

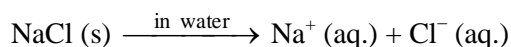
1. Basic Concepts

1.1 Solvation

When a substance is dissolved in a solvent, the solute particles are attracted by the solvent molecules. This process is called solvation. The energy released during solvation is called solvation energy.

The process is called hydration and the energy is called hydration energy if solvent is water.

Consider the example of dissolution of NaCl in water. In this process some energy is required to break the lattice (Called Lattice Energy) while some energy is released during solvation of Na^+ and Cl^- ions by water molecules. The overall process here actually is somewhat endothermic because the Lattice Energy is more than Solvation Energy and the required heat is taken from solvent molecules which results decrease in temperature. However in some other cases, the Lattice Energy is lesser than Solvation Energy which makes the dissolution process to be exothermic. The net enthalpy change during dissolution is called Enthalpy of Solution.



1.2 Solvolysis

It is a reaction of solute particles (molecules or ions) with the solvent. E.g. Hydrolysis (reaction with water), ammonolysis (reaction with ammonia) and alcoholysis (reaction with alcohol).



1.3 Hybridization of Carbon

Valence shell of carbon contains four orbitals (one s orbital and three p orbitals) and can form four bonds. Carbon can form σ (sigma) bond and π (pi) bond. π bonds are formed by sideways overlapping of pure p orbitals. So the number of p orbitals is equal to the number of π bonds of a carbon and do not participate in hybridization. Unpaired electron of carbon generally does not participate in hybridization. Similarly delocalized lone pair also does not participate in hybridization.

No. of π bonds formed by carbon	State of hybridization	Examples
0	sp^3	CH_4 , CCl_4 , $\text{CH}_3\text{-CH}_3$
1	sp^2	$\text{CH}_2 = \text{CH}_2$, $\text{H}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$
2	sp	$\text{CH} \equiv \text{CH}$, $\text{O} = \text{C} = \text{O}$

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Consequences of hybridization state

(i) Since s orbitals are smaller than p orbitals so more the s character, smaller will be the size of hybrid orbitals

$$sp < sp^2 < sp^3$$

(ii) Smaller the size of orbitals, shorter and stronger will be the bond formed by it.

$$sp < sp^2 < sp^3$$

Bond length

$$sp > sp^2 > sp^3$$

Bond strength

(iii) s orbitals are of lesser energy than p orbitals. So more the s character lesser will be the energy of hybrid orbital.

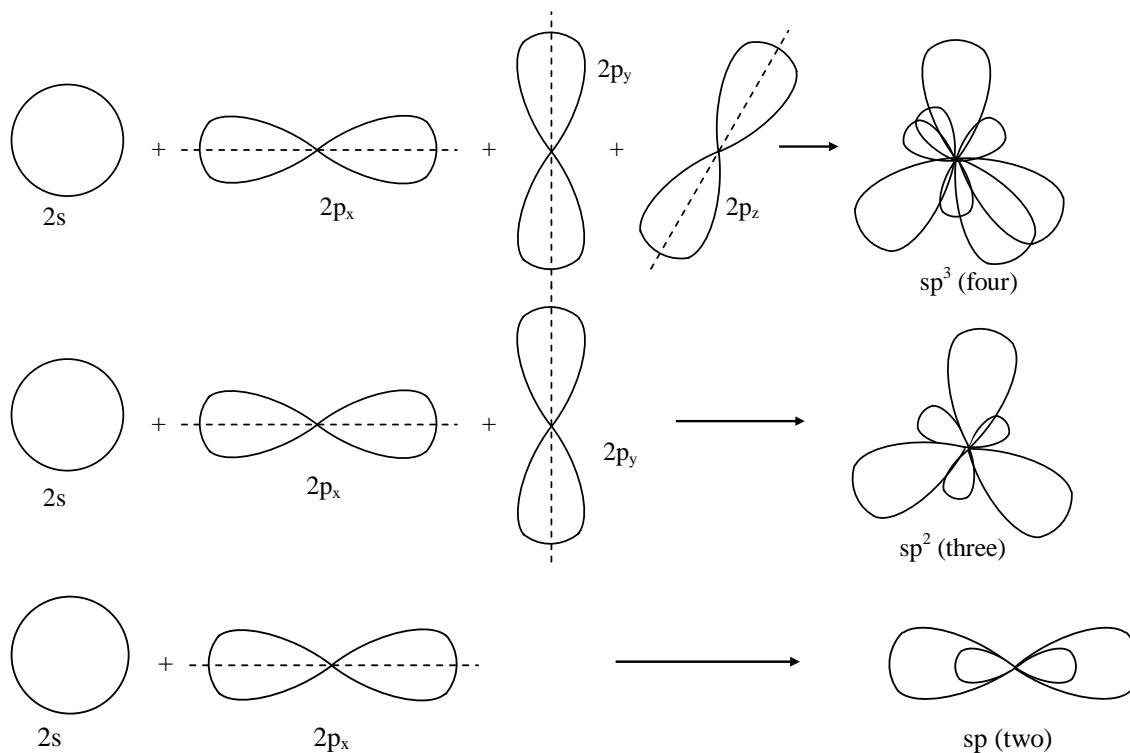
$$sp < sp^2 < sp^3$$

Order of energy

(iv) The hybrid orbitals repel each other and tend to lie far apart from each other.

