Mesomeric effect :-

The mesomeric effect takes place in unsaturated and specially in conjugated system via their π orbitals. For example, consider a carbonyl group whose all of the properties can neither satisfactorily be represented by the classical formula, I nor by extreme polar structure, II (which is attend attained due to transference of electrons to oxygen atom owing to its greater electronegativity.)

$$>C=O \qquad >\overset{+}{C}-\bar{O} \qquad >C\overset{\cdot\cdot}{=}O$$

I II III

The actual structure seems to lie somewhat in between the two forms I and II, it is a resonance hybrid of the above two extreme limits. The resonance hybrid may best be represented by the structure III in which π electrons are drawn preferencially towards oxygen rather than carbon. Now if the carbonyl group is conjugated with c=c type of system, the above polarisation is transmitted further via the π electrons.

$$H_3C-CH=CH-CHO \longleftrightarrow H_3C-CH=\overset{+}{C}H-\bar{O} \longleftrightarrow$$

$$H_3C-\overset{+}{C}H-CH=CH-\bar{O}.$$

$$H_3C-CH-CH-CH=O$$

This type of displacement of electrons may be also be caused by the presence of an hetatom having at least one lone pair of electrons in conjugated system. e.g.

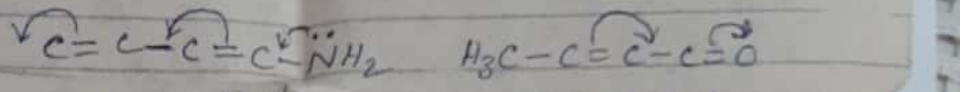
$$R_2\ddot{N}-CH=CH-CH=CH-CH_3 \longleftrightarrow$$

$$R_2\overset{+}{N}=CH-CH=CH-\bar{C}H-CH_3$$

the two extreme forms

Thus mesomeric effect may be defined as the permanent effect in which π electrons are transferred from a multiple bond to an atom, or from a multiple bond to a single covalent bond or lone pair(s) of p-electrons from an atom to the adjacent single covalent bond. In case the compound in question is having conjugated system of double bonds, the mesomeric effect is transmitted through whole of the conjugated system and thus the effect may better be known as conjugative effect

Like inductive effect, the mesomeric effect ~~(denoted~~ (denoted by m) may be +M and -M. It is +M when the transference of electron pair is away from the atom; and -M when transference of electron pair is towards the atom In general,



+M effect -M effect

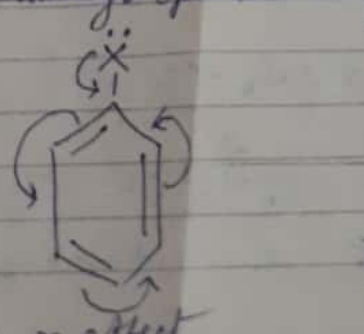
Some common atoms or group which cause +M and -M effect are given below.

+M groups $-Cl$, $-Br$, $-NH_2$, $-R_2N$, $-OH$, $-OCH_3$

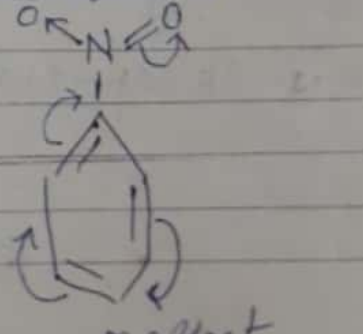
-M groups $-NO_2$, $-C\equiv N$, $>C=O$

The effect is of common occurrence in ~~arom~~ aromatic compounds where the group $\ddot{X}$ with unshared pair of electrons is attached ~~with~~ directly to the phenyl group and thus the lone pair of electrons becomes conjugated with the benzene nucleus and compound exert +M effect.

~~Since mesomeric effect is a permanent effect and always operates in a non rea~~



+M effect

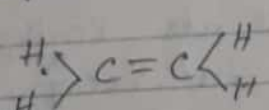


-M effect

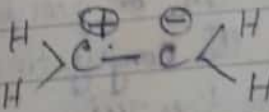
Since mesomeric effect is a permanent effect and always operates in a reagent molecule, it, like inductive effect, affects the physical properties of a molecule.

Electromeric effect:

This type of temporary displacement of electrons takes place in compounds containing multiple covalent bonds (e.g. C=C, C=O, C≡N etc) or an atom with a lone pair of electrons adjacent to a covalent bond. The effect involves complete transference of a pair of electrons from a multiple bond to an atom, or from a multiple bond to another bond, or from an atom with a free pair of electrons to a bond. It is the π electrons of a multiple bond or the p-electrons of an atom, which are transferred. Since the effect involves complete transference of electrons, it lead to the development of full + and − charges within the molecule. It is important to note that the electromeric effect is purely a temporary effect and is brought into play only at the requirement of attacking reagent; it vanishes out as soon as the attacking reagent is removed from reaction mixture. For example,



(a) Ethylene molecule before adding the reagent



(b) Ethylene molecule after adding the reagent

In the above examples as soon as the attacking reagent is removed, the charged molecule (b) reverts into its original condition (a).

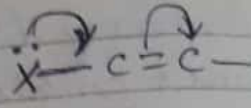
The electromeric effect takes place in the direction of the more electronegative atom and is generally shown by the curve arrow, starting at the original position of the electron pair and ending to the new position (attained by migration) of electron pair, e.g.

in the carbonyl group it operates as

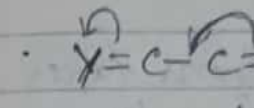
$>\overset{\curvearrowright}{C}=O \rightleftharpoons >\overset{+}{C}-\overset{-}{O}$ and not as $>\overset{\curvearrowright}{C}=O \rightleftharpoons >\overset{-}{C}-\overset{+}{O}$

The electromeric effect is represented by the symbol E which may be +E when when the displacement of electron pair is away from the atom or groups or -E when the displacement is towards the atom or group.

eg;



+E effect
(displacement away from atom X)



-E effect
(displacement towards group Y)

Now, since the electromeric effect takes place only at the requirement of reagent it always facilitates the reaction but never inhibits it. It is important to note that when the inductive effect and electromeric effects are operating in a molecule but in the opposite directions, it is the electromeric effect that usually overcomes the inductive effect.

The electromeric effect is of common occurrence during adding of polar reagents on C=C and C=O bonds.

The combined mesomeric and electromeric of the atom or group is known as its conjugative effect. Since the conjugative effect was first recognized in connection with the phenomina of tautomerism. It was previously known as (±T).