

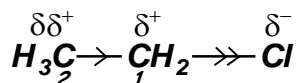
# STRUCTURE AND REACTIVITY: BASIC CONCEPTS

## INDUCTIVE EFFECT

The polarization of a bond induced by an adjacent polar bond is known as the Inductive Effect.

### Explanation

Consider the following molecule



Since, electronegativity of Cl is more than C, therefore, Cl attracts shared pair of electrons more towards itself. As a result, Cl acquires  $\delta^-$  charge and C acquires  $\delta^+$  charge and bond becomes polar. In order to remove the deficiency of electron density on carbon, it attracts electron density of second carbon atom, which thus acquires positive charge. However, this +ve charge on second carbon is less than on first C. Thus, this bond also becomes polar. Such type of polarization is called Inductive Effect.

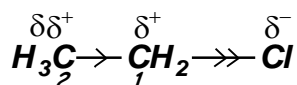
If there is a longer carbon chain in the compound. This effect operates through the chain

### Points To Be Noted

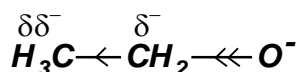
- Inductive effect operates through sigma bond
- Inductive effect goes on decreasing through the chain and practically disappears after four bonds.
- Electrons are not actually shifted from one atom to other. Instead it is only an unequal sharing of electrons between atoms.

### Generation And Direction Of Inductive Effect

Inductive effect may be generated by a permanent dipole as explained above

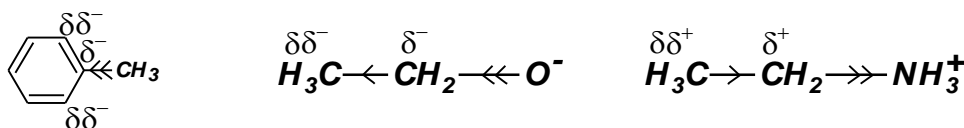


Inductive effect may also be generated by a formal charge



Direction of inductive effect may be from carbon chain to Functional group and vice versa.

### Classification Of Groups On The Basis Of Inductive Effect.



C - H is almost non-polar and carbon and hydrogen equally share electron density of bond. Based on this fact, all functional groups can be classified into electron withdrawing (-I) and electron donation (+I) groups relative to H.

A brief list of these groups, in approximately decreasing order of their strength is given below.

Electron-withdrawing groups (-I) :  $^+NR_3$ ,  $^+NH_3$ ,  $NO_2$ ,  $CN$ ,  $CO_2H$ ,  $F$ ,  $Cl$ ,  $Br$ ,  $I$ ,  $OAr$ ,  $CO_2R$ ,  $OR$ ,  $COR$ ,  $OH$ ,  $C = CR$ ,  $Ar$ ,  $CH = CR_2$

Electron-donating groups (+I)  $O^-$ ,  $CO_2^-$ ,  $CR_3$ ,  $CHR_2$ ,  $CH_2R$ ,  $CH_3$ ,  $D$

### Applications

The concept of inductive effect is widely used to explain behavior of organic compounds and organic reactions.

## Strengths of Acids

Strength of acid mainly depends upon the following factors.

- Ease of proton donation.

Generally, greater the ease with which a substance donates proton, stronger is the acid and vice versa.

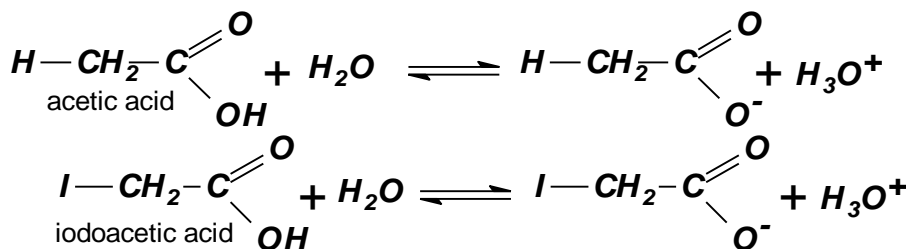
- Stability of Anion

Generally, greater the stability of anion formed after proton donation, stronger is the acid and vice versa.

### Example – 1

Iodoacetic Acid Is 50 Times More Stronger Than Acetic Acid.

