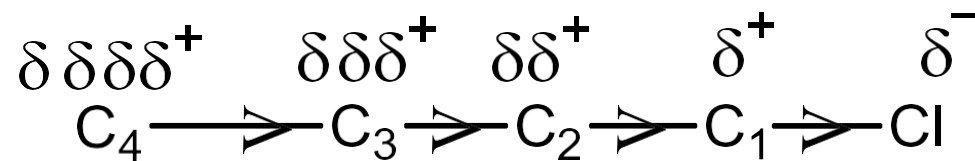


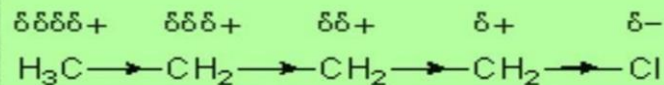
Inductive effect

It is defined as permanent displacement of an electron pair in a sigma bond towards more electronegative atom or group in a carbon chain is called as Inductive effect.

- It arises due to electro negativity difference between two atoms forming sigma bond
- It is transmitted through sigma bonds and its effect decreases as the carbon chain length increases, significant up to 3 or 4 carbon atoms after that it is negligible.
- It is denoted by \rightarrow



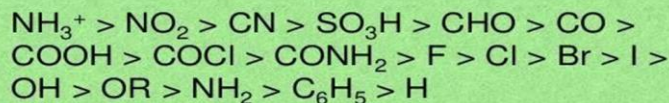
- Inductive effect weakens away along the chain and is not significant beyond 3rd carbon atom



TYPES OF INDUCTIVE EFFECT

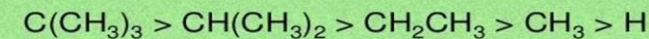
1) Negative inductive effect (-I):

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:



2) Positive inductive effect (+I):

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.

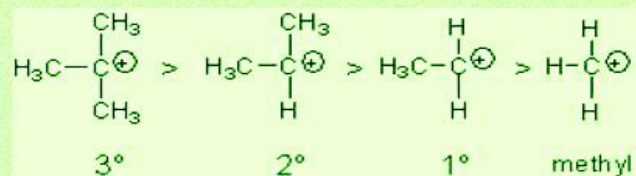


• APPLICATIONS OF INDUCTIVE EFFECT

1. Stability of carbocations:

The stability of carbocations increases with increase in number of alkyl groups due to their +I effect. The alkyl groups release electrons to carbon, bearing positive charge and thus stabilizes the ion.

The order of stability of carbocations is :



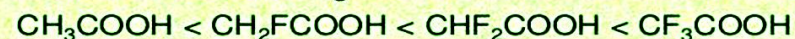
3. Acidic strength of carboxylic acids and phenols:

The electron withdrawing groups (-I) decrease the negative charge on the carboxylate ion and thus by stabilizing it. Hence the acidic strength increases when -I groups are present.

However the +I groups decrease the acidic strength.

E.g.

i) The acidic strength increases with increase in the number of electron withdrawing Fluorine atoms as shown below.

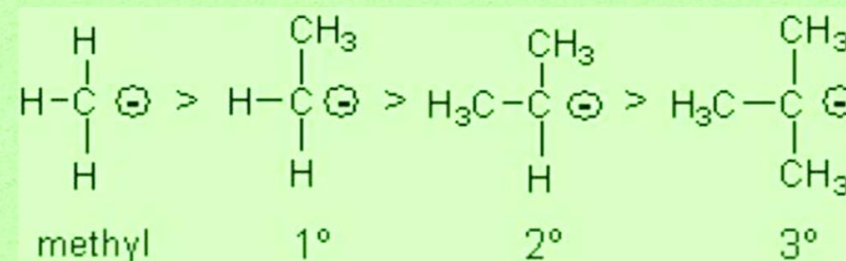


ii) Formic acid is stronger acid than acetic acid since the $-\text{CH}_3$ group destabilizes the carboxylate ion.

2. Stability of carbanions:

However the stability of carbanions decreases with increase in the number of alkyl groups since the electron donating alkyl groups destabilize the carbanions by increasing the electron density.

Thus the order of stability of carbanions is:



4. Basic strength of amines: The electron donating groups like alkyl groups increase the basic strength of amines whereas the electron withdrawing groups like aryl groups decrease the basic nature. Therefore alkyl amines are stronger Lewis bases than ammonia, whereas aryl amines are weaker than ammonia.

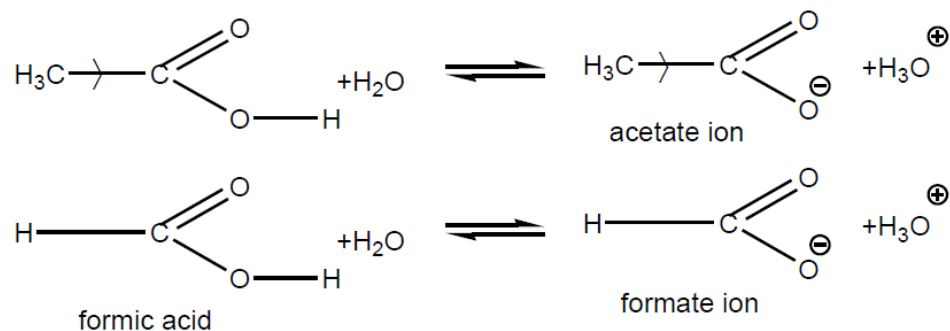
Thus the order of basic strength of alkyl and aryl amines with respect to ammonia is :



Q.1. Why Formic acid is stronger than acetic acid? Explain.

The relative acidity can be explained on the basis of stability of conjugate bases of the two acids. The following conjugate bases are formed from the corresponding acids.

In acetate ion, the electron releasing methyl group (+I effect) would intensify the negative charge on COO^- ion and thus destabilizes it. No such effect is present in formate ion (HCOO^-). Hence formate ion is more stable than acetate ion. Therefore formic acid is stronger acid than acetic acid.



Arrange the acidity order among the CH_3COOH , HCOOH , ClCH_2COOH and $\text{ClCH}_2\text{CH}_2\text{COOH}$

The proton of ethyne are more acidic than those of ethane, which in turn, are more acidic than ethane. Explain.

We can explain this on the basis of the hybridization state of carbon in each compound. The C-H bond in acetylene, ethylene and ethane are sp , sp^2 and sp^3 hybridized respectively. The sp , sp^2 and sp^3 hybrid orbitals possess 50%, 33.3% and 25% s character respectively. As the s character increases electronegativity increases. So proton release will be progressively favoured in ethane, ethylene and acetylene. Hence the acidity order $\text{CH}\equiv\text{CH} > \text{CH}_2=\text{CH}_2 > \text{CH}_3\text{CH}_3$ is justified.

Arrange the basicity order in both the medium of the following compounds:

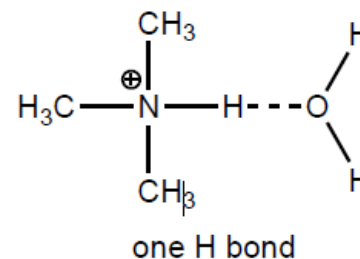
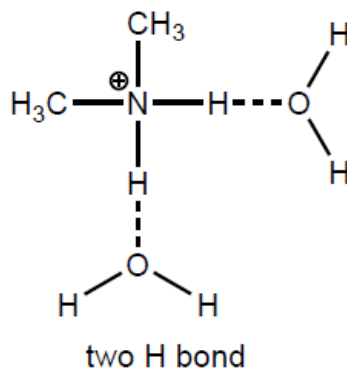
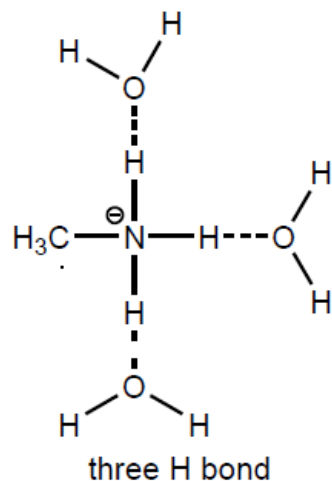
$\text{H}_3\text{C-NH}_2$, $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$ in chlorobenzene and in water.

In going from primary amine to secondary amine the electron availability on the nitrogen atom increases consequently the basicity increases, but going from secondary to tertiary the basicity decreases. This is due to the fact that the basicity not only depends on electron availability but also the stability formed when it takes a proton. The stability of the cation (onium ion) formed from tertiary amine is reduced than secondary amine as it contains one hydrogen atom which gets hydrogen bonded compare to secondary amine which contains two hydrogens having two hydrogen bonding. So secondary amine is more solvated than tertiary amine. Here the stability lost due to solvation (hydrogen bonding) is more pronounced than the inductive effect. Such kind of solvation is absent in chlorobenzene solvent.

Hence the basicity order in water is as follows: $\text{Me}_3\text{N} < \text{Me}_2\text{NH} > \text{MeNH}_2$ Secondary > tertiary > primary

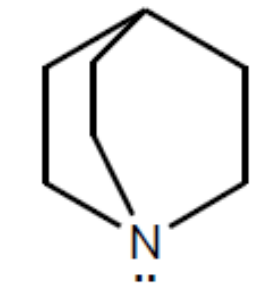
but in chlorobenzene: $\text{H}_3\text{C-NH}_2 < (\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N}$.

pK_b value = 3.27, 3.32, 3.34

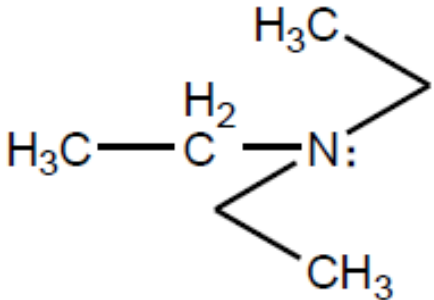


Compare the basicity between quinuclidine and triethylamine.

Both the N atom is sp^3 hybridised. In quinuclidine the N atom is tightly held back by the ring so the lone pair electrons on nitrogen is readily available for coordination than triethylamine. Because in triethylamine, the three alkyl groups are rotating around the nitrogen which block the nitrogen to donate electron towards proton. Hence quinuclidine is more basic than triethylamine.



Quinuclidine



Triethylamine

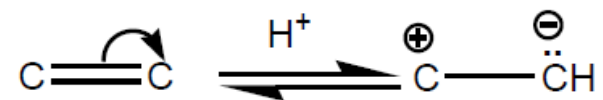
ELECTROMERIC EFFECT

The complete transfer of shared pairs of π electrons of a double bond or multiple bond to one of the bonded atoms under the influence of the attacking reagent is known as electromeric effect.



