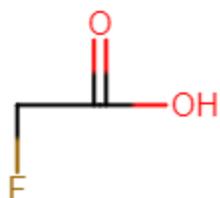
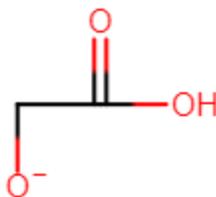
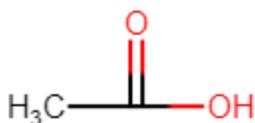


Answer: The compound with the methyl functional group (bottom) is the most stable since the CH_3 group is a +I species, which increases the stability of the carbocation. Since fluorine and chlorine are electron-withdrawing -I groups, they decrease the stability of the carbocation by increasing the magnitude of the positive charge on it. However, the compound containing fluorine is less stable than the one containing chlorine (because fluorine is more electronegative and, therefore, more electron-withdrawing).

Important Note: electron-donating species decrease the stability of carbanions and increase the stability of carbocations due to +I effect. Electron-withdrawing species increase the stability of carbanions and decrease the stability of carbocations due to -I effect.

Gauging the Acidity or Basicity of a Compound with the Inductive Effect (Solved Example)

Question: Which of the following compounds has the highest acidity?



Answer: The order of acidity is $\text{F-CH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{O}^-\text{-CH}_2\text{COOH}$

Explanation:

- The acidity of an acid is directly proportional to the stability of the corresponding conjugate base.
- The acidic part of these molecules is the carboxyl group (COOH group), whose conjugate base is the carboxylate ion (COO⁻).
- A +I group will increase the negative charge on the conjugate base, thereby decreasing its stability and, consequently, decreasing the acidity of the parent acid.
- A -I group will stabilize the negative charge of the conjugate base due to its electron-withdrawing nature. This increases the stability of the conjugate base and the acidity of the parent acid.
- Since O⁻ is an electron-donating group (or a +I group), it will decrease the acidity of the compound.
- Since F is an electron-withdrawing group, it will increase the acidity of the compound.
- Therefore, the compound at the bottom is the most acidic and the one on the top-right is the least acidic.

Remember:

- -I Groups (electron-withdrawing groups) increase acidity and decrease the basicity.
- +I Groups (electron-donating groups) decrease acidity and increase basicity.

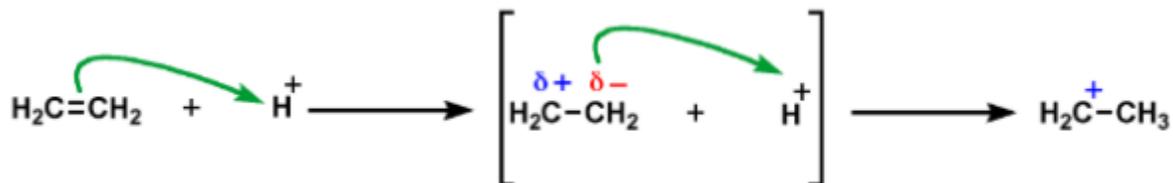
Electromeric Effect

(Main Article: [Electromeric Effect](#))

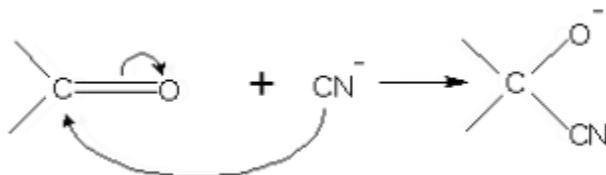
The electromeric effect involves the complete transfer of pi electrons to one of the bonded atoms in an organic compound. It is a temporary effect that occurs due to the presence of an attacking reagent (an electrophile or nucleophile that triggers the formation of a dipole in the organic compound). The electromeric effect subsides when the attacking reagent is removed from the system.

Types of Electromeric Effects

+E Effect: When the attacking reagent is an electrophile, the pi electrons shift towards the attacking reagent, which binds to the atom that retains the bond pair (and is negatively charged). **Example:** the +E effect can be observed during the protonation of alkenes (illustrated below).



-E Effect: When the attacking reagent is a nucleophile, the pi electrons shift away from the attacking reagent, which binds to the atom that lost its pi-electron (and is positively charged). **Example:** the -E effect can be observed during the addition of a nucleophile (such as a cyanide ion) to the carbonyl group of a carbonyl compound (illustrated below).

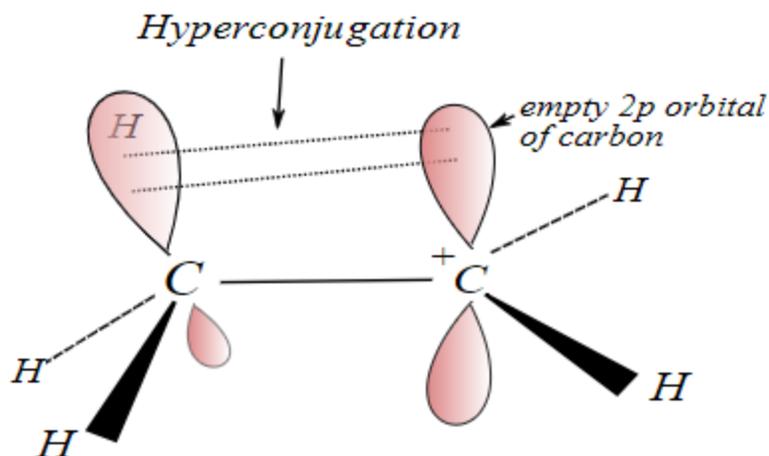


Remember:

- Electrophiles are +E groups
- Nucleophiles are -E Groups
- +E and -E effects are temporary and their presence is entirely dependent on the attacking reagent.