Both Iodoacetic acid and acetic acid ionizes in water as

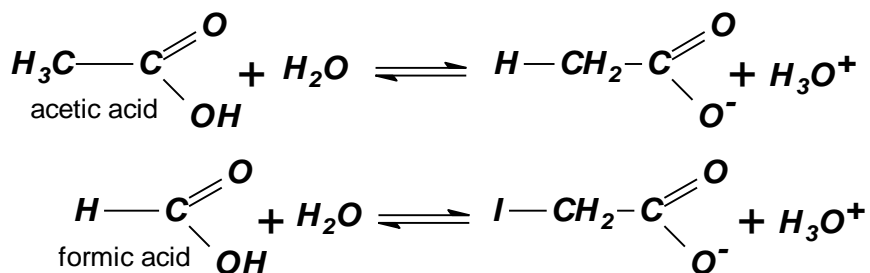


In iodoacetic acid, strong electron withdrawing effect of iodine makes the donation of proton easier. Further iodoacetate anion formed is better stabilized by strong  $-I$  effect of iodine. In acetic acid, no such ease of donation of proton and stabilization of anion is present. Hence iodoacetic acid is more stronger acid than acetic acid.

Similarly, chloroacetic acid is more stronger than iodoacetic acid. Because Cl is more electronegative than I. Therefore, Cl makes the proton donation easier and also stabilizes the anion formed better than I.

Formic Acid Is More Stronger Than Acetic Acid.

Both these acids ionizes as



$\text{CH}_3$  group in acetic acid is electron donating relative to H in formic acid. Thus methyl group makes proton donation difficult and also destabilizes the anion formed. Hence acetic acid is less acidic than formic acid.

## RESONANCE

The representation of real compound as a weighted average of two or more contributing structures is called resonance.

The real compound is called Resonance hybrid, and

The contributing structures are called resonance structures or canonical forms.

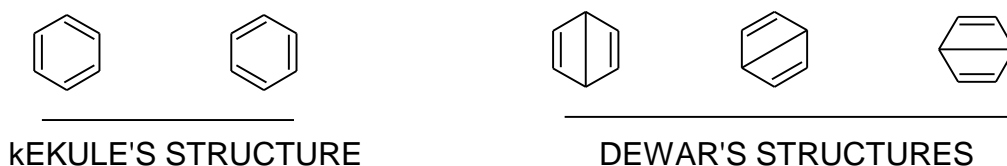
### Examples And Explanation

Consider the case of benzene. Kekule suggested following structure for benzene.

This structure shows that three C – C single bonds must have a bond length of  $1.54 \text{ \AA}$  and three C = C double bonds must have bond length of  $1.34 \text{ \AA}$ . But actually, all C to C bonds in actual benzene are identical with a bond length of  $1.42 \text{ \AA}$ . Further, above structure shows that benzene must decolorize  $\text{Br}_2$  and  $\text{KMnO}_4$  solutions like ethene. But it actually not happens. Thus above structure of benzene is not the actual structure.



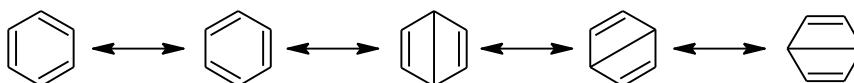
To explain this unusual behaviour of benzene, many structures were suggested for benzene.



Neither of the above structure can fully explain the actual behavior of benzene. Actual structure of benzene is in between the above structures. Thus benzene is represented by these structures in following way

This representation is called resonance. The structures are called resonance structures or canonical forms, while actual benzene is a resonance hybrid of these all structures.

Such type of unusual behaviour is very common among delocalized bonding systems.



### Points To Be Noted

- ❑ Each structure has a definite contribution towards actual molecule. Various canonical forms are not actual structures. They only exist in our theory.
- ❑ Actual molecule is a resonance hybrid of all the canonical forms.
- ❑ A resonance hybrid is always more stable ( lower energy ) than any of its canonical form.
- ❑ The difference of energy between a resonance hybrid and its most stable canonical form is called resonance energy.
- ❑ A double headed arrow is placed between canonical structures of a molecule.

Thus a delocalized chemical system is generally represented by more than one structures.

## RULES FOR WRITING RESONANCE STRUCTURES

Following rules are observed while writing resonance structures for a molecule.

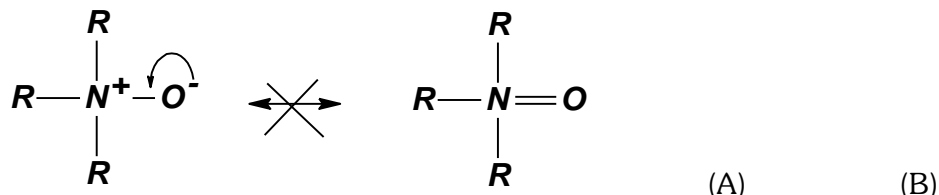
### 1) All The Structures Must Be Bonafied Lewis Structures.

i.e. Maximum number of covalent bonds that an atom can have are

1 for H          2 for halogen ( with +ve charge )          3 for oxygen ( with +ve charge )

4 for carbon    4 for nitrogen ( with +ve charge )

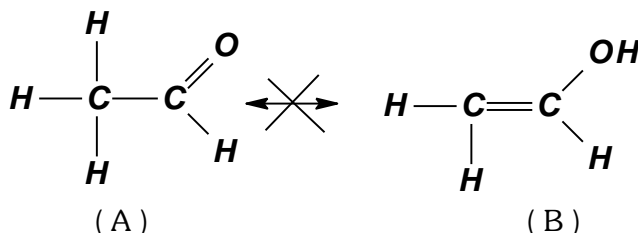
e.g.