Since the effect involves complete transference of electrons, it leads to the development of full positive charge (+) and negative charges (-) within the molecule. Electromeric effect is a temporary effect and operates in presence of attacking reagent and vanishes as soon as the attacking reagent is withdrawn.

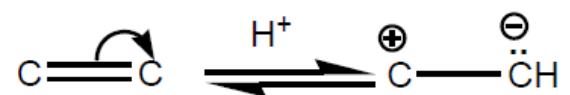
If a proton (H^+) adds to $C=C$ bond, the π bond will break and the electron pair will be transferred completely to one of the C atoms.



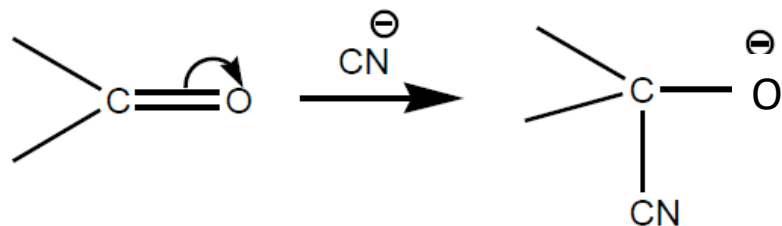
The electromeric effect has no specific direction. Its direction is always that which favours the reaction.

The effect takes place in the direction of the more electronegative element. It can be represented by the symbol E and is of two types: (i) + E effect (ii) – E effect.

+ E effect: When the displacement of an electron pair is away from the atom or group, it is called + E effect.

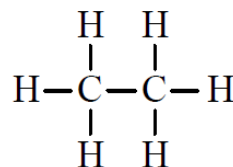


-E effect: When the displacement of an electron pair is towards the atom or group, it is called – E effect.

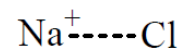


Resonance

Resonance may be defined as bonding or sharing of electrons between more than two atoms (nuclei). Typical covalent and ionic bonding involves sharing (covalent) or transferring (ionic) electron pairs between two atoms as shown in the examples of ethane and sodium chloride below. In these examples the bonding electrons are localized:



Ethane
Localized covalent bonds



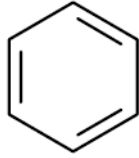
Sodium Chloride
Localized ionic bond

Resonance and Inductive Effects of Various Functional Groups

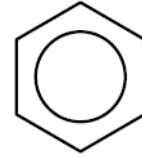
Inductive Effects: Electron- Withdrawing	Inductive Effects: Electron-Donating	Resonance Effects Electron Withdrawing	Resonance Effects Electron Donating
$-\text{NR}_3^+$ $-\text{NH}_3^+$	$-\text{O}^-$ $-\text{COO}^-$	$-\text{COOR}$ $-\text{COOH}$	$-\text{OH}$ $-\text{OR}$
$-\text{COOH}$ $-\text{COOR}$	$-\text{CH}_3$ $-\text{CHR}_2$ $-\text{CH}_2\text{R}$ $-\text{CR}_3$	$-\text{COR}$ $-\text{CHO}$	$-\text{NH}_2$ $-\text{NR}_2$
$-\text{NO}_2$ $-\text{CN}$		$-\text{SO}_2\text{R}$ $-\text{SO}_2\text{NHR}$	$-\text{NHR}_2$ $-\text{SH}$
$-\text{CHO}$ $-\text{COR}$		$-\text{NO}_2$ $-\text{CN}$	
$-\text{F}$ $-\text{Cl}$ $-\text{Br}$ $-\text{I}$ $-\text{CF}_3$		$-\text{Ar}$	
$-\text{OH}$ $-\text{OR}$			
$-\text{NH}_2$			
$-\text{SH}$ $-\text{SO}_2\text{R}$			

Resonance differs from the two examples above in that it involves the sharing of electrons between more than two atoms via delocalization. The classical example of resonance is provided by the pi-bonding system of benzene. Benzene is a six membered ring composed of six sp^2 hybridized carbon atoms in a plane and sharing 6 pi electrons. It can be represented by the "Kekule" structure shown below which suggests an "alternating" single bond-double bond bonding pattern. This representation does not really adequately reflect the true electronic character of benzene since, in reality, all six pi electrons are shared equally by the six carbons.

Thus the "inscribed" circle representation may be more accurate (although it doesn't directly indicate the number of pi electrons):



Kekule Structure
of benzene

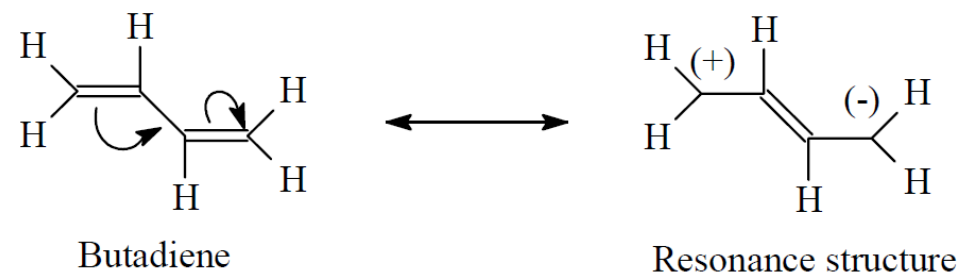


Inscribed circle
structure of benzene

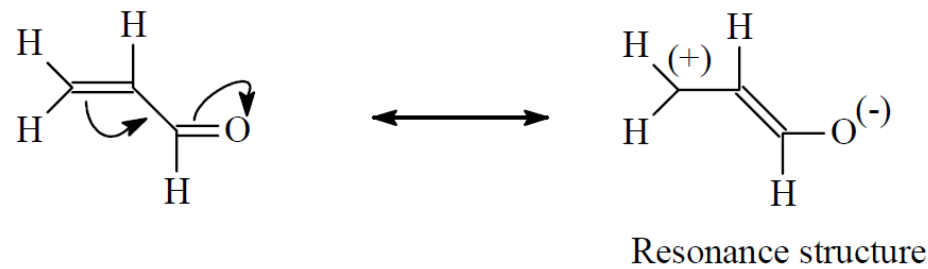
The Kekule structure of benzene does represent the electronic and structural requirements for resonance. For resonance phenomena to exist a "conjugated" electronic system must be present and the atoms involved in this system must be coplanar or capable of adopting a coplanar conformation. The type of resonance effect exerted by an atom or functional group – electron donating (+R) or withdrawing (-R) is determined by the electronic nature of the group.

Each of these characteristics/requirements of resonance are defined in more detail below:

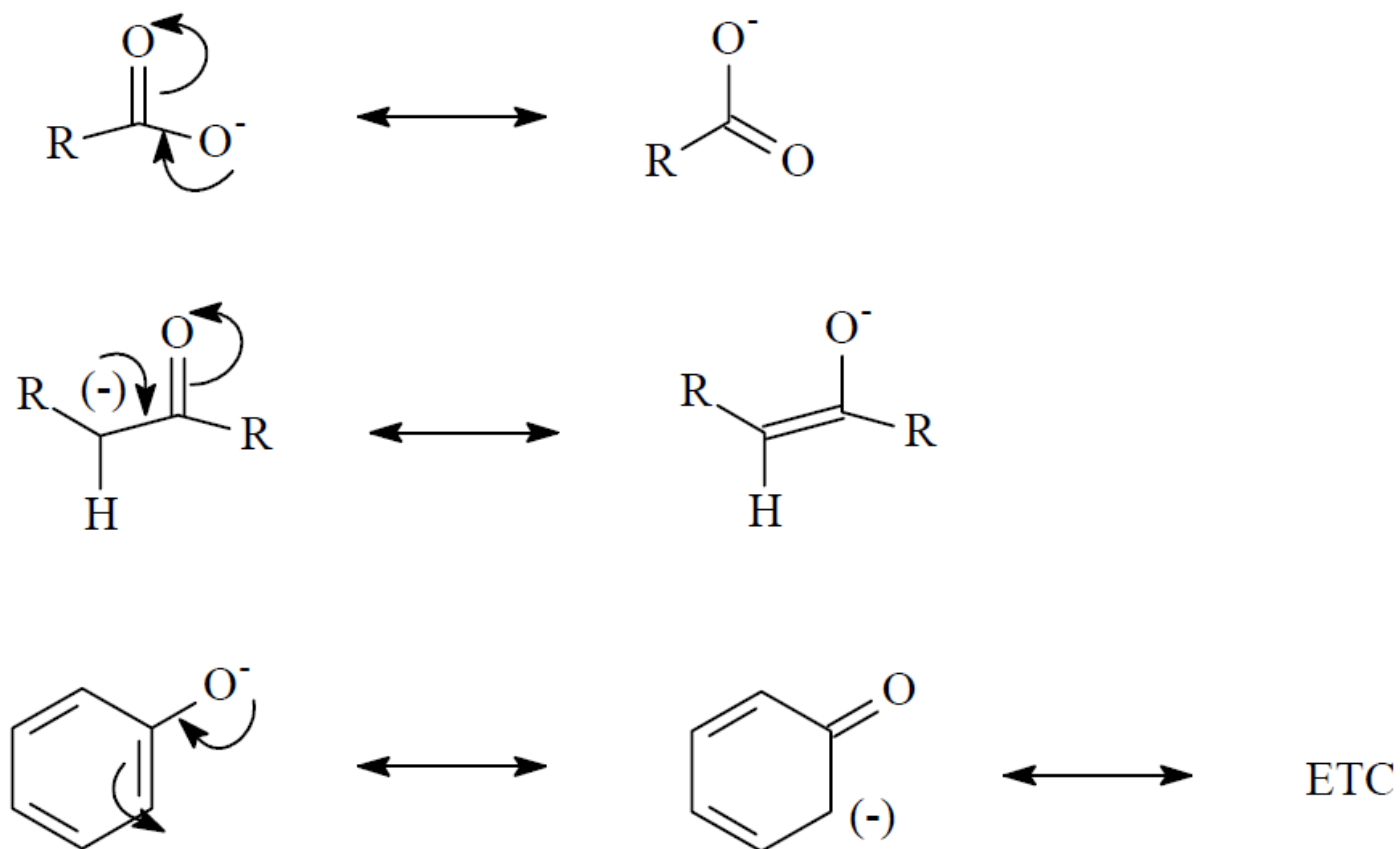
"Conjugation": An electronic configuration in which there is an alternating single bond double (pi) bond pattern, or an atom with non-bonded electron pairs (or lacking an electron pair) bound to a double bond system. The alternating single bond-double (pi) bond pattern can be illustrated by butadiene. In this example the resonance structure shows that the electrons can be "shared" or delocalized (follow the arrows) creating a cationic and an anionic center:



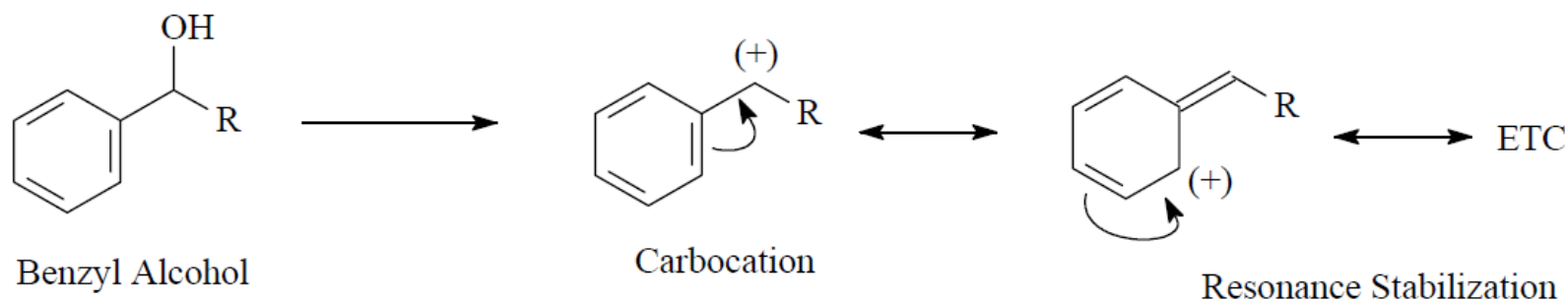
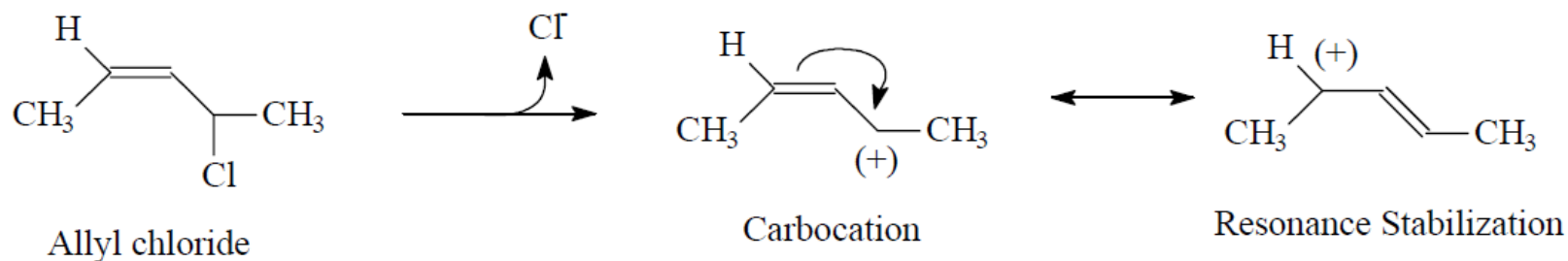
Another example of the single bond-double bond resonance pattern is in α , β -unsaturated carbonyl compounds. Here the difference in electronegativity between atoms in the pattern allows for a dipole and reactivity such as conjugate addition:



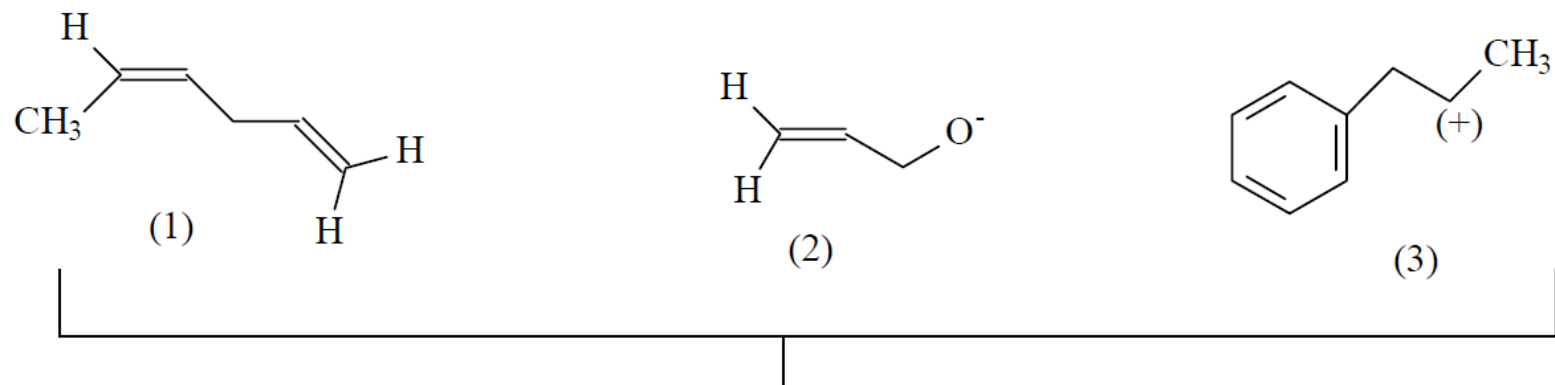
Examples of resonance resulting from atom with non-bonded electron pairs bound to a double bond system are shown below. Notice in each case below that the "resonance phenomenon" involves an electron rich atom donating a pair of electrons to an electron deficient multiple bond system, and that in actuality, the charges shown are distributed or delocalized over all of the atoms of conjugation. This resonance phenomenon is what makes carboxylic acids, and to a lesser extent phenols and protons alpha- to a carbonyl, acidic! The charged formed upon ionization can be stabilized through resonance delocalization!



Resonance can also occur in structural patterns where an atom deficient in an electron pair is bound to a double bonded system. Consider the case of the reaction of the "allyl chloride" compound below. This compound can ionize by loss of Cl^- (a good leaving group) because the charge of the resulting carbocation is stabilized by resonance delocalization of the pi (double bond) electrons. The same is true for benzyl alcohols as shown below. Benzyl alcohols can ionize because the resulting carbocation charge can be delocalized throughout the benzene ring via resonance:

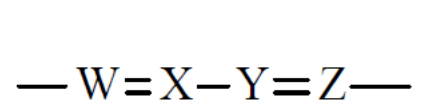


In every case above, resonance was possible because of an electronic configuration in which there is an alternating single bond-double (pi) bond pattern, or an atom with non-bonded electron pairs (or lacking an electron pair) bound to a double bond system. It is important to realize that resonance is not possible when such an electronic configuration is NOT possible. Consider the examples below. In the first example (1) resonance is not possible because the two double bonds are separated by MORE THAN one single bond. In the second example the negatively charged atom is separated from the double bond by more than one single bond and in example (3) the charge is separated from the C=C by more than a single double bond.

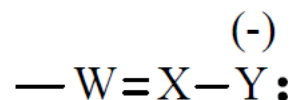


NO RESONANCE POSSIBLE!!

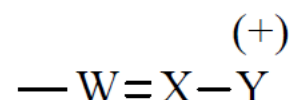
In summary, in order for resonance phenomena to occur, there must be a structural pattern characterized by the following general structures.



Conjugated "diene"

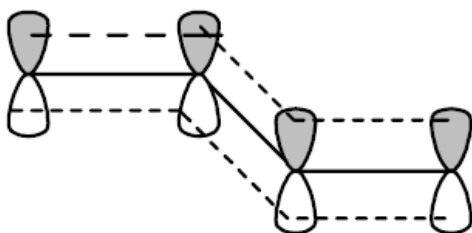


Conjugated anion

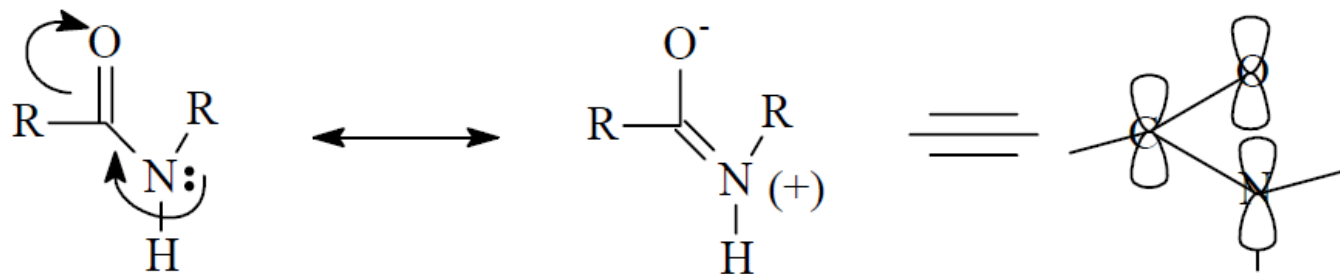


Conjugated cation

Coplanarity: In order for resonance to occur, the atoms involved in "sharing" electrons (the atoms over which the electrons are delocalized) must be able to adopt a coplanar conformation. In order for electrons to be delocalized over more than two atoms, the pi orbitals of these atoms must exist in the same plane so they can overlap. This can only occur if the atoms and orbitals involved are in the same plane:

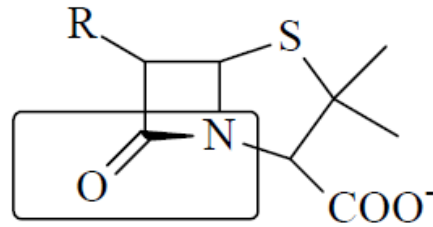


One prominent example of the requirement for coplanarity for resonance in drug science is derived from amide chemistry. Typically amides are somewhat resistant to hydrolysis because the amide nitrogen atom can donate electron density by resonance to the adjacent carbonyl and thereby reduce its electrophilicity (reactivity) toward hydrolytic nucleophiles. In order for this resonance stabilization to occur, the N-C=O atoms must be capable of existing in the same plane so their pi-orbitals can overlap:



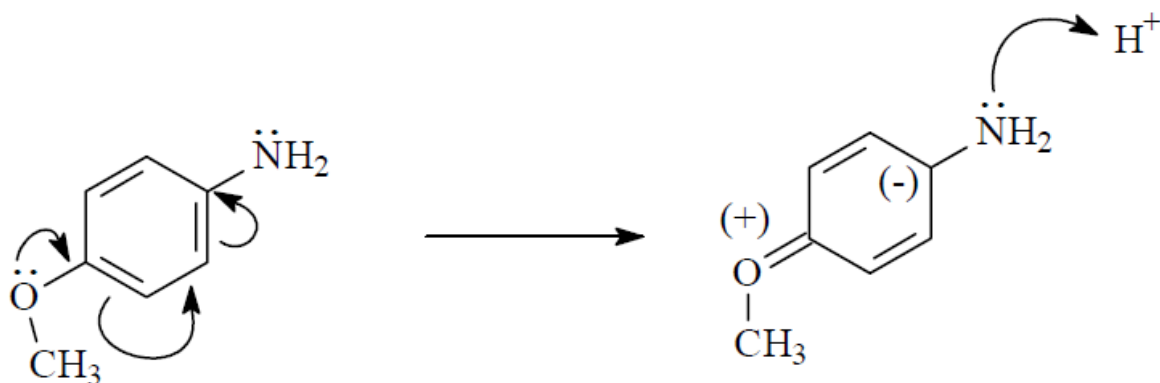
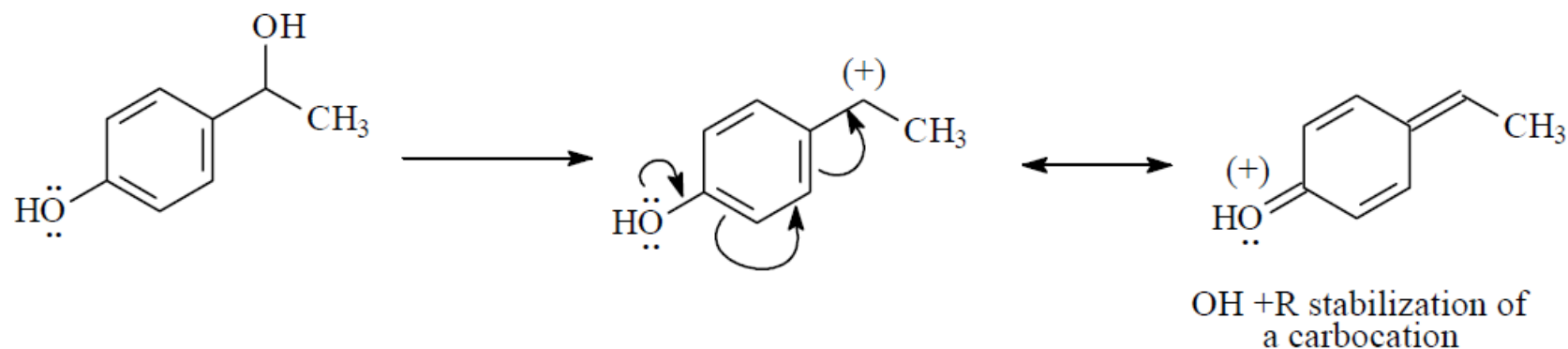
Resonance stabilization of amides

In amides where coplanarity is not possible, as in the beta-lactam antibiotics (penicillins), resonance stabilization cannot occur. In these compounds the bicyclic ring structure does not allow the amide N-C=O atoms to exist in the same plane. Thus resonance donation by N is not possible and these amides are more reactive than "typical" amides where coplanarity allows for resonance stabilization:

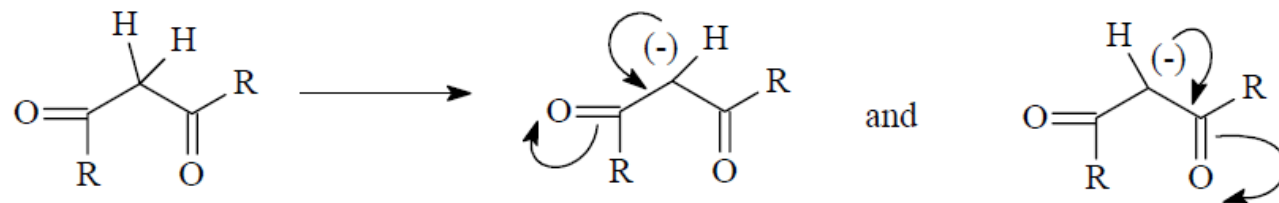
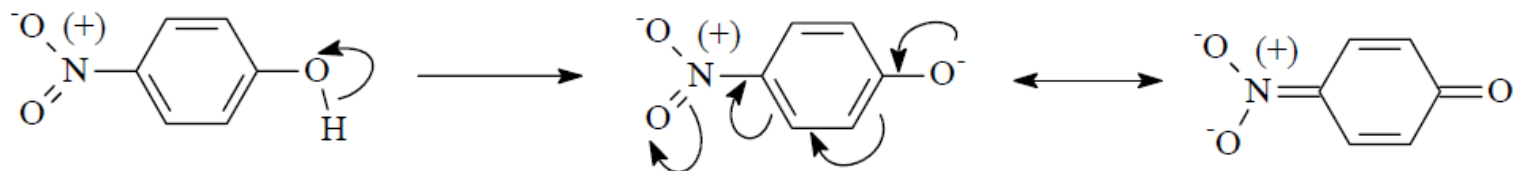


Beta-lactam amides: Non-coplanar

- Electron donating (+R) and Withdrawing (-R) Groups: electron donating and withdrawing groups by resonance are listed in the table on a previous page. Note that electron donors (+R) have at least one pair of non-bonded electrons on the atom involved in resonance (OH, OR, NRR, SR, etc.). As a result, +R groups can facilitate reactions that involve the formation of cations, and enhance the basicity of amines. This is illustrated in the examples below:



- Electron withdrawing groups (-R) are characterized by electron deficient atoms linked to a site of conjugation. As a result, -R groups can facilitate reactions that involve the formation of anions, and enhance the acidic of acids. This is illustrated in the examples below:



RESONANCE VERSUS INDUCTION:

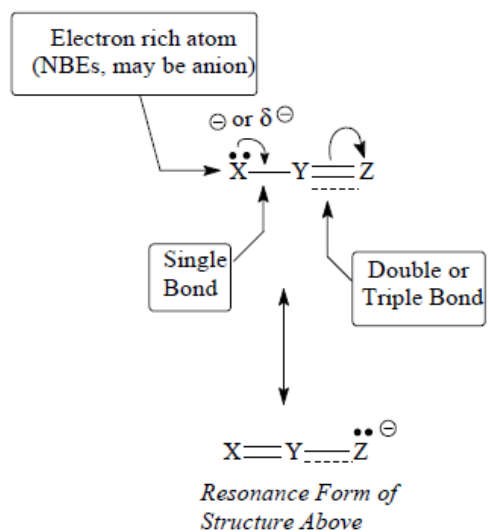
As described above, induction involves the electronic effects of atoms and functional groups through saturated carbons, and are dependent on bond valence and position.

Resonance involves the sharing or delocalization of electron pairs over more than two atoms and requires conjugation and coplanarity. To compare and contrast these two electronic effects, consider the electronic effects of the hydroxy group (OH). This group is a withdrawer by induction (-I) and an electron donor by resonance (+R).

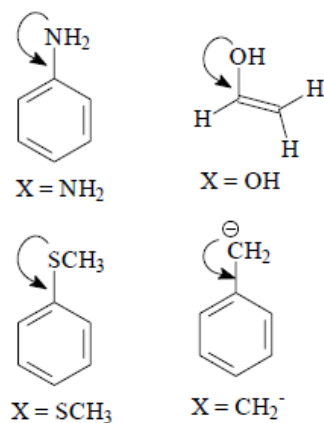
Thus when positioned within a structure where it can participate in delocalization of pi electrons, it will function as a strong electron donor. When placed in a structure where its resonance effects are "insulated" by single bonds, only its electron withdrawing inductive effect will be felt.

CONJUGATED SYSTEM

(X group is a donor by resonance, +R)

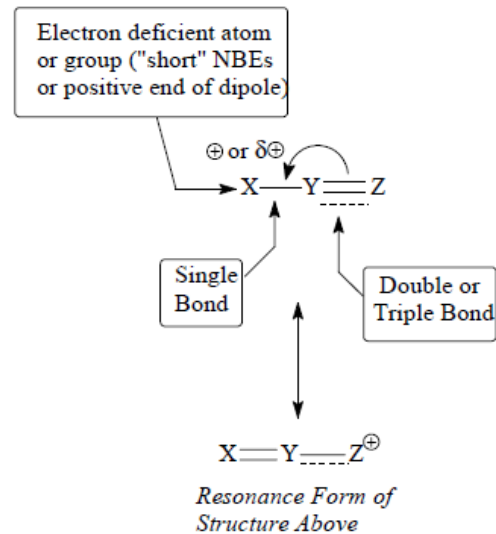


EXAMPLES OF +R GROUPS:

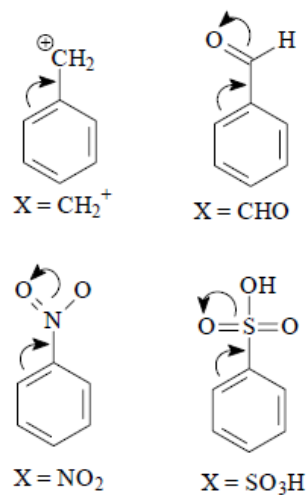


CONJUGATED SYSTEM

(X group is a withdrawer by resonance, -R)

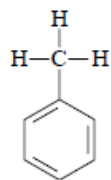


EXAMPLES OF -R GROUPS:

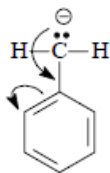


CARBON SUBSTITUENTS AND ELECTRONIC EFFECTS

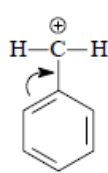
The electronic effects of an atom are a function of ionization and hybridization state as well as the nature of the structure to which they are linked (are they "in conjugation" with the structure to which they are linked):



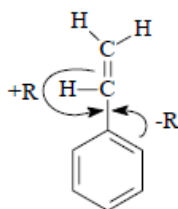
Fully saturated carbon with no NBEs. R not possible! **+I Effect**



Loss of H^+ :
Carbanion: NBE pair available for donation: **+R Effect**



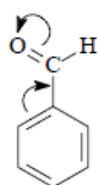
Loss of H^+ :
Carbocation: Vacant orbital ("short" a NBE) **-R Effect**



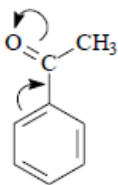
Alkene carbon: Can donate (**+R**) or withdraw (**-R**) electron density