(v) More the s character of hybrid atom, higher is its electronegativity.

Hybridization	Angle between hybrid orbitals	Arrangement of hybrid orbitals
sp^3 (four)	$109^\circ 28'$	Tetrahedral
sp^2 (three)	120°	Trigonal planar
sp (two)	180°	Linear

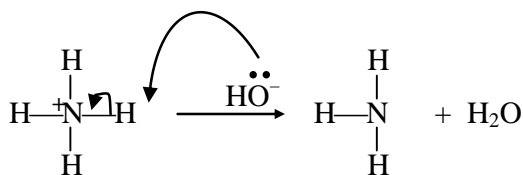


2. TYPES OF REAGENTS (in terms of covalent bond formation)

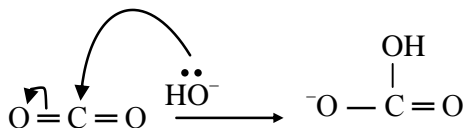
2.1 Electrophile (Electron loving species)

It is a species which can form a covalent bond by using electron pair of another species. It is represented by E^+ . The electrophile must have an atom with a vacant orbital or a polarized π bond. The positive charge is not necessary and all cations are not electrophiles. All electrophiles are Lewis acids. e.g. H^+ , NO^+ , X^+ , CH_3^+ , BF_3 , $AlCl_3$, $O=C=O$, SO_3 , $H-C\equiv N$ etc. Polarization of π bond is necessary because if the polarization is not there, the electron rich π bond will not allow the filled orbital of other species to approach itself. The electrophilic site must not have negative charge because it will not allow the filled orbital of other species to approach itself.

Some cations like H_3O^+ , NH_4^+ , CH_3-X etc are not absolute electrophiles but a source of electrophile H^+ or CH_3^+ . These are better called as source of electrophiles but may be sometimes termed as electrophile.



Not an absolute electrophile but
a source of electrophile, H^+

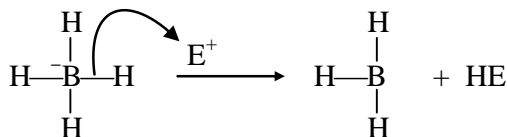


an absolute electrophile due to
presence of polarized π bond
because it reacts in totality

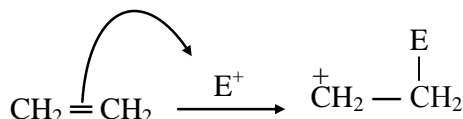
2.2 Nucleophile (Nucleus loving or positive charge loving)

It is a species which form a covalent bond using its own electron pair with other species. These are generally represented by Nu^- . The negative charge is not necessary. The nucleophile must have a lone pair or a π bond (polarized or non polarized). The nucleophilic site must not be positively charged. All nucleophiles are Lewis bases. E.g. H^- , X^- , HO^- , RO^- , $RCOO^-$, H_2N^- , NH_3 , H_2O , ROH , CO_2 , SO_3 etc.

Some anions are not absolute nucleophiles due to absence of lone pairs and π bond but are source of nucleophiles (like H^-). Some examples are BH_4^- , AlH_4^- . These are also sometimes called nucleophiles.



Not an absolute nucleophile but
a source of nucleophile, H^-



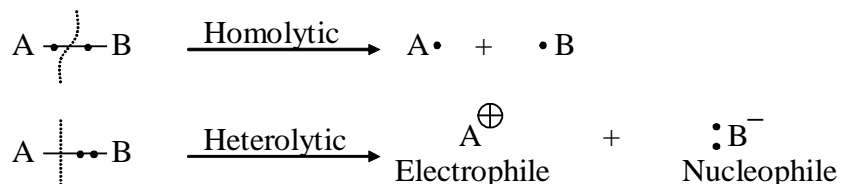
an absolute nucleophile due to presence of π bond because it reacts in totality

2.3 Free Radical

It is a species having an unpaired electron. These species can form a bond by sharing their unpaired electron. E.g. H^\cdot , X^\cdot (halogen atom), $\text{R}-\text{O}^\cdot$ etc.

3. MODES OF BOND CLEAVAGE

Bond Cleavage:



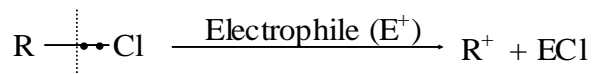
3.1 FACTORS AFFECTING MODE OF BOND CLEAVAGE

Electro-negativity difference: Higher the difference in electro-negativities of the bonded atoms, more will be chances of heterolytic bond cleavage.