Structure ( B ) is not a valid Lewis structure since it contains 5 covalent bond for nitrogen.

### 2) The Position Of Nuclei Must Be Same In All Canonical Forms

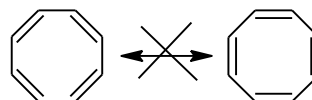
Various canonical forms are written only by delocalization of electrons.



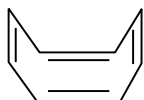
Structure ( B ) is not a valid canonical form of acetaldehyde since it involves the transfer of proton.

### 3) All The Atoms Involved In Resonance Must Lie In Same Plane, In Order To Have Maximum Overlap Between p – Orbitals.

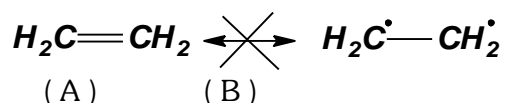
Cyclooctatetraene does not show resonance



Because cyclooctatetraene has a tub – shaped structure in which all the atoms do not lie in the same plane. Thus resonance is impossible.

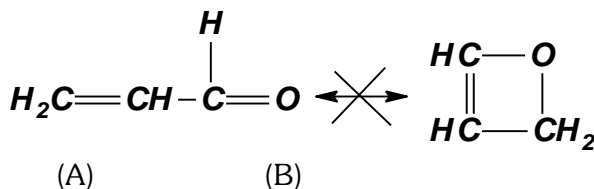


### 4) The Number Of Unpaired Electrons Must Be Same In All Canonical Forms.



Structure ( B ) is not possible, as it contains unpaired electrons. It is actually an excited form of ethylene.

### 5) Structure With Distorted Bond Angle And Bond Length Are Not Possible.

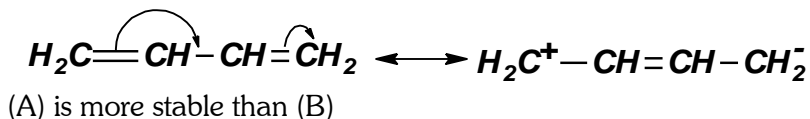


( B ) is not a canonical form of acrolein.

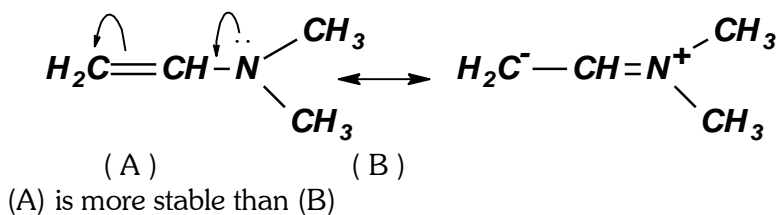
## CONTRIBUTION OF RESONANCE STRUCTURES

Various canonical forms of a compound contribute differently.  
Contribution of canonical forms can be judged by following rules.  
Other things being equal

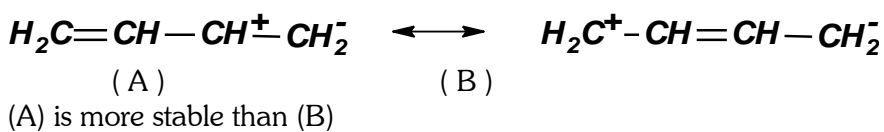
- 1) The Greater The Number of Covalent Bonds, The Greater The Stability.



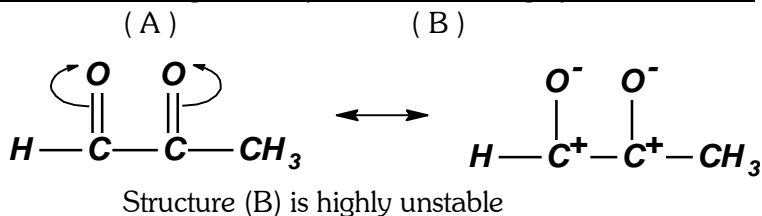
- 2) Structure Without Charge Are More Stable Than With Charge.



