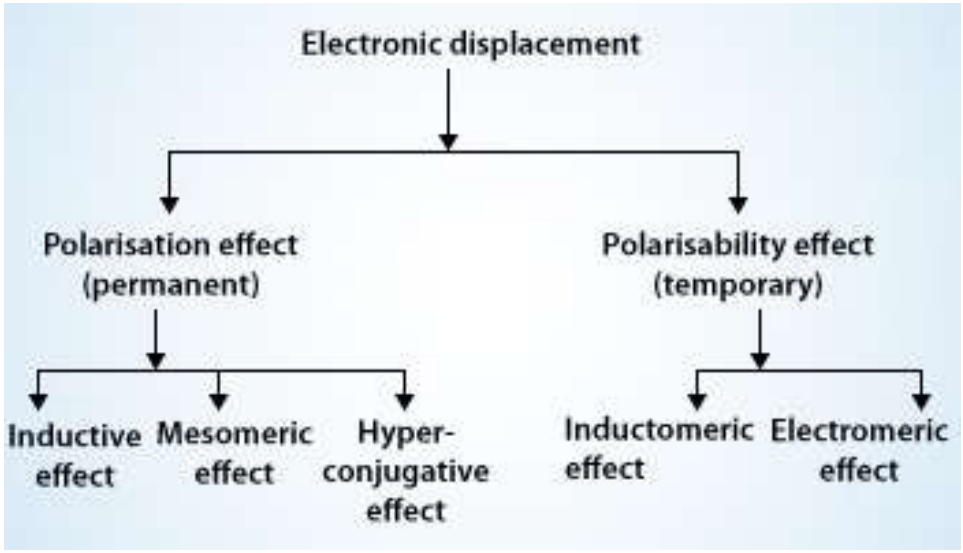
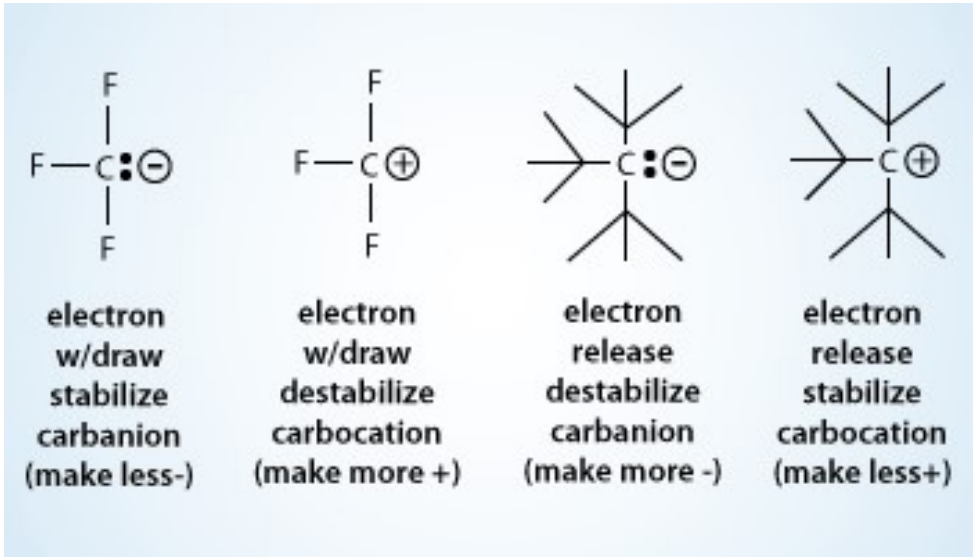
ELECTRONIC DISPLACEMENTS



The reagent attacking on a covalent bond, bears always either a negative or a positive charge. For a reaction to take place with the reagent on the covalent bond, the latter should possess opposite charge centers to that of reagent molecule. The substrate molecule is usually an electrically neutral molecule. It should develop polarity on some of its carbon atoms or substituents connected together. This is made possible by the displacement of the bonding electrons.