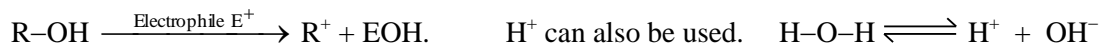
Type of solvent used: Higher the polarity of the solvent, more will be chances of heterolytic cleavage. This is because polar solvents can solvate the ions more easily whereas, nonpolar solvents can solvate the neutral species more easily.

Types of Reagent Used for the bond cleavage:

Electrophilic and nucleophilic reagents cannot do homolytic cleavage but can do heterolytic cleavage.

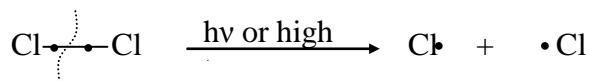


H^+ should not be used to remove Cl^- because HCl is a strong acid i.e the reaction, $\text{H}-\text{Cl} \rightarrow \text{H}^+ + \text{Cl}^-$, has very high tendency to occur in forward direction and very less tendency to occur in backward direction. Hence H^+ has very less tendency to remove any halide ion.

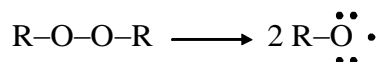


Radical reagents cannot do heterolytic cleavage but can do homolytic bond cleavage.

Homolytic cleavage requires high energy due to which it is favoured at high temperature and presence of light.

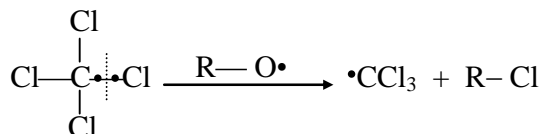
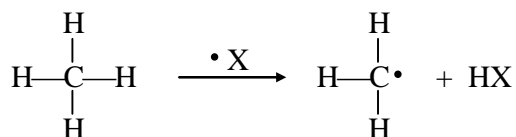
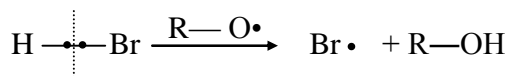


However, if two adjacent atoms having lone pairs belong to 2nd period, the repulsion between lone pairs dominates to weaken the bond, making homolytic cleavage easier. Other free radicals are generated by heating peroxides which dissociate easily to generate RO[•] radicals that react further to generate other radicals.

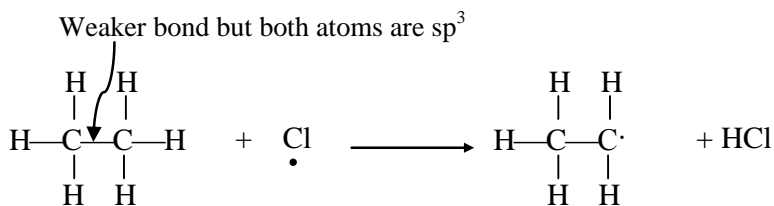
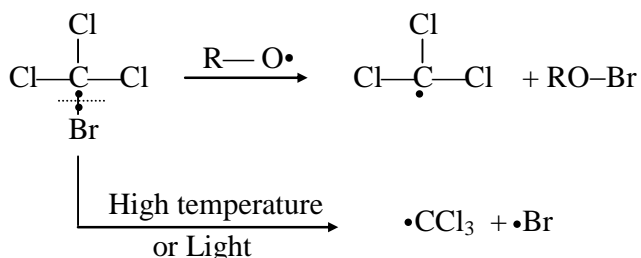


3.2 Homolytic cleavage by a free radical

(i) During homolytic cleavage, the radical reagent prefers to combine with smaller atom as it will form a stronger bond. However, if smaller atom is highly surrounded, radical reagent will combine with the surrounding atom.



(ii) During homolytic cleavage, the radical reagent prefers to break weaker bond (bond of larger atoms) however, if both the atoms of weaker bond are three dimensionally surrounded by other atoms it may break other bonds.

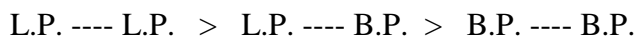


4. REPULSIVE FORCES IN A MOLECULE

There are several types of repulsive forces and strains present in a molecule. They decide several characteristic properties of the molecule. Some important repulsive forces are:

4.1 Lewis Repulsion

According to Lewis the valence electron pairs around an atom repel each other and tend to lie far apart from each other. This repulsion is more by a lone pair than by a bond pair because the lone pair is present in the orbital of central atom only while the bond pair is present in the orbitals of central atom as well as the surrounding atom that are overlapped with each other. Therefore, lone pair is present in lesser space than the bond pair i.e. lone pair has higher electron density than the bond pair. Consecutively, the repulsion between lone pairs will be maximum and that between bond pairs is minimum. This repulsion between valence electron pairs around an atom is called Lewis Repulsion.