Hyperconjugation

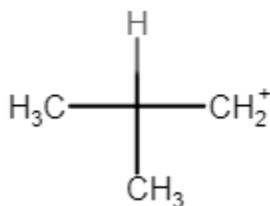
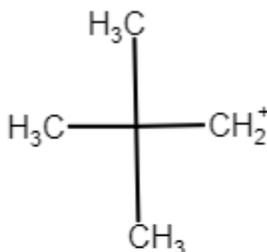
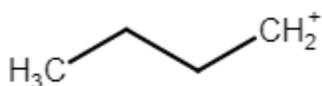
Carbocations are stabilized by adjacent sigma bonds that donate electrons to vacant p-orbitals. This effect is a permanent effect and is called hyperconjugation (also called no-bond resonance). Here, the delocalization of the positive charge increases the stability of the compound.



The stability added by hyperconjugation is directly proportional to the total number of hyperconjugating structures which is, in turn, directly proportional to the total number of alpha hydrogens.

Gauging the Stability of Carbocations with Hyperconjugation (Solved Example)

Question: Rank the following carbocations in the increasing order of stability.



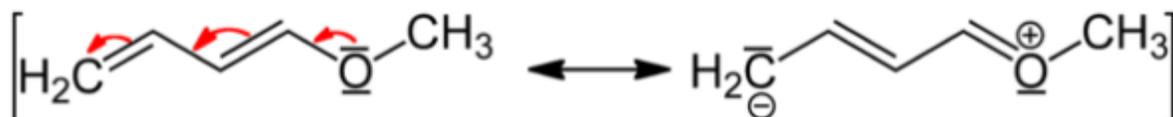
Answer: The total number of alpha-hydrogens is proportional to the stability of the carbocation (due to hyperconjugation). Therefore, the bottom-left and the top-left compounds are the most stable and the top-right compound is the least stable.

Mesomeric Effect

The mesomeric effect involves the delocalization of electrons over a network of pi bonds. The polarity that arises in organic compounds due to the interactions between two pi bonds (or a pi bond and a lone pair) is a consequence of the mesomeric effect. This effect can stabilize both negative and positive charges.

Types of Mesomeric Effects

+M Effect: It involves the donation of electrons by a pi-system. Electrons typically move away from +M groups. An illustration detailing the +M effect in a methoxy ether molecule is provided below.



Examples of +M groups: O^- , NH_2 , and OH groups. These groups usually contain a lone pair or a pi bond.

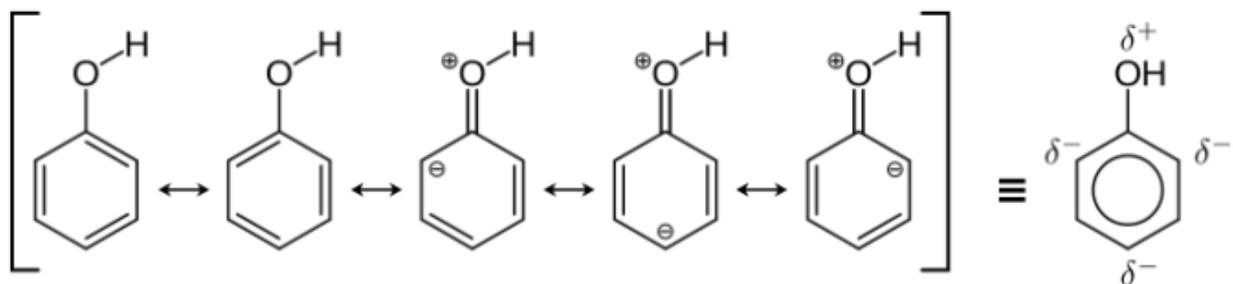
-M Effect: It involves the acceptance of electrons by a pi-system. Electrons typically move towards -M groups, as illustrated below.



Examples of -M groups: CHO and NO_2 groups.

Mesomeric Effect in Phenol (Example)

The OH group in a phenol molecule exhibits a +M effect, resulting in the delocalization of a lone pair of electrons (belonging to the oxygen atom) over the aromatic system (illustrated below).



From the illustration, it can be observed the electron densities are particularly high at the ortho and para positions of the aromatic ring. This makes the phenol molecule particularly susceptible to electrophilic substitutions at the ortho and para positions.