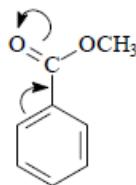
The electronic effects of an atoms are determined or modified by the nature of the functionality in which they are incorporated:



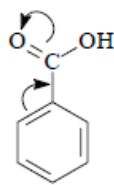
Aldehydes



Ketones

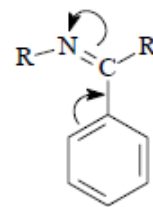


Esters

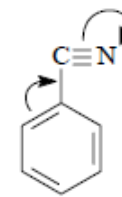


Carboxylic Acids

Carbonyl-containing functional groups (aldehydes, ketones, ester, acids) in conjugation with an aromatic ring (or other site of potential resonance) can withdraw electron density by resonance (**-R**) as shown above. These functional groups also withdraw electron density weakly by induction. The same is true, to a lesser degree, for analogues of the compounds above where the carbonyl oxygen is replaced by an atom of the same group (sulfur), or multiple bonded atom of the same row (as in nitrogen shown below)



Imines

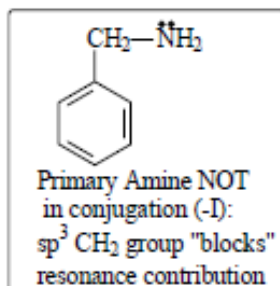
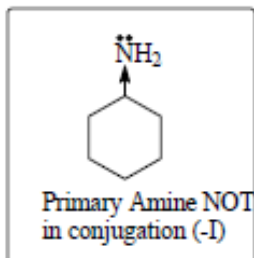
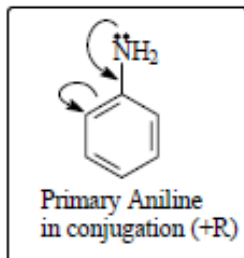


Nitriles

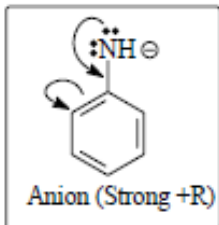
Unsaturated carbon-nitrogen functionality (imines and nitriles and similar structures) in conjugation with an aromatic system, like the carbonyl-containing functional groups can also withdraw electron density by resonance (**-R**) as shown above. These functional groups also withdraw electron density weakly by induction.

THE ELECTRONIC EFFECTS OF NITROGEN SUBSTITUENTS

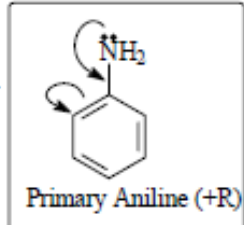
Electronic effects of an atom determined by nature of bonding and potential for conjugation:



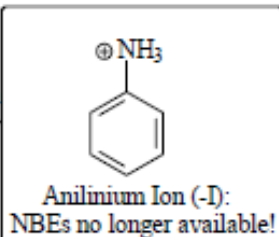
Electronic effects of an atom determined by the ionization state:



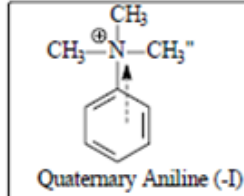
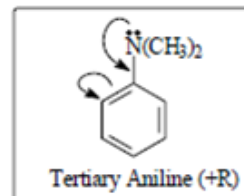
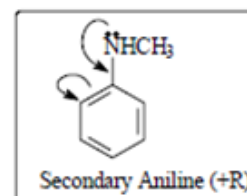
Loss of H^+



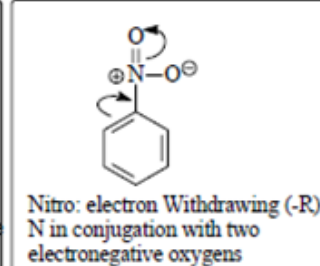
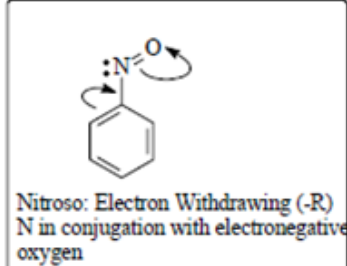
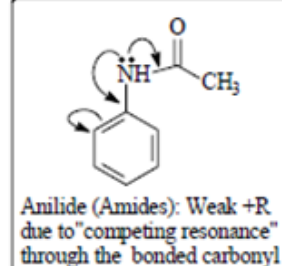
Protonation



Alkyl substitution does not change the nature of potential electronic effects of an atom, unless alkyl substitution changes the bonding order (i.e. "occupies" nitrogen's lone pair of NBEs):

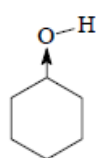


The electronic effects of an atoms are determined or modified by the nature of the functionality in which they are incorporated:

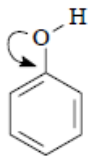


OXYGEN AND OTHER GROUP 6 ATOM SUBSTITUENTS AND ELECTRONIC EFFECTS

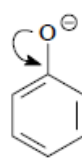
The electronic effects of an atom are a function of ionization and hybridization state as well as the nature of the structure to which they are linked (are they "in conjugation" with the structure to which they are linked):



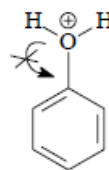
Fully saturated oxygen with two pairs of NBEs but not in conjugation. Only electronegative effect (**-I Effect**)



Fully saturated oxygen with two pairs of NBEs in conjugation. **+R Effect**



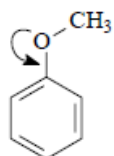
Loss of H^+ : (Anion): NBEs available for donation: **+R Effect**



Loss of H^+ : "Onium ion": Full valence cation (electron deficient, but R not possible): **-I Effect**

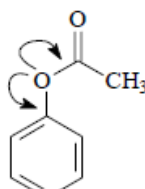


The electronic effects of an atoms are determined or modified by the nature of the functionality in which they are incorporated:



Ether

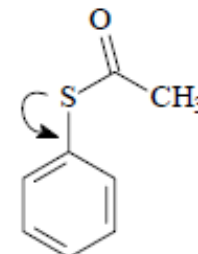
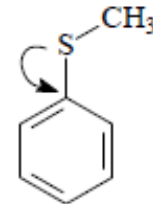
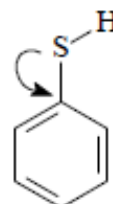
Still a +R group, but not capable of ionization



"Reverse" Ester

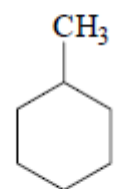
Still a +R group, but the carbonyl bonded to O (and in conjugation) reduces strength of donation by electron withdrawal

Atoms of the same group (i.e: O and S) are capable of exerting the same electronic effects (I and R), but the strength of the effect is dependent on the distance of the valence electrons from the nucleus

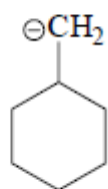
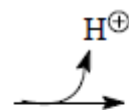


RELATIVE ACIDITIES OF ALKANES, ALCOHOLS, PHENOLS AND CARBOXYLIC ACIDS

(Increasing acidity and polarity at physiologic pH from lkanes to carboxylic acids)



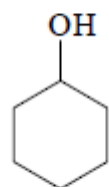
Alkane
(pKa 40)



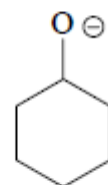
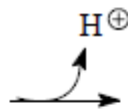
**Conjugate
Base**

Negative charge formed
on electropositive carbon
group (+I, unstable) and
no resonance stabilization

Non-polar compound
(hydrocarbon only) that
does not ionize at
physiologic pH



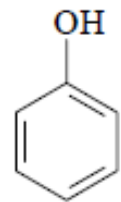
Alcohol
(pKa 16)



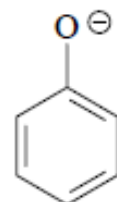
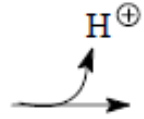
**Conjugate
Base**

Negative charge formed on
electronegative oxygen, but
no resonance stabilization

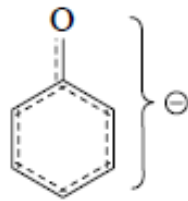
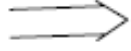
More polar than the
hydrocarbon above due to
O-H dipoles, but does not
ionize at physiologic pH



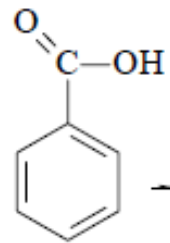
Phenol
(pKa 10)



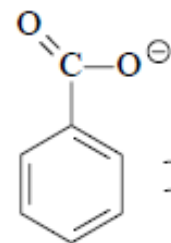
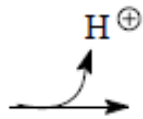
Conjugate
Base



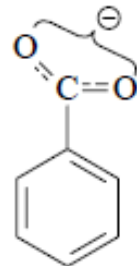
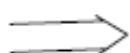
Negative charge formed on electronegative oxygen, and stabilized by resonance over 1 "O" and 6 "Cs": Weak acid at phys. pH (7): Non-ionized/Ionized = 1000/1 Somewhat polar compound under physiologic conditions!!