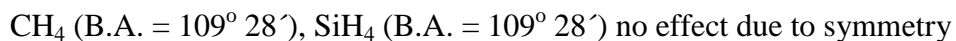


Lewis repulsions, along with other factors like hybridization etc., mainly decide the bond angles in a molecule. Consider the following molecules which have sp^3 hybrid central atom. Presence of one lone pair in NH_3 decreases the angle between the bonds from $109^\circ 28'$ to 107° . Presence of two lone pairs in H_2O decreases the bond angle further to 104.5° .



The repulsion by bond pair also depends on the electronegativity of the central atom and the electronegativity of the surrounding atom.

When electronegativity of central atom is increased, the electron cloud will move towards the central atom which decreases the distance between the bond pairs and strengthens the repulsive force between them. This will favour an increase in the bond angle at the central atom if the electron cloud is not symmetrical.

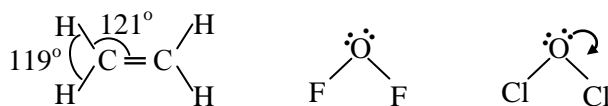


When electronegativity of surrounding atom is increased, the electron cloud will move towards the surrounding atom which increases the distance between the bond pairs and weakens the repulsive force between them. This will favour a decrease in the bond angle at the central atom if the electron cloud is not symmetrical.

CF_4 (B.A. = $109^\circ 28'$), CCl_4 (B.A. = $109^\circ 28'$), CBr_4 (B.A. = $109^\circ 28'$), no effect due to symmetry



Bond angle also depends on several other factors like resonance etc. which affects the electron density of a particular bond. Repulsion by double bonds is slightly more than repulsion by single bonds.

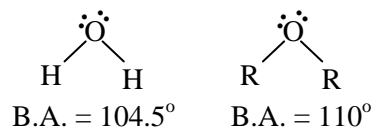


Bond angle of OF_2 is much smaller than the bond angle in OCl_2 which can be partly attributed to lesser electronegativity of Cl, partly to resonance of lone pair in OCl_2 which increases the electron density in bond pair and partly to change in hybridization from sp^3 to sp^2 .

4.2 Steric Repulsion or Van der Waal's Repulsion

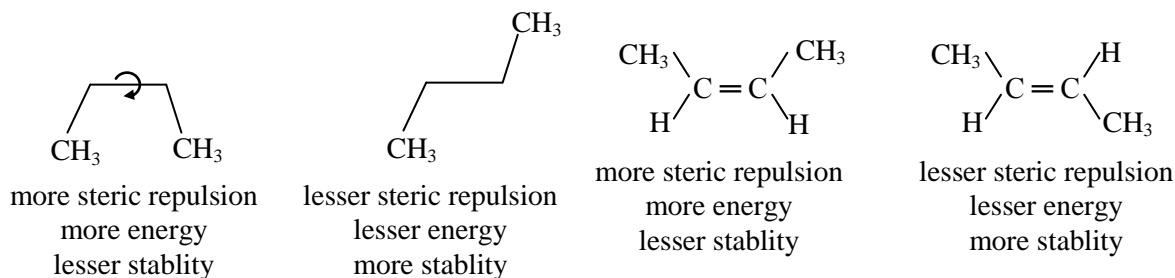
Any two atoms or groups that are not directly bonded to each other repel each other. This repulsion is mainly due to other electron clouds around the atoms and groups. Bigger groups have more steric repulsion than smaller groups. This steric repulsion is negligible between hydrogen.

Steric repulsion of the groups attached to common atom will have its effect on the bond angle. Consider the bond angles in H_2O and R_2O (ether).



In above case both the molecules have sp^3 hybrid oxygen atom with two lone pairs and two bond pairs. The Lewis repulsion by lone pair is more and the steric repulsion by hydrogen is negligible. Therefore the bond angle in H_2O is lesser than the ideal tetrahedral bond angle of $109^\circ 28'$. In ether molecule also the repulsion by lone pair is more but the Lewis repulsion of bond pairs and the steric repulsion of alkyl groups collectively has slightly dominated the Lewis repulsion of lone pairs. Therefore, the actual bond angle is slightly more than ideal tetrahedral bond angle.

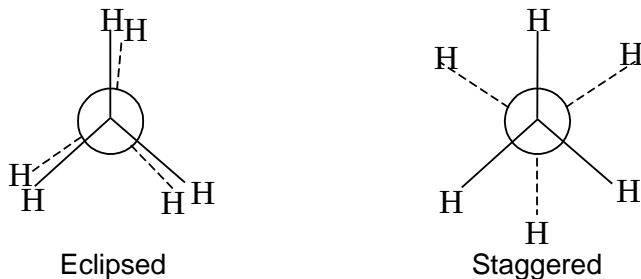
Steric repulsion of the groups attached to adjacent atoms hardly affects the bond angle because these groups can move away by rotating the connected bond. However, they have significant effect on the energy of the molecule and stability of various stereo chemical possibilities.



