

# CHEMISTRY

**Live** eBook



## 01. Resonance

If a single structure can not explain all of the properties of a molecule then more than one structures are required then it is said that molecule is showing resonance. It is due to the delocalization of electrons within the molecule.

All the contributing structures in the resonance are called **resonating structures** or **canonical structures**.

- These structures are helpful in explanation of chemical reactivity or the chemical reaction of the compound.
  - (i) Resonating structures are not the real structures.
  - (ii) The real structure is a hybrid of all resonating structures which is called as **resonance hybrid**.

## 02. Conditions for Resonance

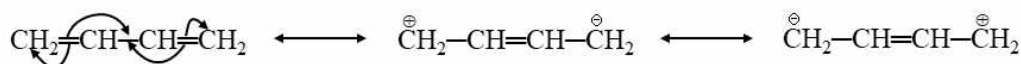
- (i) System must be planar.
- (ii) System must be in conjugation (i.e. parallel p orbitals are required)

Following type of conjugation may be present in a molecule :-

- (i)  $\pi \rightarrow \pi$  conjugation :

If there are two  $\pi$  bonds at alternate positions then  $e^-$  of one  $\pi$  bond are transferred towards another  $\pi$  bond. (According to I-effect).

*Example*



- (ii) Lone pair  $\rightarrow \pi$  conjugation :

If there is one lone pair or a negative charge and one  $\pi$  bond are at alternate position then  $e^-$  of lone pair or negative charge are transferred towards  $\pi$  bond.

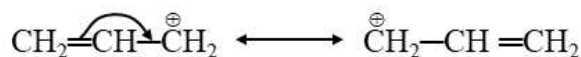
*Example*



- (iii)  $\pi \rightarrow +ve$  charge conjugation :

If there is one positive charge and one  $\pi$  bond are at alternate position then  $e^-$  of  $\pi$  bond are transferred towards positive charge.

*Example*



- (iv)  $\pi \rightarrow$  unpaired  $e^-$  conjugation :

If there is one free  $e^-$  and one  $\pi$  bond are at alternate position.

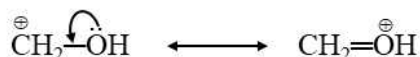
### Example



(v) **Lone → +ve charge conjugation :**

If there is one lone pair or negative charge and one positive charge are at adjacent atoms then  $e^-$  of lone pair or negative charge are transferred towards positive charge.

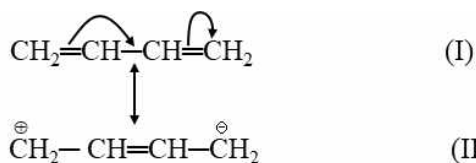
### Example



## 03. Deciding the Most Stable Canonical Form

Following conditions will correspond towards the determination of most stable canonical form:-

- (i) More the no. of covalent bonds/ $\pi$  bonds in the structure, more stable the canonical form is



(I) → no. of covalent bonds ⇒ 11  
no. of  $\pi$  bonds ⇒ 2

(II) → no. of covalent bonds ⇒ 10  
no. of  $\pi$  bonds ⇒ 1

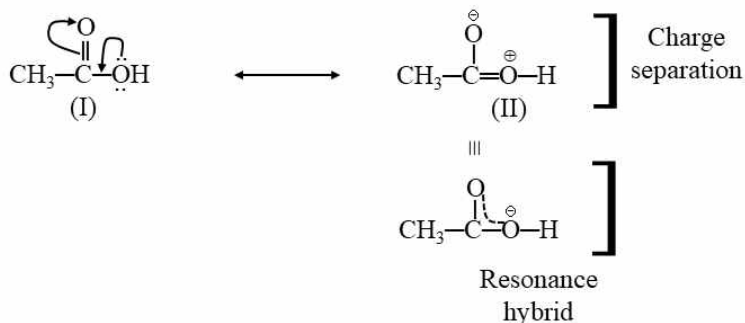
∴ I > II

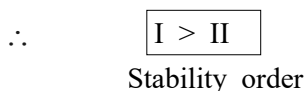
Stability order

- (ii) Indistinguishable structures contribute equally towards the resonance energy.

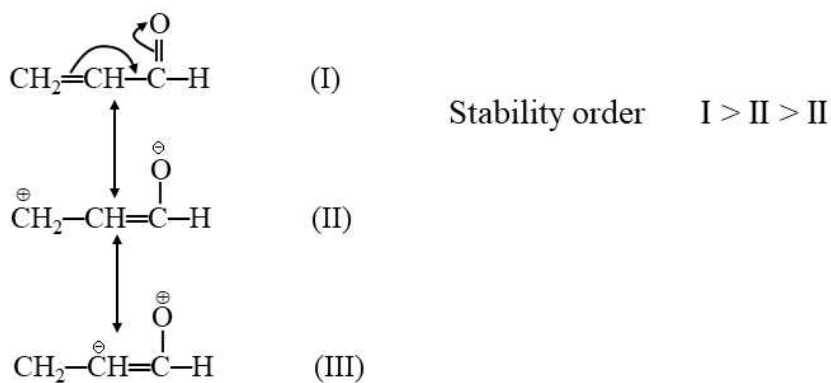


- (iii) More the charge separation i.e. the distance between the positive and negative charges in the resonance structure, more unstable is the canonical form