Carboxylic Acid
(pKa 4)

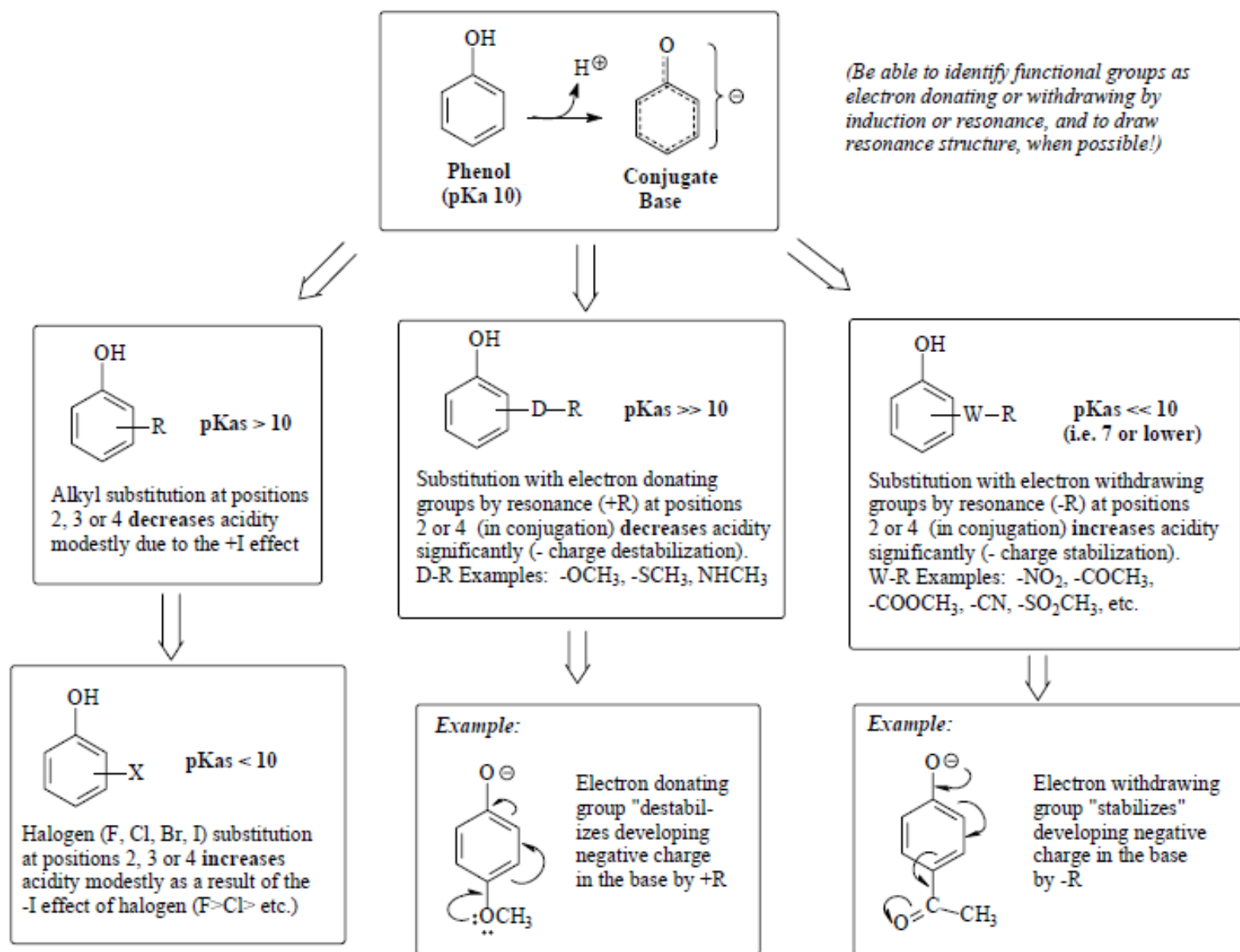


Conjugate
Base



Negative charge formed on electronegative oxygen, and stabilized by resonance over 2 "Os" and 1 "C". Stronger acid than the phenol. Ionization at phys. pH (7): Ionized/Non-ionized = 1000/1 Very polar compound under physiologic conditions!!

RELATIVE ACIDITIES OF PHENOLS: SUBSTITUENT EFFECTS

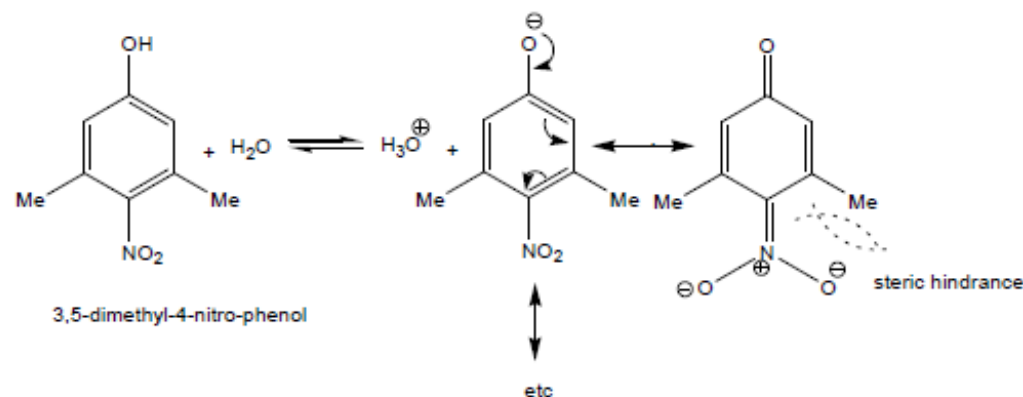
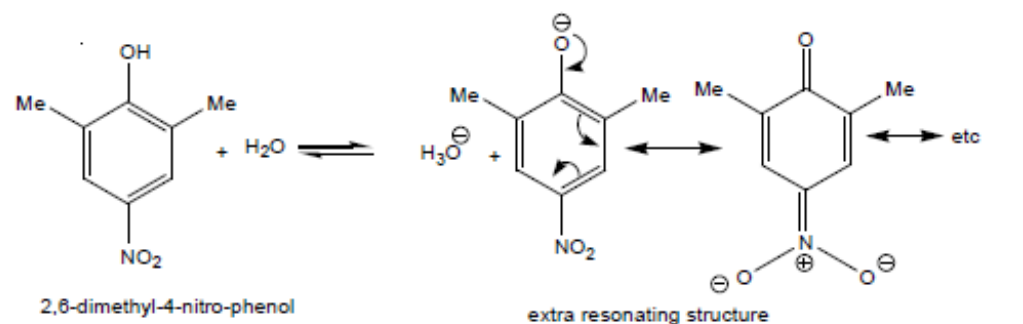


STERIC INHIBITION OF RESONANCE

An essential requirement for resonance is that the involved atom in resonating structure must be co-planar or nearly planar. Thus if co-planarity is partially reduced or completely reduced/prevented by the steric effect of a group, resonance is diminished or prevented. This phenomena is known as **steric inhibition of resonance**. It has effects on

- Acidity
- Basicity
- Bond length and bond strength
- Dipolemoments
- Reactivity

Acidity: The greater acidity of 2,6-dimethyl 4-nitro phenol(I) than 3,5 isomer(II) can be explained with the help of Steric inhibition of resonance. The acidity can be judged by comparing the stability of the conjugate bases.

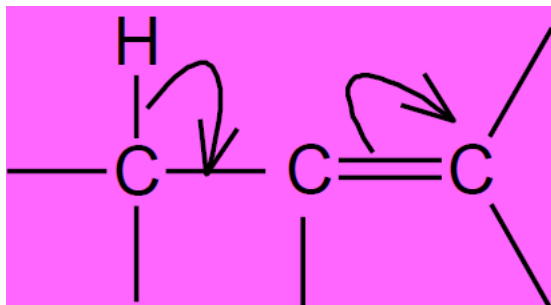


In 3,5-dimethyl -4-nitro phenoxide ion , the two methyl groups and the nitro group are in close proximity. Due to their bulk, the nitro group rotates round the C-N bond to avoid interaction between the methyl groups. In doing so, the p-orbital of N atom no longer remains parallel to the p-orbital of the ring carbon. Hence the NO_2 group cannot delocalize the $-ve$ charge by $-R$ effect of NO_2 group. Such kind of situation is absent for 2,6 isomer.

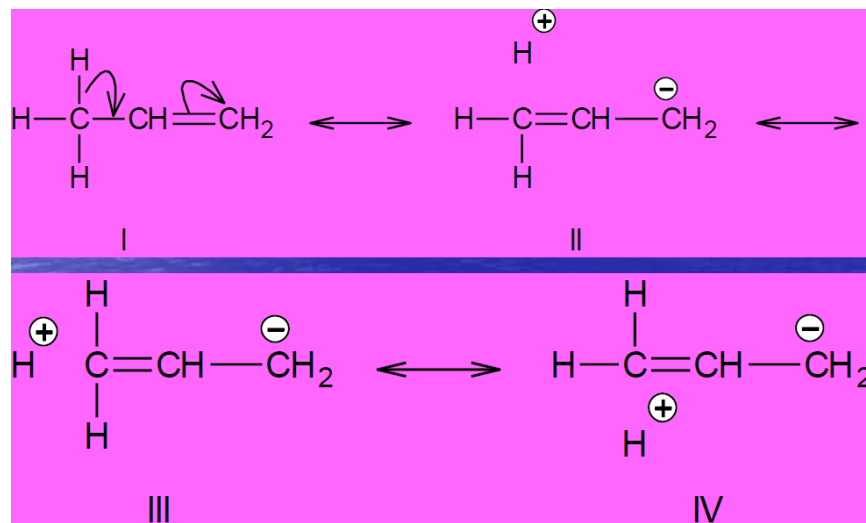
So 2,6-dimethyl 4-nitro phenoxide ion has extra resonating structure than 3,5 dimethyl 4-nitro phenoxide ion . Hence 2,6-dimethyl 4-nitro phenoxide ion is more stable than 3,5 isomer. Therefore 2,6-dimethyl 4-nitro phenol has higher acidity than 3,5 isomer.

Hyperconjugation

Baker and Nathan suggested that an alkyl group with at least one H atom on the **alpha** carbon atom when attached to an unsaturated C atom, is able to release electron by a mechanism similar to that of electromeric effect



This type of electron release due to presence of the system $\text{H}-\text{C}-\text{C}=\text{C}$ is known as hyperconjugation. For example, Propylene may be regarded as the resonance hybrid of the following structures due to hyperconjugation.

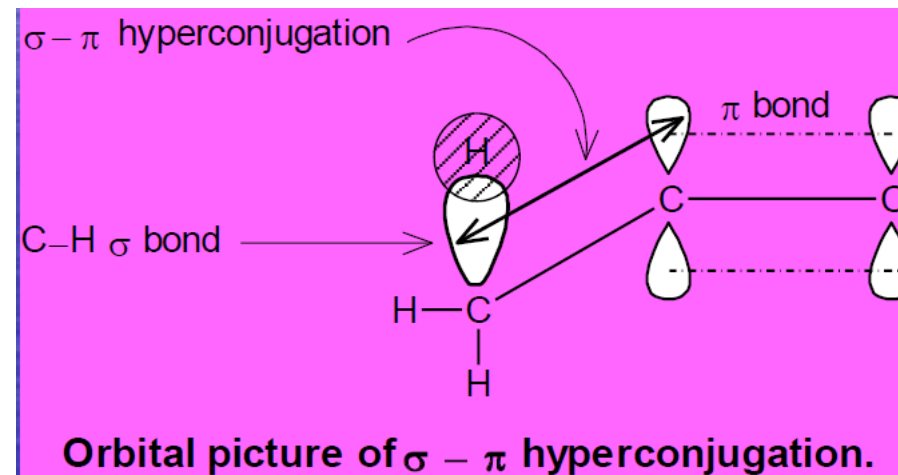


The various hyperconjugation forms of propylene are called contributing structures. In fact, the hyperconjugation effect is similar to the resonance effect.

