



Sri Ramakrishna Mission Vidyalaya College of Arts and Science
 (An Government Aided Autonomous Institution Affiliated to Bharathiar University)
 (Reaccredited by NAAC with A+ grade)
Coimbatore-641 020
Department of Chemistry

Programme: BSc Chemistry

Course: General Chemistry-I

Course Code: 23UCH1C01

UNIT – III: Electronic effects and reaction intermediates: Polar, non-polar molecules, electron donating and withdrawing groups. Polar effects- inductive, mesomeric, electromeric, resonance, hyperconjugation and steric effects. Homolytic and heterolytic fission.

Polar and non-polar molecules:

In simple terms, polar means oppositely charged, and non-polar means equally charged. Covalent bonds can be polar or non-polar. To understand the difference between polar and non-polar bonds, it is essential to comprehend electronegativity.

What is electronegativity?

Electronegativity is the measurement of how much an atom wants to bond to another atom. Electronegativity increases from left to right and down each column on the periodic table.

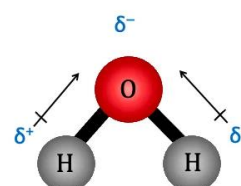
The Pauling scale describes the electronegativity of an element, with a scale from 0.7 to 4. Fluorine is the most electronegative element, with an electronegativity of 4. Caesium is the least electronegative element with an electronegativity of 0.7.

H 2.1																	He ---
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne ---
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.2	S 2.5	Cl 3.0	Ar ---
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn ---
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7															

Polar bond:

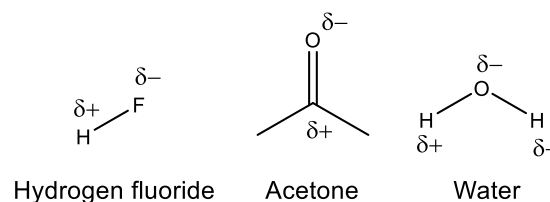
A polar bond is a type of covalent bond. A bond between two or more atoms is polar if the atoms have significantly different electronegativities (>0.4). Polar bonds do not share electrons equally, meaning the negative charge from the electrons is not evenly distributed in the molecule. This causes a dipole moment.

A dipole moment occurs when one end of the bond is positive, and the other end is negative. A classic example of a polar bond is the bond in water between hydrogen and oxygen. The bond is classified as a polar bond because it has a large electronegativity difference of 1.4. The electrons in hydrogen are more attracted to the electrons in oxygen because oxygen is more electronegative.



Polar Molecules:

A polar molecule is a molecule that has one end is slightly positive and another end is slightly negative. They are generally asymmetrical, with an uneven distribution of the electrons. If a molecule is non-polar, then the molecules either share the electrons evenly, e.g. they have a non-polar bond, or the polar bonds are symmetric, in the cases of carbon dioxide or carbon tetrachloride. In those molecules, there are dipoles but they cancel out due to the symmetry. Examples: HF, Water, Acetone, NH_3 , CH_3OH , PCl_3



Non-polar bond:

Non-polar bonds are also a type of covalent bond. Unlike polar bonds, non-polar bonds share electrons equally.

A bond between two atoms or more atoms is non-polar if the atoms have the same electronegativity or a difference in electronegativities that is less than 0.4. An example of a non-polar bond is the bond in chlorine. Chlorine contains two chlorine atoms. The electrons are shared equally because the electronegativity difference between the two atoms is zero.



Nonpolar Molecules:

Nonpolar molecule, there are no positive or negative poles formed in the molecule. Any charges are distributed evenly across the molecule. Nonpolar molecules are generally symmetrical.

For example, the tetrahedral molecule carbon tetrachloride. Another example is boron trifluoride, which is trigonal planar. In symmetrical molecules, the dipole charges cancel out. Nonpolar molecules usually will dissolve well in nonpolar solvents, but tend to be insoluble in water.

Examples: Benzene, CH_4 , CCl_4 , BF_3 , N_2 , Hexane



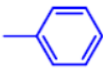
Scan here to watch polar and non-polar molecules:

Electron donating groups:

An electron donating group (EDG) is an atom or functional group that donates some of its electron density into a conjugated π system via resonance (or mesomerism) or inductive effects (or induction)—called +M or +I effects, respectively—thus making the π system more nucleophilic.