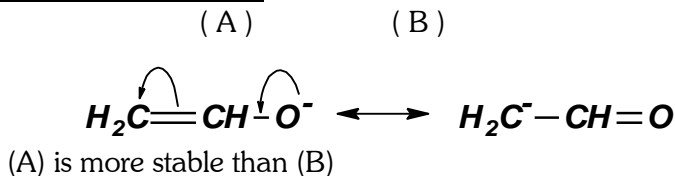
- 3) The less charge separation, The greater the stability.



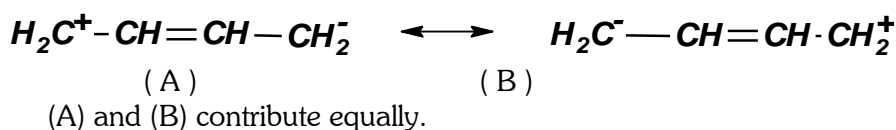
- 4) Structure with like charges on adjacent atoms is highly unfavourable.



- 5) Structure with negative charge on more electronegativity element are more stable than structure with Negative Charge On Less E.N. Element.



- 6) Equivalent Canonical Forms Contribute Equally.



## STABILITY OF RESONANCE HYBRID

The stability of a resonance hybrid can be decided by following simple rules

Greater the number of principal contributing forms

And

More nearly equal their contribution.

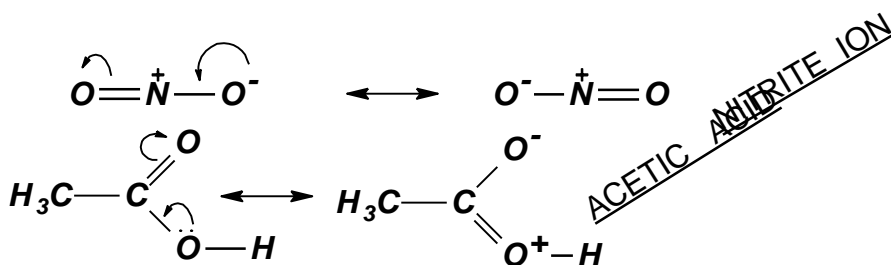
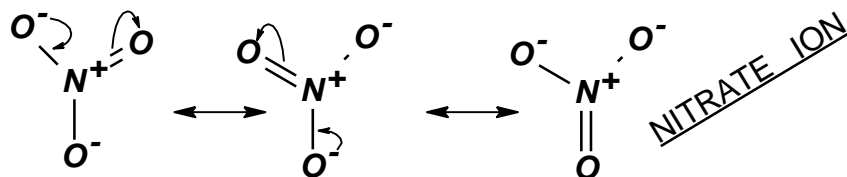
Greater the stability.

### Examples

#### □ Nitrate And Nitrite Ions

The canonical forms of nitrate and nitrite ion are given below.

Since nitrate ion has more canonical forms than nitrite ion, therefore, it is more stable than nitrite ion.s

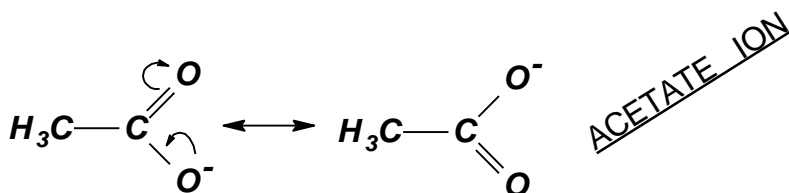


#### □ Acetic Acid And Acetate Ion.

Both acetic acid and acetate ion have two canonical forms each.

Since two canonical forms of acetate ion contribute equally while that of acetic acid not.

Thus acetate ion is more stable than acetic acid.



## RESONANCE ENERGY


The difference of energy between a resonance hybrid and its most stable canonical form is called Resonance Energy.

### Example And Explanation

Resonance energy of a compound can be estimated by comparing its observed heat of hydrogenation with that calculated for most stable canonical form.

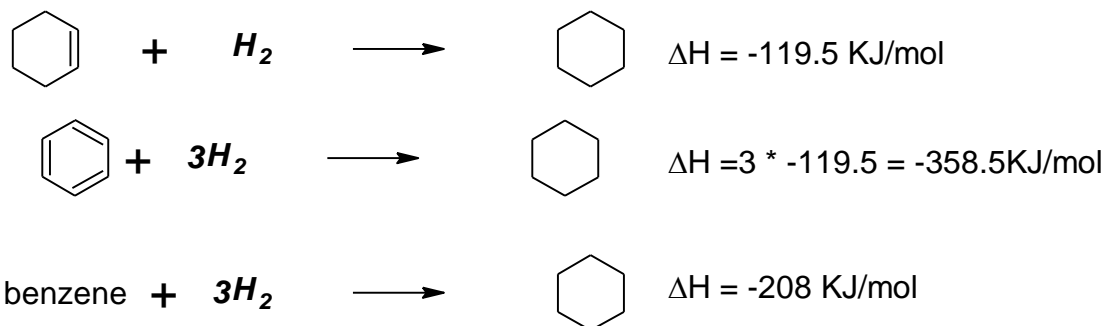
e.g.