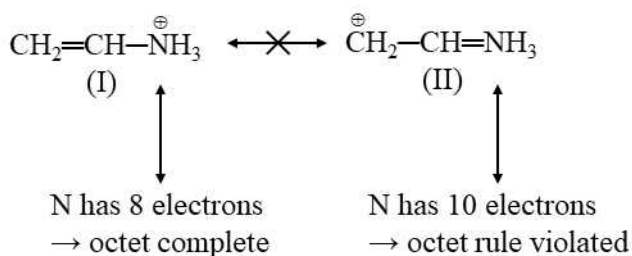




- (iv) Structures with positive charge on electronegative atom and negative charge on electropositive atom contribute least



- (v) In case of atoms of the second period in the periodic table, such resonance structures which violate the octet rule should not be considered.



∴ (II) → not a resonating structure.

#### 04. What are EWG & ERG?

##### Electron withdrawing groups (EWGs)

The groups/substituents which have tendency to attract shared pair of electrons or have positive charge over them.

eg :  $\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{COOH}$ ,  $-\text{CHO}$  etc.

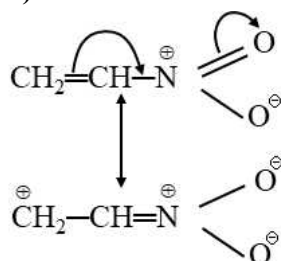
##### Electron releasing groups (ERGs)

The groups/substituents which have tendency to donate the extra lone pair of electrons present with them or have negative charge over them

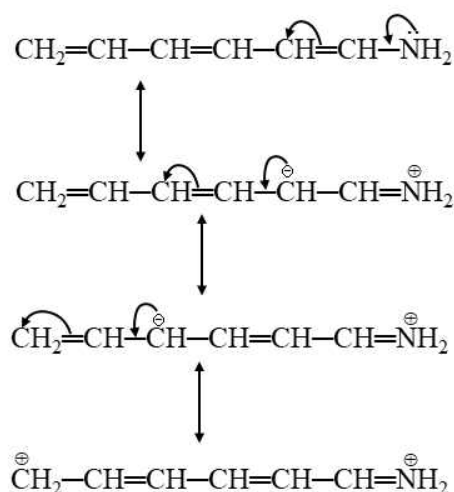
eg :  $(\text{CH}_3)_3\text{C}-$ ,  $(\text{CH}_3)_2\text{CH}-$ ,  $-\ddot{\text{N}}\text{H}_2$ ,  $-\ddot{\text{O}}\text{H}$ , etc

## 05. Resonance Effect/Mesomeric Effect

- Polarity developed in conjugate system by the complete transfer of non-bonding electron or  $\pi$ -bond electron due to the group or atom attached with conjugated system is known as mesomeric effect.
- If transfer of  $\pi$ -bond electron takes place from conjugated system to group then it is known as **negative mesomeric (-M)** effect.



- For  $-M$  effect, group should have either positive charge or should have vacant orbital.
- Due to  $-M$  effect positive charge comes over conjugate system or due to  $-M$  effect electron density decrease in conjugate system, such type of conjugate system will be more reactive towards nucleophile or will be less reactive towards electrophile.
- **Group which shows  $-M$  effect are -**  
 $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{CHO}$ ,  $-\text{COR}$ ,  $-\text{COOH}$ ,  $-\text{COOR}$ ,  $-\text{COX}$ ,  $-\text{CONH}_2$  etc.
- If transfer of non bonding electron takes place from group to conjugate system then it is known as positive **mesomeric (+M)** effect.



- For  $+M$  effect, group should have either be lone pair of electron or should have negative charge.
- Due to  $+M$  effect negative charge comes over conjugate system or electron density increase on conjugate system such type of conjugate system will be more reactive towards electrophile or will be less reactive towards nucleophile.
- **Group which shows  $+M$  effect are -**  
 $-\overset{\ominus}{\text{O}}$ ,  $-\overset{\ominus}{\text{NH}}$ ,  $-\text{NR}_2$ ,  $-\text{NHR}$ ,  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{OR}$ ,  $-\text{SH}$  -  $\text{SR}$ ,  $-\text{F}$ ,  $-\text{Cl}$ ,  $-\text{NHCOR}$ ,  $-\text{O}-\text{COR}$  etc.

- In mesomeric effect polarity or charge migrate from one end to another end. During charge transfer, energy releases from the conjugate system which increase the stability of conjugate system also.

## 06. Applications of Resonance Effect

(a) **Acidic strength :**

$$\text{Acidic strength} \propto -M \propto -I \propto \frac{1}{+M} \propto \frac{1}{+I}$$

(b) **Basic strength :**

If there is more resonance of lone pair or negative charge then it will be more stable, means less basicity.

$$\text{Basic strength} \propto +M \propto +I \propto \frac{1}{-M} \propto \frac{1}{-I}$$