Because of these electronic effects, an aromatic ring to which such a group is attached is more likely to participate in electrophilic substitution reaction. EDGs are therefore often known as activating groups, though steric effects can interfere with the reaction. Electron withdrawing groups:

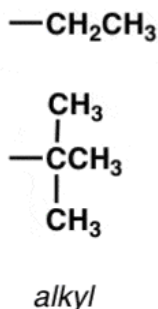
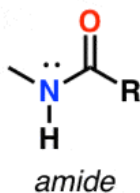
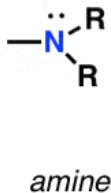
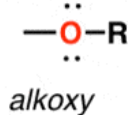
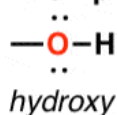
An electron withdrawing group (EWG) is an atom or functional group that withdraws some of its electron density into a conjugated π system via resonance (or mesomerism) or inductive effects (or induction)—called -M or -I effects, respectively thus making the π system more electrophilic.

Electron-donating Groups ←			Electron-withdrawing Groups →		
π donors	σ donors		Halogens	Carbonyls	Other
—NH_2 or —NR_2 —OH or —OR —N—C(=O)—R	—R 	—H	—F: —Cl: —Br: —I:	—C(=O)—R —C(=O)—OH —C(=O)—OR	$\text{—SO}_3\text{H}$ —CN —NO_2 —NR_3^+ —CF_3
← Ortho/Para Directors				Meta Directors →	

Activating and Deactivating Groups

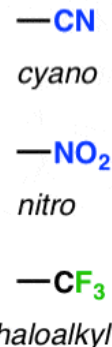
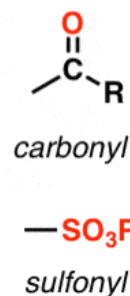
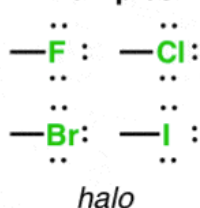
Activating groups increase the rate of reaction in electrophilic aromatic substitution reactions, relative to H

Examples



Deactivating groups decrease the rate of reaction in electrophilic aromatic substitution reactions, relative to H

Examples

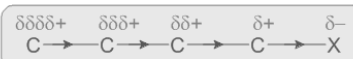


Inductive Effect:

The inductive effect refers to the phenomenon wherein a permanent dipole arises in a given molecule due to the unequal sharing of the bonding electrons in the molecule.

Inductive effect

Polarization of sigma bond when an electronegative atom or group (X) withdraws electron pair of sigma bond towards itself.



Polarization is transmitted through σ -bonds by creating a permanent dipole in the molecule. Polarization fades away from right to left

Salient Features:

- It arises due to electronegativity difference between two atoms forming a sigma bond.
- It is transmitted through the sigma bonds. No pi bonds are involved.
- The magnitude of inductive effect decreases while moving away from the groups causing it.
- It is a permanent effect. It may create permanent dipole in the molecule.
- In general, the inductive effect is relatively weak and is overshadowed by other electronic effects like resonance effect, hyperconjugation etc.
- It influences the chemical and physical properties of compounds.

Negative Inductive effect: The electron withdrawing nature of groups or atoms is called as negative inductive effect. It is indicated by $-I$. Following are the examples of groups in the decreasing order of their $-I$ effect: $\text{NH}_3^+ > \text{NO}_2 > \text{CN} > \text{SO}_3\text{H} > \text{CHO} > \text{CO} > \text{COOH} > \text{COCl} > \text{CONH}_2 > \text{F} > \text{Cl} > \text{Br} > \text{I} > \text{OH} > \text{OR} > \text{NH}_2 > \text{C}_6\text{H}_5 > \text{H}$

Positive Inductive Effect: It refers to the electron releasing nature of the groups or atoms and is denoted by $+I$. Following are the examples of groups in the decreasing order of their $+I$ effect. $\text{C}(\text{CH}_3)_3 > \text{CH}(\text{CH}_3)_2 > \text{CH}_2\text{CH}_3 > \text{CH}_3 > \text{H}$.

Scan here to watch about the inductive effect.