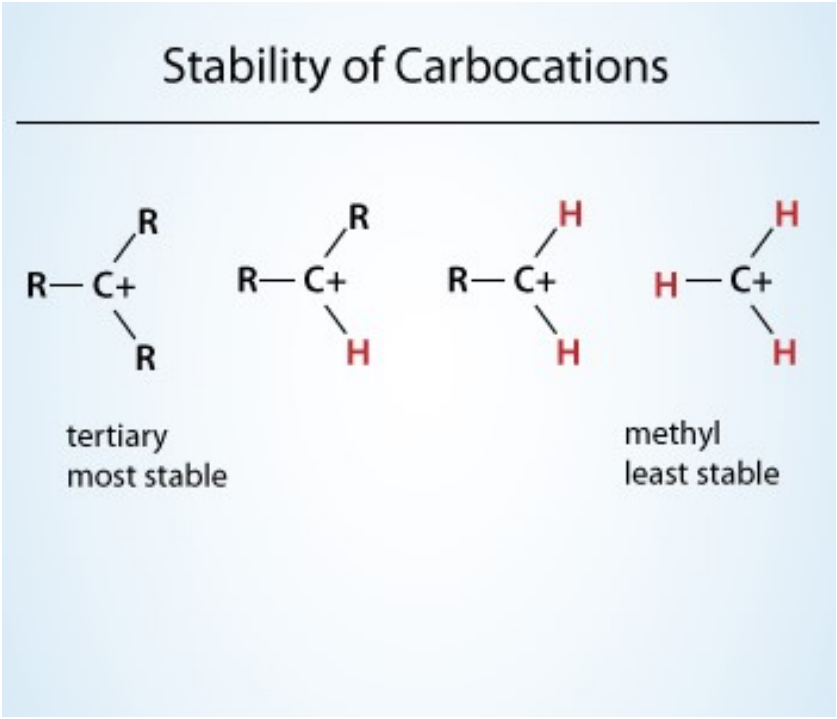
The electronic displacement in molecules may be due to certain effects, some of which are permanent (Inductive and Mesomeric effects) and others are temporary (Electromeric effect). The former effects are permanently operating in the molecule and are known as polarization effects, while the latter are brought into play by the attacking reagent.As soon as the attacking reagent is removed, the electronic displacement disappears. Such effects are known as the polarizability effects.



INDUCTIVE EFFECT.

Inductive effect:

Inductive effect may be defined as the permanent displacement of electrons forming a covalent bond towards the more electronegative element or group. The inductive effect is represented by the symbol →, the arrow pointing towards the more electronegative element or group of elements. This inductive effect is divided into two types depending on their strength of electron withdrawing or electron releasing tendency with respect to hydrogen.



POSITIVE INDUCTIVE EFFECT

Alkyl groups show positive inductive effect. Positive inductive effect stabilizes the carbocation, so if number of alkyl groups attached is more that is a stable carbocation.

Negative Inductive Effect:

Any atom or group attracting electrons more strongly than hydrogen is said to have a –I effect (electron–attracting or electron–withdrawing). Ex: NO_2, Cl, Br, I, F, COOH, OCH_3 etc.,

The atoms or groups which cause negative inductive effect, in the order of decreasing effect are as follows:

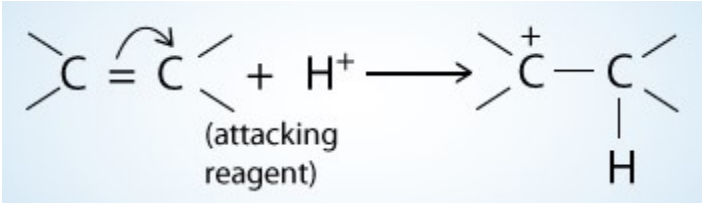
$N^+(CH_3)_3 > NO_2 > CN > F > COOH > CI > Br > I > CF_3 > OH > OCH_3 > C_6H_5 > H$

Positive inductive effect(Electron donating):