Consider the case of benzene. It's most stable canonical form is cyclohexatriene.

For one double bond  heat of hydrogenation is approximately  $-119.5$  KJ/mol.  
Thus for 3 double bonds of cyclohexatriene heat of hydrogenation will be  $3 \times -119.5 = -358.5$  KJ/mol

Heat of hydrogenation of actual benzene is  $-208$  KJ/mol.

These can be summarized as



The difference is  $(-358.5) - (-208) = -150.5$  KJ/mol

The resonance energy of benzene is therefore  $150.5$  KJ/mol. Thus benzene is said to be resonance stabilized by an amount equal to  $150.5$  KJ/mol. This is called resonance energy.

### Points To Be Noted

The resonance energy increases as the number of principal canonical forms increases for a compound.  
e.g. Resonance energies for different aromatic compound is given below

Benzene	( 2 canonical forms )	150.5 KJ/mol
Naphthalene	( 3 canonical forms )	255 KJ/mol
Anthracene	( 4 canonical forms )	351 KJ/mol
Phenanthrene	( 5 canonical forms )	384.5 KJ/mol

More equally contributing are the canonical forms, greater the resonance energy.

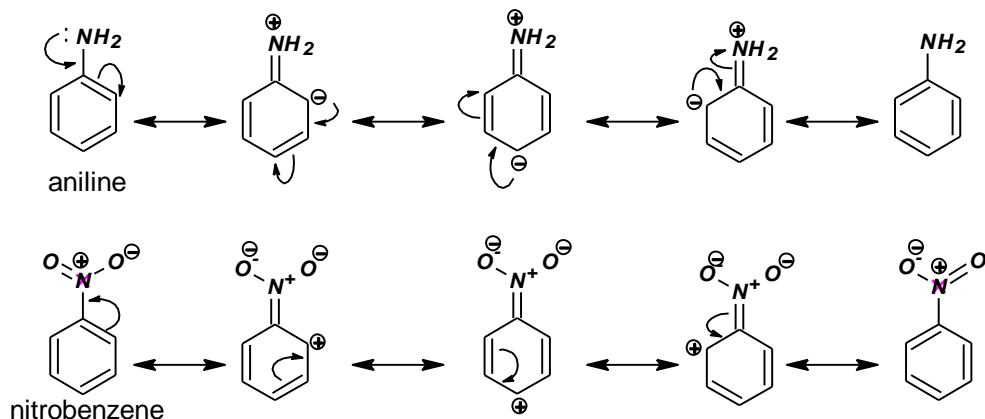
Generally, greater the resonance energy, more is the stability of a compound and vice versa.

## RESONANCE EFFECT OR MESOMERIC EFFECT

The decrease in electron density at one position in a molecule, with corresponding increase in electron density at some other position is called Resonance Effect or Mesomeric Effect.

### Examples And Explanation

In delocalized chemical systems, electron density spread over various atoms.  
e.g. consider the case of Aniline and nitrobenzene



In case of Aniline,  $-\text{NH}_2$  group donates electron to ring while in nitrobenzene, nitro group withdraws electrons from the ring. Thus mesomeric effect may be classified as positive or negative.

If a group donates electron, it is called electron donating group and indicated by  $+M$ .

If a group withdraws electrons, it is called electron withdrawing group denoted by  $-M$ .

Generally,

A group containing lone pair of electrons, attached to an unsaturated system donates electrons to unsaturated system. It is called electron donating group

A group containing a multiple bond, involving an E.N. atom, attached to an unsaturated system withdraws electrons from unsaturated system.

It is called electron withdrawing group.

Common  $+M$  and  $-M$  groups are given below.