Since structures II, III, and IV have no definite bond between the alpha carbon atom and one of the H atoms, hyperconjugation is also known as no bond resonance. It is also known as second order resonance or Baker-Nathan effect.

The orbital concept of hyperconjugation may be explained with the help of propylene. In this concept, the electron pair of C-H bond (sigma bond) is involved in conjugation with the pi electron pair of the double bond.

Therefore, hyperconjugation involves delocalization of sigma electrons of C-H bond through overlapping of p orbital of double bond as shown below



Structural requirements of hyperconjugation:

Any organic compound can show hyperconjugation if it will fulfill the following conditions

1. Compound should have sp^2 hybrid carbon of alkene, arenes, carbocations and free radicals
2. α Carbon atom with respect to sp^2 hybrid C atom should have at least one hydrogen atom and α carbon atom should be sp^3 hybridized.

Thus, hyperconjugation is of following types:

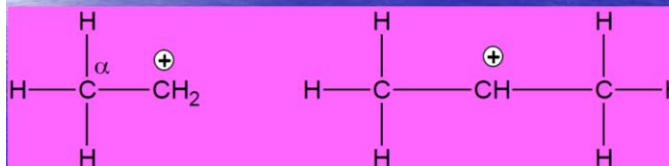
(i) σ (C–H), π conjugation:

- This type of conjugation occurs in alkenes and alkyl substituted aromatic compounds.



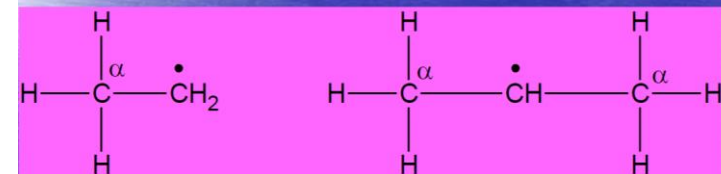
(ii) σ (C–H), positive charge (vacant p-orbital) conjugation:

- This type of conjugation occurs in alkyl carbocations.



(iii) σ (C–H), odd electron (incomplete p-orbital) conjugation:

- This type of conjugation occurs in alkyl free radicals.



Applications:

Stability of alkenes

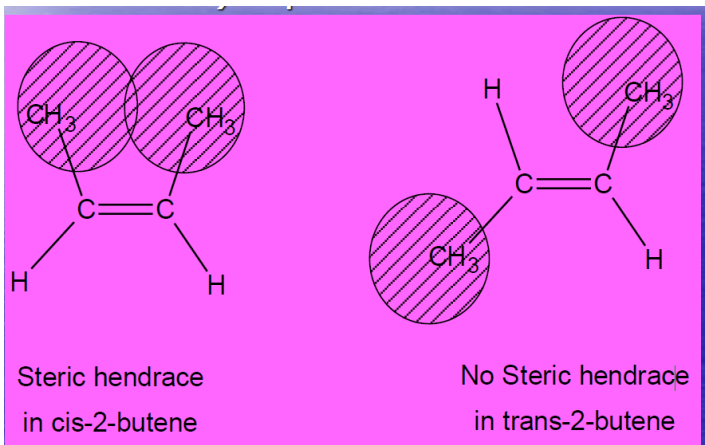
Heat of hydrogenation shows that the greater the number of alkyl groups attached to the double bonded C atom, greater is the stability of alkene (lower is the heat of hydrogenation) Thus on the basis of heat of hydrogenation, the order of stability of different alkenes have been found to be Tetrasubstituted> Trisubstituted > Disubstituted> Monosubstituted Ethylene

Trans 2 Butene is more stable than cis 2 butene, in which two methyl groups are close together and hence their electronic cloud (steric hindrance) repel each other

The order of stability of substituted alkenes can also be explained on the basis of hyperconjugation.

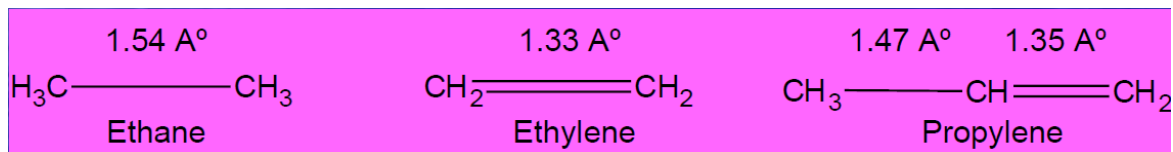
Alkenes				
No. of α - H atoms	12	9	6	3
No. of Resonating structures	13	10	7	4

The greater the number of resonating structures of a molecule, greater will be its stability.



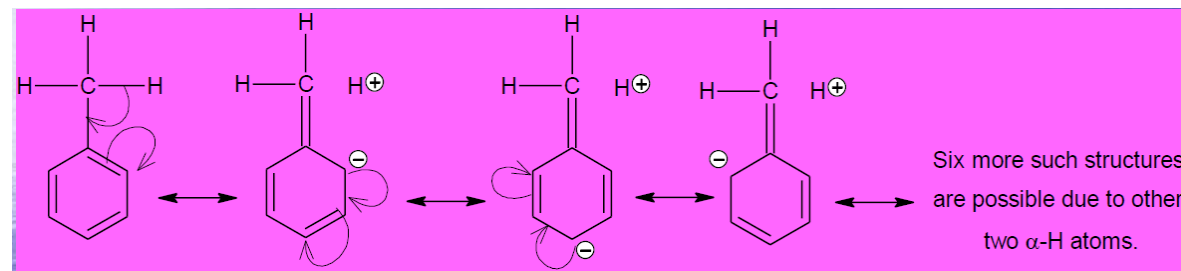
2. Abnormal bond lengths:

In hyperconjugation a single bond acquires a double bond character and vice versa, hence abnormality in bond lengths is observed in the compounds showing hyperconjugation. For example, Ethane and ethylene, C-C and C=C bonds show normal length 1.54 Å and 1.33 Å, respectively due to no hyperconjugation in the compounds but in propene, the bond lengths are 1.47 Å and 1.35 Å for C-C and C=C bonds, respectively. This change in bond lengths may be explained by hyperconjugation.



3. Directive influence of alkyl groups:

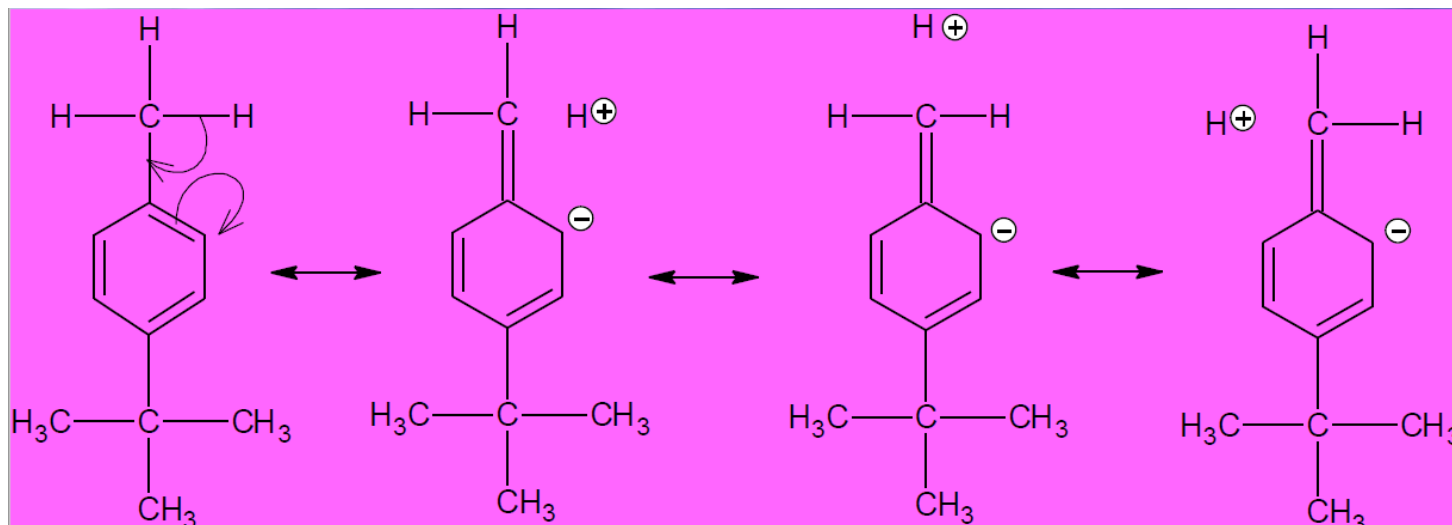
- The $-\text{CH}_3$ and other alkyl groups are o- and p- directing which can be explained on the basis of hyperconjugation as follows:



As a result of hyperconjugation, electron density at o- and p- position (w.r.t. methyl group) increases and therefore electrophilic substitution in toluene takes place at o- and p- positions. Thus alkyl groups are o- and p- directing.

4. Orienting power of methyl group in p substituted toluene:

In p-t-butyl toluene, further substitution occurs at o position with respect to methyl group even though the inductive effect of t butyl group is far greater than methyl group. This anomaly is due to greater hyperconjugative effect of methyl group (having 3 α -H atoms) which increases the electron density at o-position w r t methyl group than t-butyl groups which have no α -H atoms and hence no hyperconjugation occurs. Here hyperconjugation overweighs inductive effect.