4.3 Dihedral repulsion or Torsional repulsion

The Repulsion between two non adjacent bonds is called dihedral repulsion or torsional repulsion. This repulsion hardly affects the bond angle but has a significant effect on the energy of the molecule and also affects the dihedral angle between these non adjacent bonds. *Dihedral angle is defined as the apparent angle between two non adjacent bonds when seen from the axis passing through the connecting bond.*

Following are the Newman projections showing the Dihedral angle 0° and 60° in eclipsed and staggered conformers of ethane respectively.



Dihedral repulsions in eclipsed conformer make it less stable than staggered conformer. It must be noticed that Steric repulsion of groups attached to adjacent atoms also affect the dihedral angle.

4.4 Strain in Ring Systems

Molecules which contain rings comprise an important subset of organic compounds. In many respects their behavior and properties are identical to those of functionally analogous open-chain systems. In other respects, however, the greater structural order imposed by a ring causes the properties of cyclic compounds to be quite different than analogous open-chain systems. These differences arise from the need to accommodate preferred bond angles and conformations in structures which restrict the adoption of optimal geometries.

As we have seen previously, molecules with saturated carbon atoms have preferred bond angles of about 109° around the carbons and they are found primarily in staggered, anti conformations. This geometry allows the optimal overlap of all the interacting orbitals and yields the greatest amount of bond energy. Consequently the molecule has a lower energy than any other geometry and is thus the most stable. It is possible to measure the heats of combustion for a series of saturated hydrocarbons and thereby determine how much energy is released ($-\Delta H_{\text{comb}}$) when a $-\text{CH}_2-$ group in a saturated hydrocarbon reacts with oxygen. Thus the heat of combustion of an open-chain methylene group is -157.4 kcal/mol. (The heat of combustion is negative because heat is evolved.)



By a similar method, the heats of combustion of methylene groups in various ring compounds can be determined and the results are presented in Table 1.1. These data show that only cyclohexane and rings larger than C₁₃ have methylene groups of the same energy as methylene groups in open-chain systems. Since in every case the products of combustion (1 CO₂ and 1 H₂O) are the same, any differences in the heats of combustion must reside in the methylene groups themselves. The value of 157.4 kcal/mol represents the least amount of energy that can be

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released by combustion since an open-chain methylene group is at the lowest energy possible for that unit. All other values are equal to or higher than 157.4 kcal/mol.

A value of $-\Delta H_{\text{comb}}/-\text{CH}_2\text{-unit} = 157.4$ kcal/mol (as in cyclohexane) indicates that a methylene group in that compound is as stable as one in an open-chain system and thus it is at the lowest possible energy. A value of $-\Delta H_{\text{comb}}/-\text{CH}_2\text{-unit} > 157.4$ kcal/mol means that a methylene group in that ring system is *less stable* and therefore of *higher energy* than a methylene group in an open-chain compound by an amount equal to the difference between its $-\Delta H_{\text{comb}}$ and 157.4. These differences are shown in the third column of Table 1.1. Finally, since each ring system contains a different number of methylene groups, the total increase in energy of the ring system due to all the methylene groups is found by multiplying the $\Delta(-\Delta H_{\text{comb}})$ by the number of methylene groups in the molecule. This is shown in the last column as total strain. Strain can be defined as an increase in energy of a molecule (making it *less stable*) which results from any structural feature which causes nonoptimal overlap of atomic orbitals. Imperfect overlap leads to weaker bonds so less energy is derived from bond formation. Strain energy is the increase in energy due to imperfect overlap compared to the energy of an analogous system which has optimal overlap and the most bonding energy possible.

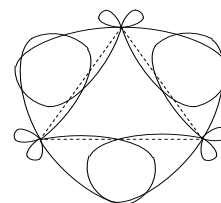
Table 1.1 Heats of Combustion of Methylene Groups in Cyclic Hydrocarbons

Hydrocarbon	$-\Delta H_{\text{comb}}/-\text{CH}_2\text{-unit}$ (kcal/mol)	$-(\Delta H_{\text{comb}})$ vs. Open Chain (kcal/mol)	Total Strain (kcal/mol)
Open chain	157.4	0	0
Cyclopropane	166.5	9.1	27.3
Cyclobutane	163.8	6.4	25.6
Cyclopentane	158.7	1.3	6.5
Cyclohexane	157.4	0	0
Cycloheptane	158.3	0.9	6.3
Cyclooctane	158.6	1.2	9.6
Cyclononane	158.8	1.4	12.6
Cyclodecane	158.6	1.2	12.0
Cycloundecane	158.4	1.0	11.0
Cyclododecane	157.8	0.4	4.8
Cyclotridecane	157.7	0.3	3.9
Cyclotetradecane	157.4	0	0