Electron-donating groups ( $+M$ ):  $\text{O}^-$ ,  $\text{NR}_2$ ,  $\text{NHR}$ ,  $\text{NH}_2$ ,  $\text{OR}$ ,  $\text{OH}$ ,  $\text{OCOR}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{Cl}$ ,  $\text{F}$ ,  $\text{R}$ ,  $\text{Ar}$

Electron-withdrawing groups ( $-M$ ):  $\text{NO}_2$ ,  $\text{CN}$ ,  $\text{COOH}$ ,  $\text{COOR}$ ,  $\text{CONH}_2$ ,  $\text{CONHR}$ ,  $\text{CONR}_2$ ,  $\text{CHO}$ ,  $\text{COR}$ ,  $\text{Ar}$

### Points To Be Noted

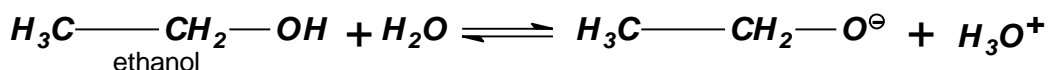
- A  $+M$  or a  $-M$  group causes resonance effect only when attached to an unsaturated system, because resonance effect operates through  $\pi$  - electrons.
- The electrons are not actually donated or withdrawn. Rather, it is only the change in distribution of electron density in the molecule.

### Applications

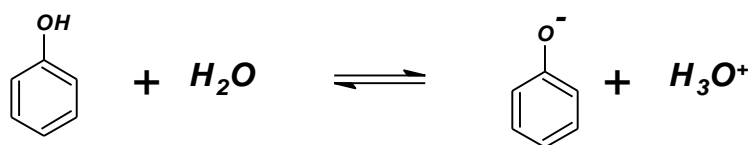
- Strength Of Acids

Phenol is a stronger acid than ethanol

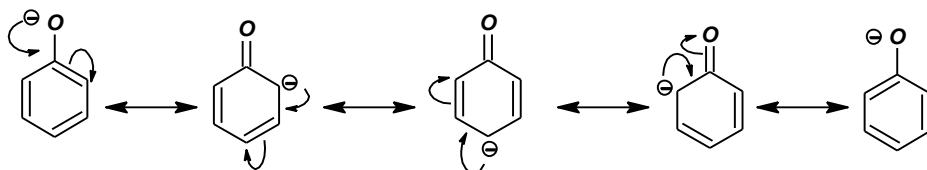
The acidity of both phenol and ethanol is due to the dissociation of  $\text{O}-\text{H}$  bond.







Greater acidity of phenol is due to greater stability of phenoxide ion, because phenoxide ion is resonance stabilized by delocalization of negative charge.

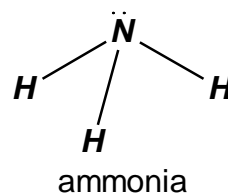
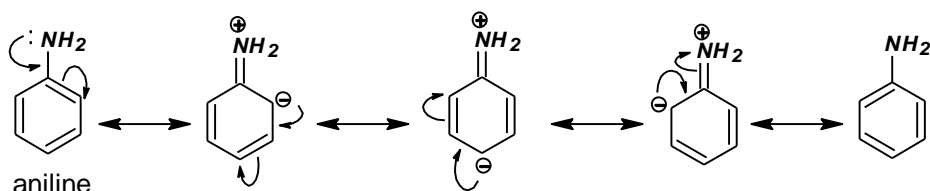


Such type of delocalization is not possible in ethoxide ion. Hence, phenol is more acidic than ethanol.

### Strength of Bases

#### ***NH<sub>3</sub> is more acidic than Aniline***

In Aniline lone pair of nitrogen is delocalized over the aromatic ring, hence it is not readily available to donate. But in NH<sub>3</sub>, lone pair is concentrated on nitrogen and can be easily donated. Hence, NH<sub>3</sub> is a stronger base than aniline.



## STERIC INHIBITION OF RESONANCE

According to rule of resonance

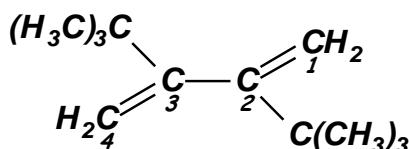
All the atoms involved in resonance must lie in the same plane ( i.e. coplanar ) in order to have maximum overlap between p – orbitals.

Any structural feature of a molecule, that disturbs the co – planarity of atoms, due to steric hindrance, results in the inhibition of resonance. This phenomenon is called steric inhibition of resonance.

### Examples

#### □ 2,3 – Diterbutyl Butadiene

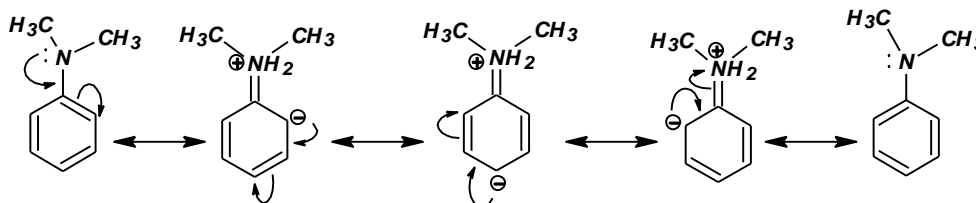
Bulky groups, present at 2 and 3 carbons twist the molecule resulting in the loss of co – planarity of C – 2 and C – 3 , thus resonance is inhibited between two conjugated double bonds.