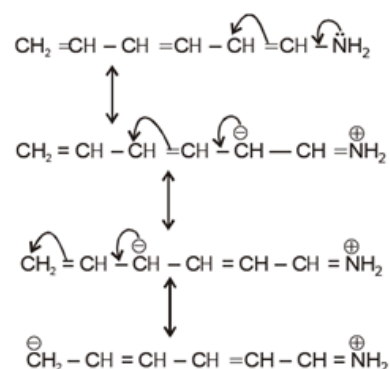
Mesomeric Effect:

Mesomeric effect is the polarity produced in a molecule or a conjugated system by the movement of π electrons towards or away from a substituent group.

Also, we can say that an atom or group of atoms that donates/withdraws electrons through resonance is called mesomeric effect. Thus, electron releasing or electron-withdrawing effects occur to the substituents by delocalization of π -electrons. Conjugation is a necessary criterion for mesomeric effect. It is represented by M , and such effect can be analyzed in various canonical forms.

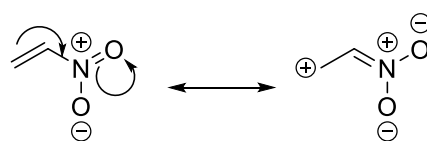
$+M$ effect (positive mesomeric effect)

When the π electrons move away from the particular group towards the rest of the molecule, the electron density of the molecule/conjugated system increases. Such an effect is called positive mesomeric effect ($+M$ effect). It is shown by electron-releasing substituent. Some of the $+M$ substituents are $-\text{OH}$, $-\text{SH}$, $-\text{OR}$, $-\text{OCOR}$, $-\text{NH}_2$, $-\text{NR}_2$, $-\text{NHCOR}$, Ph , $-\text{CH}_3$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, etc.



$-M$ effect (negative mesomeric effect)

When the π electrons are moved from the rest of the molecule to a particular group, the electron density of the molecule/conjugated system decreases. Such an effect is called negative mesomeric effect ($-M$ effect). It is shown by electron-withdrawing substituent. Some of the $-M$ substituents are NO_2 , $-\text{CN}$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{CONH}_2$, $-\text{COO}^-$, $-\text{CHO}$, $-\text{COR}$, and so on.



Scan to watch the about Mesomeric effect.



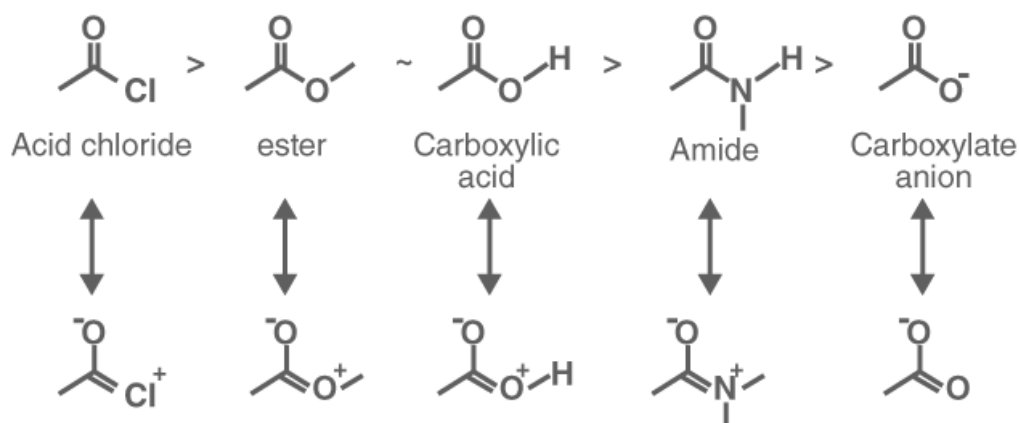
The main difference between resonance and the mesomeric effect is that the resonance effect describes how a molecule's lone pair of electrons and bond pair of electrons determine its chemical structure, whereas the mesomeric effect describes how a molecule's chemical structure is stabilized by using a functional group.

Resonance Effect:

The polarity induced in a molecule by the interaction of a lone pair of electrons with a pi bond or the interaction of two pi bonds in nearby atoms is known as the resonance effect.

Positive Resonance Effect: The electrons are transferred away from an atom or substituent group bound to the conjugated system in this process. For example – -OH, -SH, -OR, -SR.