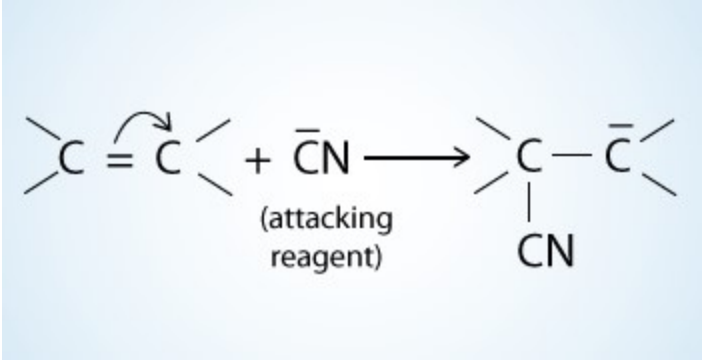
If an atom or group attracts electrons less strongly than hydrogen, it is said to have +I effect (electron repelling or electron–releasing). Ex: CH_3, C_2H_5, Me_2CH and Me_3C groups. As the number of alkyl groups attached to carbon increases, the positive inductive effect increases.

Groups in the decreasing order of their +I effect:

$(CH_3)_3C > (CH_3)_2CH > CH_3CH_2CH_2 > CH_3 > H$



Positive Electromeric Effect (+R effect).In this effect the p–electrons of the multiple bond are transferred to that atom to which the reagent gets attached.



Negative Electromeric Effect (–E effect). In this effect the Π – electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached.

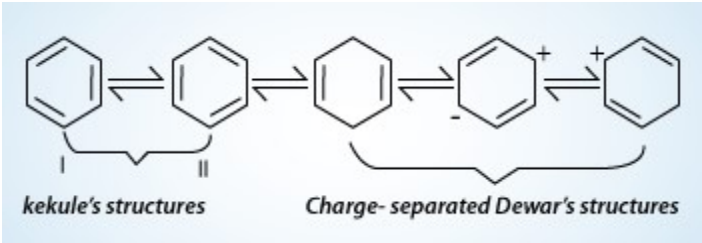
Electromeric effect:

The movement of electrons from one atom to another at the demand of attacking reagent in multi bonded atoms is called electromeric effect, denoted as E effect. This type of temporary displacement of electrons take place in compounds containing multiple covalent bonds (Eg: 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 transfer of Π–electrons of a multiple bond, or the Π–electrons of an atom, with in the molecule. It leads to the development '+' and '–' charges in the molecule.

The electromeric effect is purely a temporary effect and is brought into play only when the molecules containing multiple bonds or an atom with a lone pair of electrons adjacent to covalent bond are treated with attacking reagent. It vanishes as soon as the attacking reagent is removed from reaction mixture.



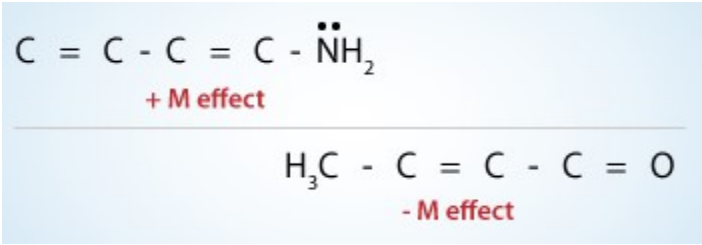
RESONANCE HYBRID STRUCTURES OF BENZENE

Since, the forms I and II are the most contributing, hence benzene is represented as a hybrid structure of these two structures

Resonance and Mesomeric Effect:

The phenomenon in which two or more structures can be written for the true structure of a molecule, but none of them can be said to represent it uniquely, is referred to as resonance or mesomerism. The true structure of the molecule is said to be a resonance hybrid of the various possible alternative structures which themselves are known as resonating structures or canonical structures.

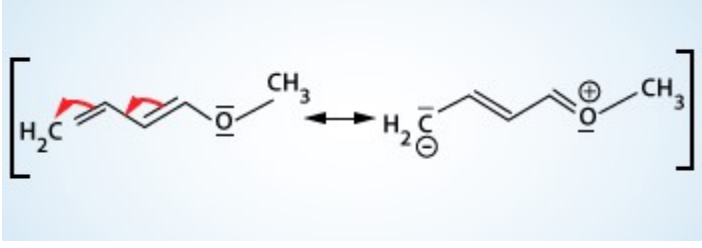
Every two adjacent resonating structures are represented by inserting a double headed arrow between them. The actual structure of benzene may be represented in two ways as shown in the adjacent figure.