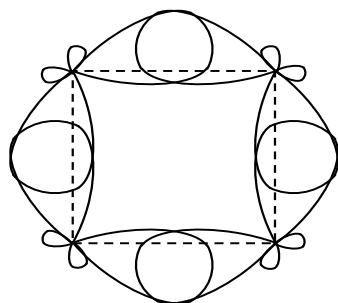
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The methylene groups of cyclopropane are less stable by 9.1 kcal/mol than the methylene groups in open-chain hydrocarbons, and cyclopropane itself contains 27.3 kcal/mol of strain energy because there are three such methylene groups. Cyclopropane is a strained molecule because the three-membered ring requires that the bond angles at carbon be 60° when saturated carbon normally has bond angles of 109° . The distortion of bond angles from the normal tetrahedral geometry leads to increased energy or strain. The smaller bond angles prevent normal overlap along the internuclear axis (dotted line). Overlap occurs outside the internuclear axis and a “bent” bond is formed (also referred to as a τ bond). The τ bond is weaker than a σ bond due to nonoptimal overlap and thus is of higher energy. This special type of bond can be considered as a σ bond having some π character. This type of strain is termed *angle strain* (sometimes called *Baeyer's strain*). It comes about because normal bond angles are not possible and thus nonoptimal overlap results.

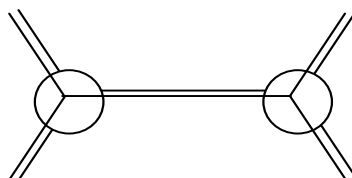
Angle strain in cyclopropane is manifested chemically by greater chemical reactivity of the τ bonds. Thus cyclopropane reacts with bromine, acids, and can be hydrogenated in stark contrast to an unstrained alkane, which is inert to these reagents.



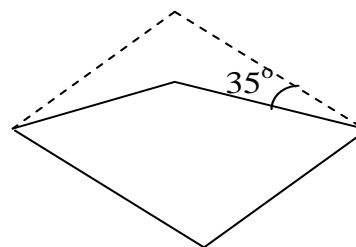
Cyclobutane also exhibits angle strain since 90° bond angles are required by the four-membered ring instead of the preferred tetrahedral geometry. As expected, however, the amount of angle strain is less than in cyclopropane. The ring bonds of cyclobutane are still τ bonds, but they are closer to the internuclear axis and the overlap is better. Consequently they are more stable (stronger) than the τ bonds in cyclopropane. The greater bond strength is manifested by a lower chemical reactivity. Cyclobutane is more like an unstrained alkane and does not react with bromine or acids, although it can be hydrogenated under high pressure.



bent bond τ bond



eclipsing interactions



fold angle = 35°

To achieve a bond angle of 90° , cyclobutane must be planar. This would force the adjacent C–H bonds to be eclipsed and would also raise the energy of the system. As a compromise, cyclobutane folds diagonally by 35° . While this raises the angle strain somewhat, it decreases the eclipsing interactions so that the lowest possible energy is attained. While each methylene group is less strained than one in cyclopropane, the total molecular strain is similar to that of cyclopropane.

If planar, cyclopentane should have minimal strain energy since the internal angles of a regular pentagon (108°) are very close to the normal tetrahedral angle. In fact, cyclopentane is strained by 6.5 kcal/mol. If it were planar, all the hydrogen atoms around the cyclopentane ring would be

eclipsed. This results in a second type of strain called *torsional strain*. Torsional strain is an increase in energy due to enforced eclipsing interactions. To reduce the torsional strain, cyclopentane adopts an “envelope” conformation in which one apex is bent out of the molecular plane by some 20° . This introduces some angle strain but reduces the torsional strain and is the lowest energy structure that the molecule can achieve.

Any one of the five methylene groups of cyclopentane can be bent out of plane; thus cyclopentane is a dynamic system which undergoes a series of conformational changes between different envelope conformations.

The methylene groups of cyclohexane have the same ΔH_{comb} as methylene groups in open-chain systems and thus cyclohexane is unstrained. It was originally predicted by Baeyer that cyclohexane should have angle strain due to required bond angles of 120° for a planar structure. In fact, cyclohexane adopts a puckered conformation in which all the bond angles are 109° and all the hydrogens are perfectly staggered. The chair conformation of cyclohexane and its conformational ramifications will be discussed later. It is also expected that rings larger than C6 could adopt puckered structures and thus maintain normal bond angles and staggered groups. As such they should be unstrained. In fact, it is seen in Table 1.1 that ring systems between 7 and 13 members are all strained to some degree. This strain results from the fact that puckering causes some hydrogens across the ring to approach each other closer than the sum of their Van der Waal's radii. These transannular interactions cause an adjustment in the conformational structure and raise the energy of the ring system. This increase in energy seen in medium-sized rings (C7–C13) is called transannular strain. After the ring size has reached C14, the interior of the ring is large enough to minimize transannular strain. Consequently the ΔH_{comb} returns to the normal value of 157.4 kcal/mol found in unstrained systems.