Comparison Between Inductive and Mesomeric Effects

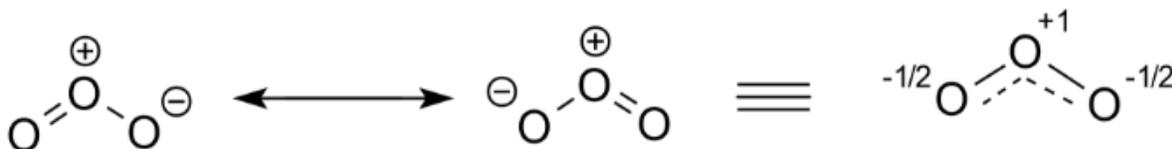
- Inductive effects are typically weaker than mesomeric effects.
- The stability offered by a +M group to an anion is generally greater than that offered by a +I group.
- The distances over which mesomeric effects are effective are much greater than the distances over which inductive effects are effective. This is because mesomeric effects are dependent on the positions of the +M and -M groups in the molecule.

Resonance Effect

(Main Article: [Resonance Effect](#))

The resonance effect involves the delocalization of pi electrons and lone pairs over molecules. This results in several hypothetical molecular structures known as resonance structures. It occurs at an intramolecular level and does not alter the structural arrangement of atoms in the molecule (the arrangement of electrons can vary).

The stabilization offered by resonance is greatest when an equivalent resonating structure (known as a resonance hybrid) can be drawn for the molecule. An illustration detailing the resonance of an ozone molecule is provided below.



Types of Resonance Effects

+R Effect: It occurs when a lone pair of electrons is released into a molecule. +R effects usually involve the transmission of a negative charge throughout the molecule due to the delocalization of a lone pair of electrons. The electron-donating agent obtains a positive charge when its lone pair undergoes delocalization.

-R Effect: It occurs primarily due to electron-withdrawing species or species with vacant p or d orbitals. -R effects usually feature the transmission of a positive charge through the molecule (the electrons are delocalized into the electron-withdrawing group from the rest of the molecule).

Isomerism

Isomerism is a phenomenon in which multiple compounds have the same chemical formula but feature different chemical structures. The chemical compounds that exhibit isomerism are called isomers.

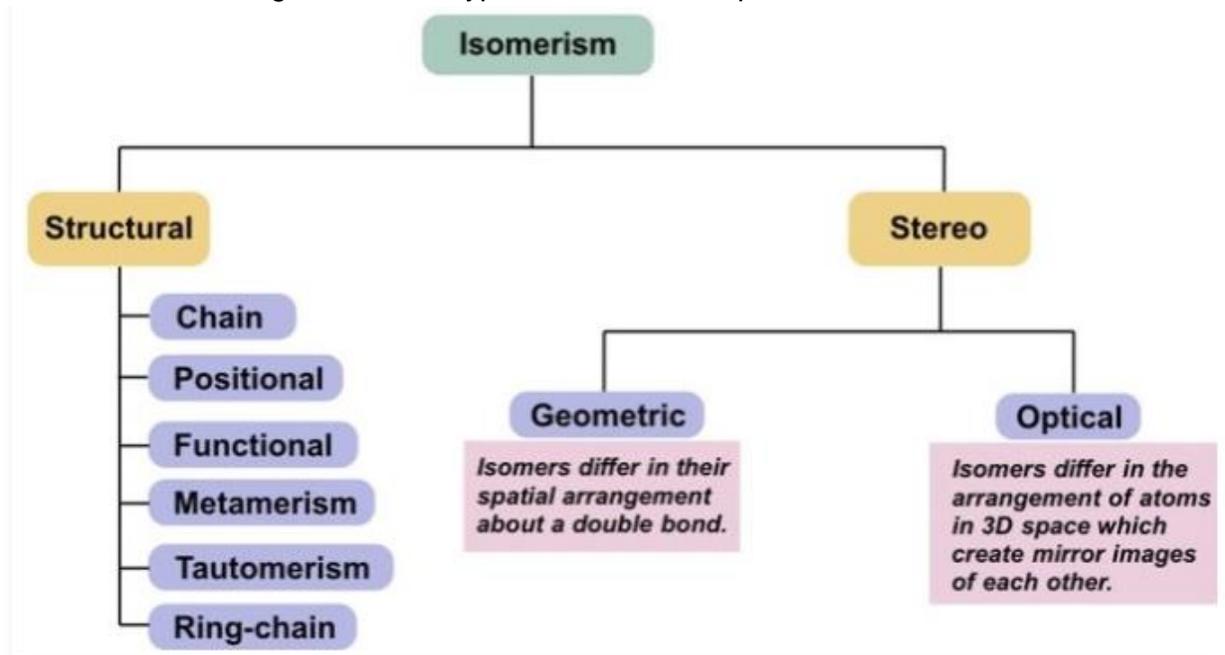
Isomerism can be broadly classified into two categories:

1. Structural isomerism
2. Stereoisomerism

Structural isomerism, also known as constitutional isomerism, features molecules with the same chemical formulae but differently arranged atoms.

Stereoisomerism is the phenomenon in which multiple molecules have the same chemical formulae but different three-dimensional orientations of the atoms.

An illustration detailing the different types of isomerism is provided below.



For an in-depth explanation about the different types of isomerism, visit our [primary isomerism page](#).

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