#### □ 2,6,N,N – Tetramethyl Aniline Is More Stronger Base Than N,N – Dimethyl Aniline

In N,N – dimethyl Aniline, dimethyl amino group and aromatic ring are co-planar, thus lone pair of N is delocalized over the ring and is not readily available to donate.

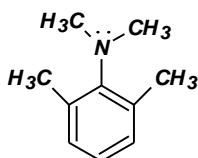
In 2,6,N,N – tetramethyl Aniline, two bulky groups present at the ortho position pushes the dimethyl amino



group out of the plane of aromatic Ring. Thus dimethylamino group and benzene ring does not remain co-planar and resonance is inhibited.

Hence, 2,6,N,N – tetramethyl Aniline is more stronger base than

N,N – dimethyl Aniline.

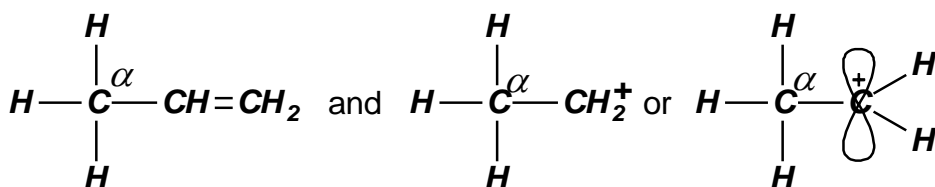


N,N,2,6-tetramethylaniline

## HYPERCONJUGATION

The conjugation of  $\sigma$  – electrons of a C – H bond with  $\pi$  – electrons of the unsaturated system or with  $\pi$  – orbital is called hyperconjugation.

Some examples of hyperconjugative systems are



### Examples And Explanation

In hyperconjugative system,  $\sigma$  – electrons of a C – H bond in a – carbon are delocalized with p – orbital of a C=C bond or a carbocation

e.g.

In structure, there is no bond between C and H. such type of delocalization is called no – bond resonance.

The hydrogen atom doesn't actually leave the molecule. Rather, net effect of no – bond resonance is that C – H bond become weaker than a normal C – H bond and there develops a double bond character between C – 2 and C – 3, resulting in strengthening and shortening of bond.

### Applications

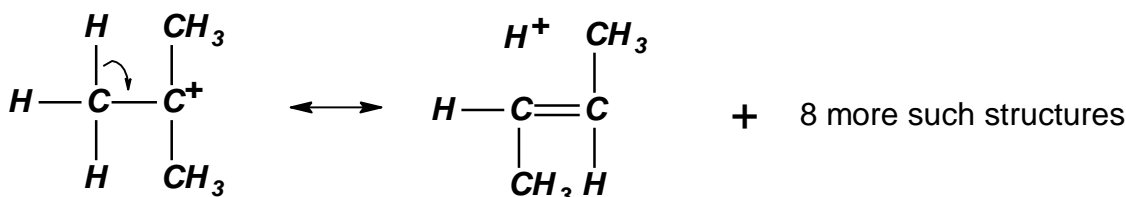
The concept of hyperconjugation has helped explain many phenomena.

#### □ Stabilities

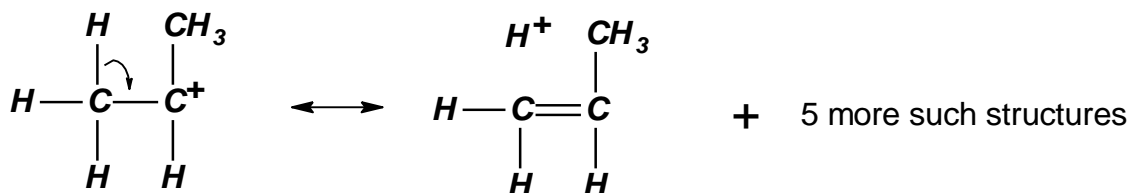
Ter Carbocation ( Or Ter Free Radical ) Is More Stable Than Secondary which in turn, is More Stable Than Primary.

It can be explained on the basis of hyperconjugation.