It must be emphasized that *angle strain*, *torsional strain*, and *transannular strain* are simply terms invented by chemists to categorize structural features in rings which lead to increased energy (strain). The molecules themselves adopt structures which are the most stable and have the greatest amount of bonding energy. Nevertheless, strain is an important feature in molecules to keep in mind since it is manifested by altered chemical reactivity.

For example, molecules which have significant angle strain such as cyclopropanes, epoxides, and aziridines undergo ring cleavage reaction very readily. Such reactions are very exergic because the strain energy is released upon ring opening. The exergic nature of these ring-opening reactions means that they have early transition states and generally have low activation energies. Conversely the formation of small rings requires that the strain energy must be added to the products in order for them to form. Medium rings are difficult to form by intramolecular ring-closing reactions because the transannular strain in the products increases the energy of the transition state leading to those products. Thus the energy barrier to ring closure is raised and the intramolecular ring closure slows down significantly. Consequently intermolecular reactions (and not intramolecular ring-closing reactions) predominate. Transannular strain is not the only factor influencing these processes, but it is a major factor. Saturated six-membered rings are easy to produce because they are unstrained. They are also resistant to ring-opening reactions for the same reason. Consequently saturated six-membered rings are the most common ring systems in the natural world.

Some Important Consequences of Ring Strain:

- (i) The carbon carbon bonds in cyclopropane show a considerable π bond character.
- (ii) Smaller rings (upto six membered rings) cannot have sp hybrid atom.
- (iii) Bridgehead atoms should not be sp^2 hybrid and can not be planar.
- (iv) Double bonds of smaller rings (upto six membered rings) do not exist in trans form.

5. Factors Affecting Electron Density (Electronic displacement)

There are various factors which affect the electron density in a particular part of species. Some of these factors are permanent (inductive and mesomeric effects) whereas some others are temporary (electromeric effect).

5.1 Inductive effect

It is a well known fact that if a covalent bond is formed between atoms of different electronegativities, the shared electrons shift towards more electronegative atom. This permanent but slight shifting of electrons due to electronegativity difference is called inductive effect (I effect). It is always measured with reference to hydrogen and is of two types:

- (a) **Positive inductive effect (+I effect):** The inductive effect of an atom or group of atoms, from which the shared electron go away (electrons are pushed away by it w.r.t. hydrogen), is called +I effect. E.g. alkyl groups, $-O^-$, $-SiH_3$ etc.
- (b) **Negative inductive effect (-I effect):** The inductive effect of an atom or group of atoms, towards which the electrons are shifting (electrons are attracted or pulled by it w.r.t. hydrogen), is called -I effect.

Electron attracting groups (-I effect)

$-NR_3^+$, $-SR_2^+$, $-NH_3^+$, $-NO_2$, $-SO_2R$, $-CN$, $-CO_2H$, $-F$, $-Cl$, $-Br$, $-I$, $-OAr$, $-COOR$, $-OR$, $-COR$, $-SH$, $-OH$, $-C\equiv CR$, $-Ar$, $-CH=CR_2$

Electron repelling groups (+ I effect)

$-O^-$, $-CO_2^-$ $>$ R_3C- $>$ R_2CH- $>$ RCH_2- $>$ CH_3 $>$ $-D$ $>$ H where R is any alkyl group.

Note:

- More the electronegativity of the atom attached, more will be the inductive (-I) effect.
- Bigger the alkyl group, more will be the inductive (+I) effect.
- More the number of alkyl groups, more will be the inductive (+I) effect.
- Inductive effect of a group decreases when its distance increases.

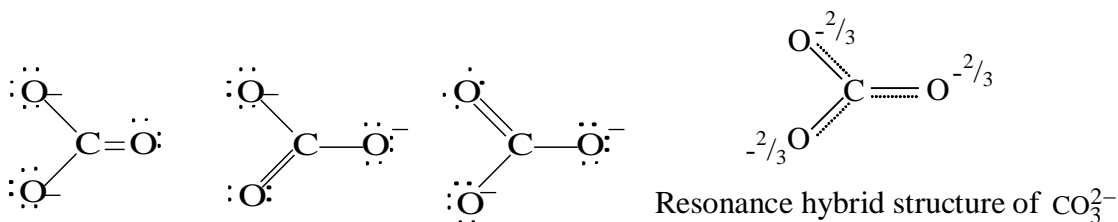
Importance of inductive effect

- (i) Acidic strength of carboxylic acid can be explained on the basis of inductive effects.
- (ii) Basic strength of amines can be explained on the basis of inductive effect.
- (iii) Reactivity of various reactants and stability of various intermediates can be explained.