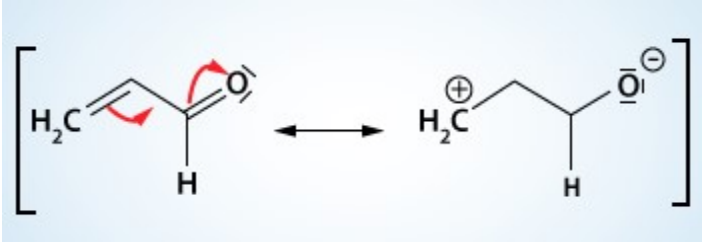
Necessary conditions for resonance:

- All the resonating structures must have the same arrangement of atomic nuclei.
- The resonating structures must have the same number of paired and unpaired electrons. However, they differ in the way of distribution of electrons.
- The energies of the various limiting structures must be same or nearly the same.
- Resonating structures must be planar.

All the resonating structures do not contribute equal to the real molecule and hence only the major contributing forms are used while representing a resonance hybrid.



+M EFFECT OF A METHOXY GROUP IN AN ETHER

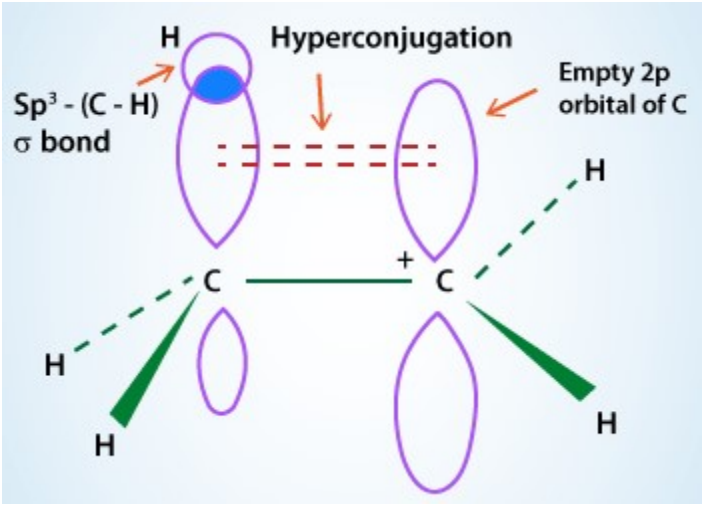


−M EFFECT OF A CARBONYL GROUP IN PROP–2–ENAL

The mesomeric effect may be defined as the permanent effect in which p electrons are transfered 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.

Like inductive effect, the mesomeric effect (denoted by M) may be +M and −M. +M effect is shown by groups containing lone pair of electrons such as – Cl, – Br, – I, – NH_2, – NR_2, – OH, – OCH_3 etc. –M effect is shown by the groups containing electro negative atoms such as – NO_2, – CN, > C = O.

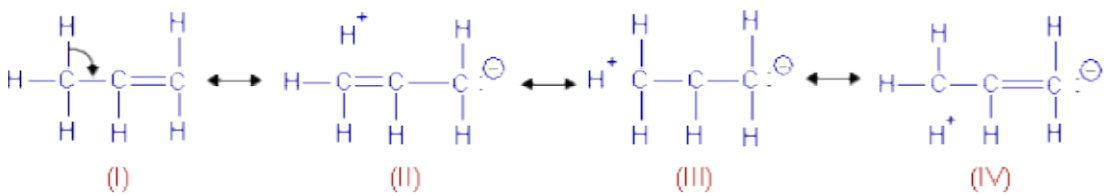
Some common atoms or groups which cause +M and –M effects are given below: Positive mesomeric effect, +M groups: – Cl, – Br, – I, – NH_2, – NR_2, – OH, – OCH_3. Negative mesomeric effect, –M groups: – NO_2, – CN, > C = O.



Hyper conjugation:

Alkyl groups with at least one hydrogen atom on the α–carbon atom, attached to an unsaturated carbon atom(H – C – C = C system), are able to release electrons by a mechanism similar to that of the electromeric effect. This process of transfer of electrons participating in a single bond into the adjacent p–orbitals is known as hyper conjugation.

The delocalization involves s and p orbitals (or p orbitals in case of free radicals). Thus it is also known as s–p conjugation.



No bond resonance structures shown by propene due to hyperconjugation.