For ter – carbonium ion

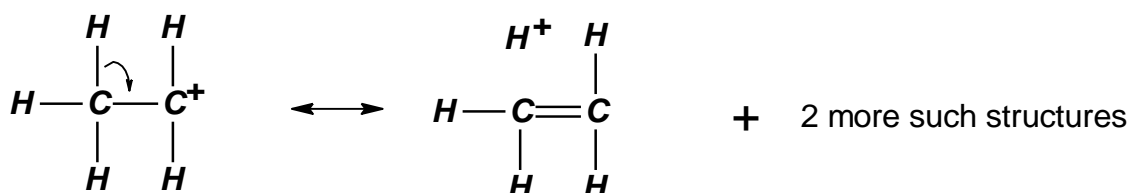


For sec – carbonium ion



For pri – carbonium ion

Since ter carbonium ion has more canonical forms than sec, which have more canonical forms than pri. And



since greater the number of principal canonical forms greater is the stability. Hence, order of stability of carbonium ions is

ter > sec > pri

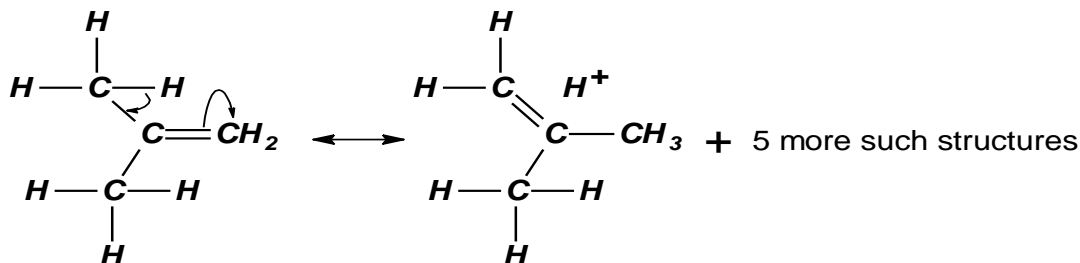
Similarly, for free radicals, the order of stability is also

ter > sec > pri

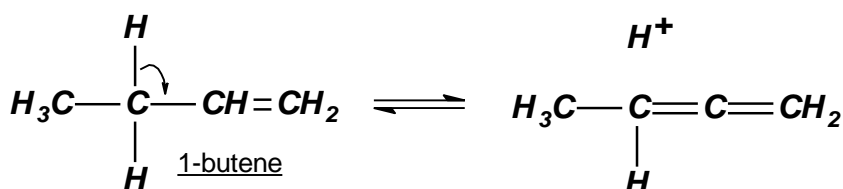
### Example – 2

#### Isobutylene Is More Stable Than 1 – Butene

For isobutylene



For 1 – butene

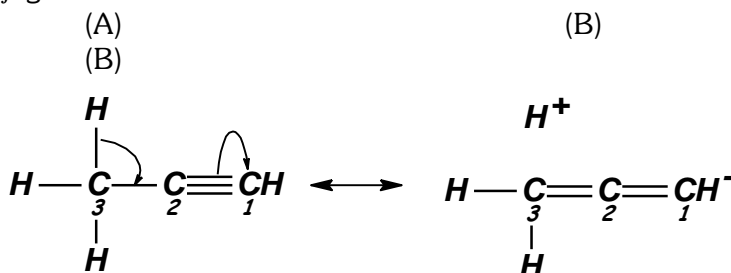


Since isobutylene has more canonical forms than 1 – butene. Therefore, isobutylene is more stable than 1 – butene.

### □ Bond Lengths

In 1 – Propyne  $\text{CH}_3 - \text{C}$  Bond Length Is Shorter (  $1.46 \text{ \AA}$  ) Than Expected (  $1.54 \text{ \AA}$  ).

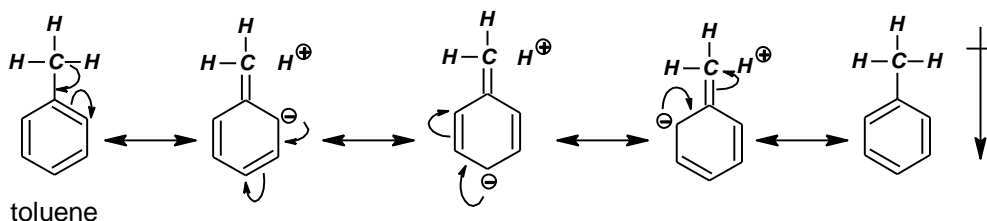
It is due to hyperconjugation



In structure (B), there develop on double bond character between C – 2 and C – 3, resulting in the shortening of bond than normal. Similarly, unusual bond energies for organic compounds has been explained on the basis of hyperconjugation.

### Dipole Moment

#### Toluene Has Dipole Moment Due To Hyperconjugation



Thus, in toluene, poles have been created due to hyperconjugation, which give rise to dipole moment for toluene.