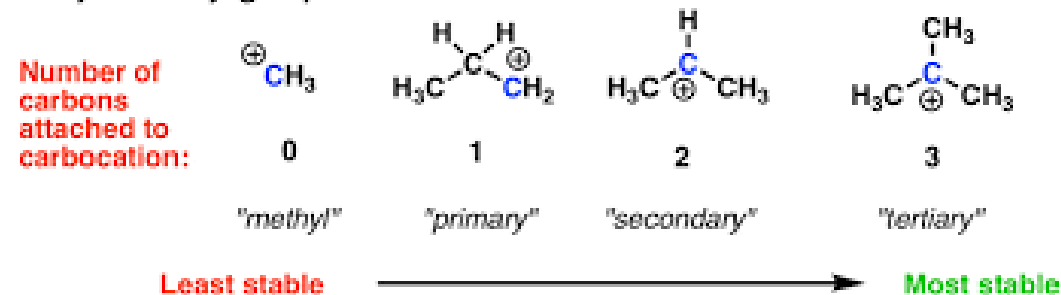


Stability of free radicals and carbocations:

Stability of alkyl carbocations:

- The order of stability of different alkyl carbocations is:

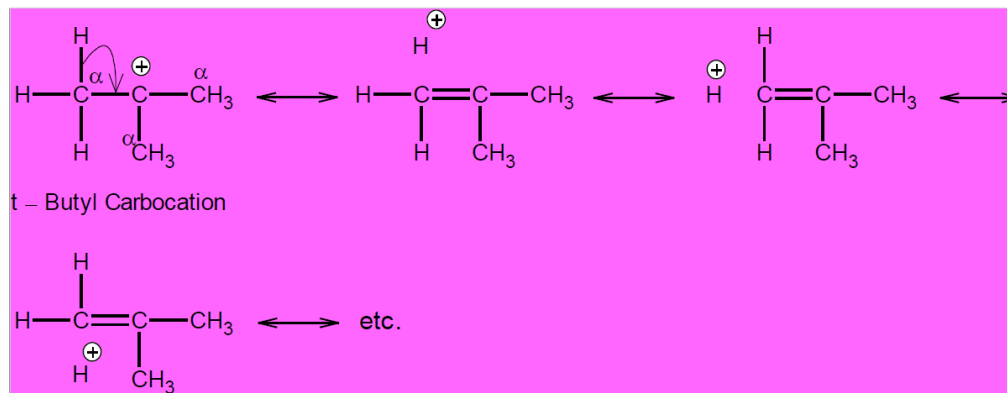
1. Adjacent alkyl groups stabilize carbocations



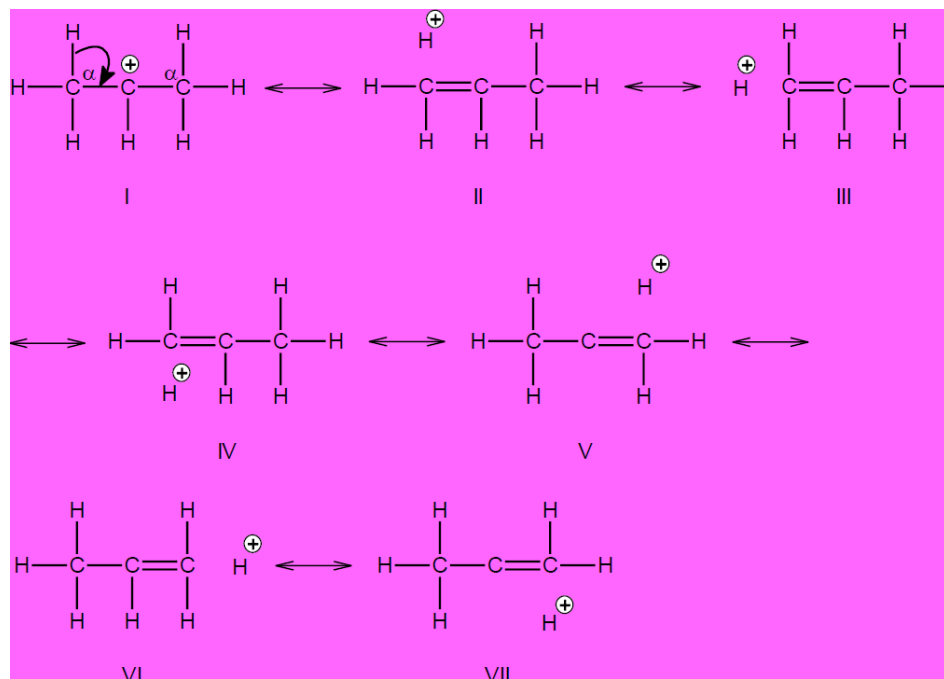
This order of stability of alkyl carbocations can be explained on the basis of inductive effect & hyperconjugation as follows:

Hyperconjugation states that greater the number of α -hydrogen atoms on a carbocation greater is the number of hyperconjugative structures (greater the dispersion of positive charge) and hence more is the stability of carbocation. Thus t-butyl carbocation (3°) with nine α hydrogen atoms has one usual and nine hyperconjugative structures, is more stable than isopropyl carbocation (2°) with six α hydrogen atoms, having one usual and six hyperconjugative structures, which, in turn, is more stable than ethyl carbocation (1°) with three α -hydrogens, having one usual three hyperconjugative structures, while methyl carbocation with no α -hydrogen, has one usual and no hyperconjugative structure, is least stable.

One usual and nine hyperconjugative structures of t butyl carbocation (3°)



One usual and six hyperconjugative structures of isopropyl carbocation (2°)

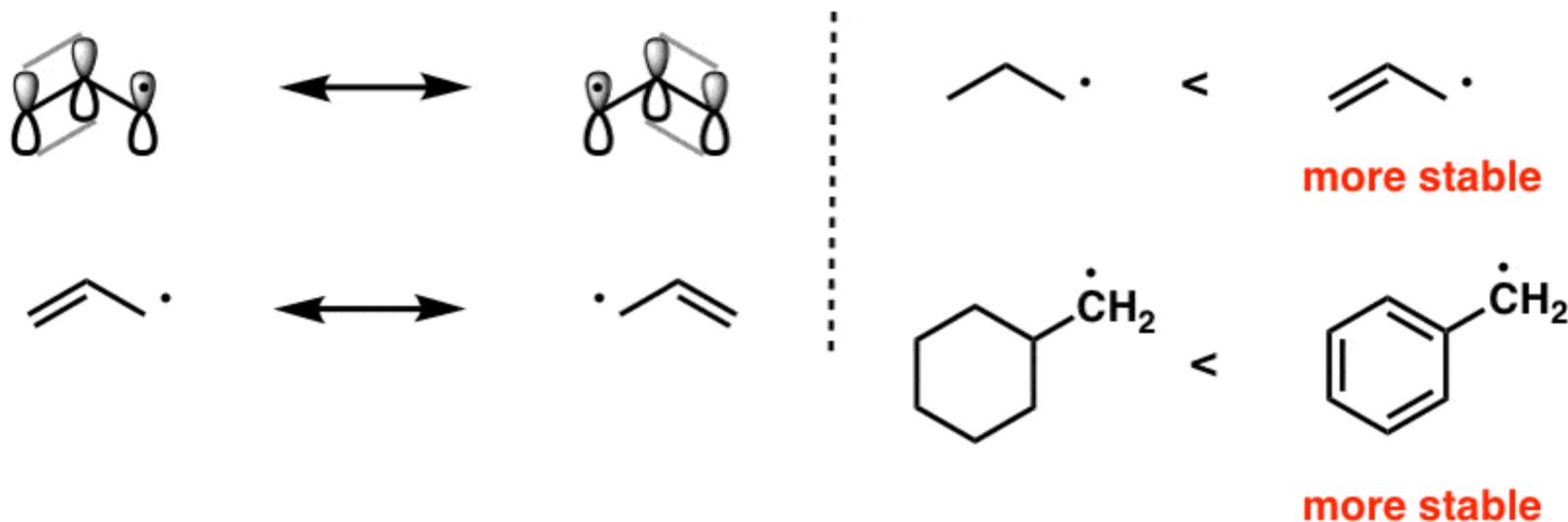


Free Radicals Are Stabilized By Resonance

The geometry of free radicals is generally that of a "shallow pyramid"

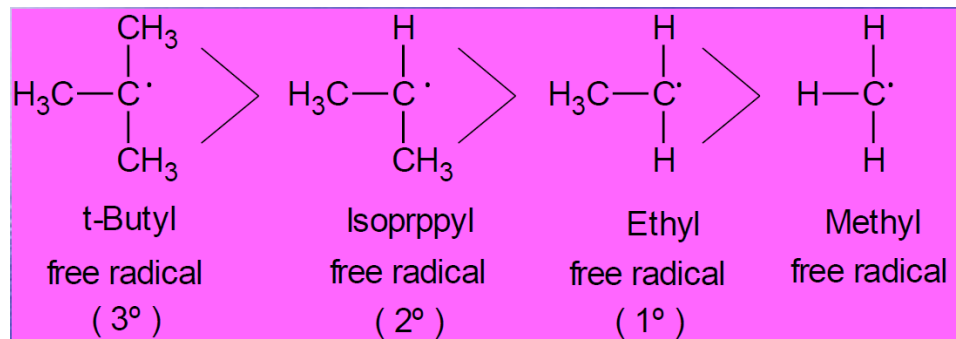


This means the partially filled p orbital can participate in resonance with adjacent p orbitals - **leading to greater stability**

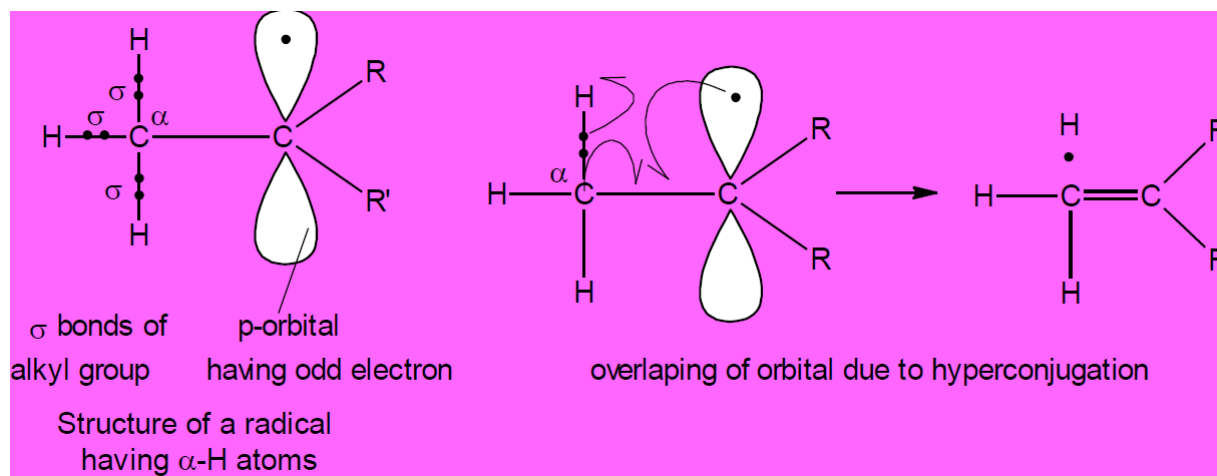


Stability of alkyl free radicals:

The order of stability of different alkyl free radicals is as follows:



The above order of stability can be explained on the basis of hyperconjugation.



One usual and three hyperconjugative structures of ethyl free radical 1°)