Negative Resonance Effect: The electrons are transferred towards the atom or substituent group associated with the conjugated system in this effect. For example - -NO₂, C=O, -COOH, -C≡N.



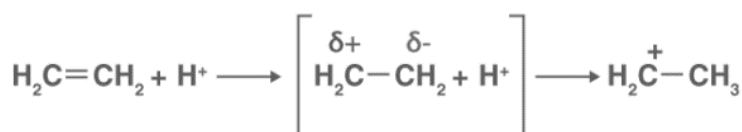
Scan here to watch the Resonance effect.

**Electromeric Effect:**

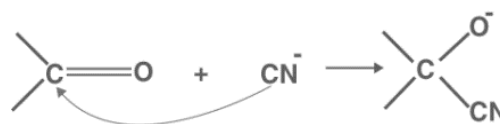
The instantaneous formation of a dipole in the molecule of an organic compound due to the complete transfer of shared pi electron pairs to one of the atoms under the influence of an attacking reagent is referred to as the Electromeric effect.

+E effect:

This effect occurs when the electron pair of the pi bond is moved towards the attacking reagent. The +E effect can be observed in the addition of acid to alkenes. The attacking reagent attaches itself to the atom which obtained an electron pair in the transfer.

**-E Effect:**

This effect occurs when the electron pair of the pi bond is moved away from the attacking reagent. The attacking reagent attaches itself to the positively charged atom in the molecule, i.e. the atom which lost the electron pair in the transfer.



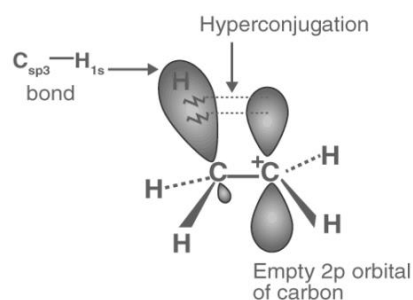
Scan here to watch about Electromeric effect.



Hyperconjugation:

Hyperconjugation is the stabilising interaction that results from the interaction of the electrons in a σ -bond (usually C-H or C-C) with an adjacent empty or partially filled p-orbital or a π -orbital to give an extended molecular orbital that increases the stability of the system.

From the figure, we observe that one of the three C-H bonds of the methyl group can align in the plane of the empty p orbital and the electrons constituting the C-H bond in a plane with this p orbital can then be delocalized into the empty p orbital.



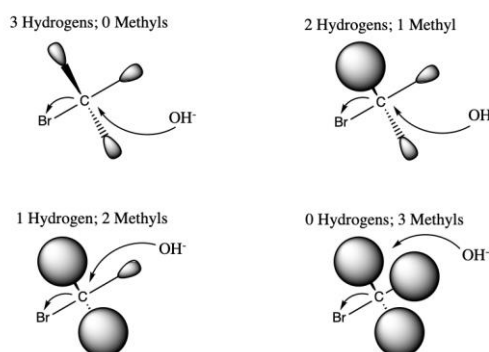
Scan here to watch about Hyperconjugation



Steric Effects:

Steric hindrance is to describe how a molecule's physical structure can affect its ability to react. When a molecule is bulky, meaning it has multiple bonds to compounds or groups other than hydrogen, it can slow down or even prevent another molecule in the desired reaction.

Eg: A simple way to see the effects of steric hindrance is in a reaction between a nucleophile and an electrophile. We can use the same nucleophile, HO^- , and change the bulk of the electrophile by adding more CH_3 groups. As shown in the diagram below, as more methyl groups are added to the molecule, there is less space for the covalent bond to the electrophile to form. Therefore, as the steric bulk increases, a molecule can be hindered from performing different reactions.



Homolytic fission:

Homolytic fission is a type of bond fission that involves the dissociation of a given molecule wherein one electron is retained by each of the original fragments of the molecule. Therefore, when a neutrally charged molecule is subjected to homolytic fission, two free radicals are obtained as the product



Heterolytic fission:

Heterolytic fission is a type of bond fission in which a covalent bond between two chemical species is broken in an unequal manner, resulting in the bond pair of electrons being retained by one of the chemical species.

When a neutrally charged molecule undergoes heterolytic fission, one of the products will have a positive charge whereas the other product will have a negative charge.