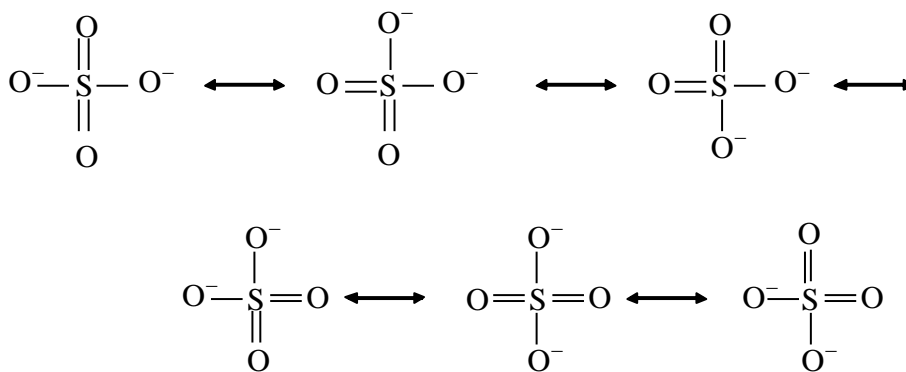
5.2 Resonance and Resonance Effect

Resonance

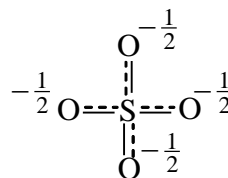
Sometimes it is possible to write more than one structures for a species, which have same arrangement of atoms and differ in the positions of π bonds and lone pairs only. None of these structures is able to explain the actual behaviour of that species. The actual behaviour of that species, however, can be explained by the average structure of all possible structures. This average structure is called resonance hybrid structure of that species and various possible structures are called resonating structures or canonical structures or contributing structures. The resonating structures of CO_3^{2-} (carbonate ion) can be written as given below. In actual structure of CO_3^{2-} ions, all carbon-oxygen bonds are identical as shown below in resonance hybrid structure.



Similarly resonance structures of SO_4^{2-} ions can be written as



The actual resonance hybrid structure may be written as



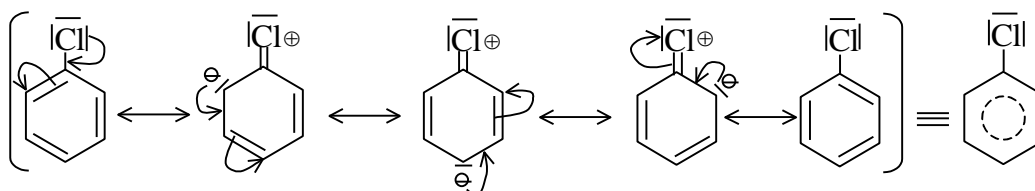
Similarly the Resonance structures of Benzene and the resonance hybrid can be written as



RULES FOR WRITING RESONATING STRUCTURES

A scholar must remember that the different resonating structures of a species must have

1. All the canonical forms must be bonafide Lewis structures. For instance, none of them can have more than 8 valence electrons if d subshell is absent.
2. The positions of the nuclei must be the same in all structures. This means that when we draw the various canonical forms, we cannot change the relative position of atoms but can change relative position of electron pairs.



The resonance interaction of chlorine with the benzene ring can be represented as above. In all structures explaining resonance, the sigma bonds are not involved, only the π or unshared electrons are put in different ways. This means that if we write one canonical form for a molecule, we can write the others by merely moving π and unshared electrons.

3. All atoms taking part in resonance i.e. covered by delocalized electrons, must lie in a plane or nearly so. This of course does not apply to atoms, which have the same bonding in all the canonical forms. The reason for planarity is maximum overlap of the p-orbitals.
4. All canonical form \ominus must have the same number of unpaired electrons.

Thus $^+\text{CH}_2\text{--CH=CH--CH}_2^-$ is a valid canonical form but $\dot{\text{C}}\text{H}_2\text{--CH=CH--}\dot{\text{C}}\text{H}_2$ is not a valid canonical form for 1,3-butadiene.

5. The energy of the actual molecule is lower than that of any canonical form or contributing form obviously. Therefore, delocalization is a stabilizing phenomenon. More the number of contributing structures, more is the stability of resonance hybrid with respect to most stable canonical structure.
6. All canonical forms do not contribute equally to the true molecule. Each form contributes in proportion to its stability, the most stable form contributing most. Thus, for ethylene, the form $\bar{\text{C}}\text{H}_2\text{--}\overset{+}{\text{C}}\text{H}_2$ has such a high energy compared to $\text{CH}_2\text{=CH}_2$ that it essentially does not contribute at all. Equivalent canonical forms contribute equally. The greater the number of significant structures that can be written and the more nearly equal they are, the greater the resonance energy, other things being equal.

The resonating structures differ only in the arrangement of electrons in different resonating forms.

CHARACTERISTICS OF RESONANCE

- (i) The contributing structures do not have any real existence. Only the resonance hybrid has the real existence.
- (ii) Resonance hybrid is the weighted average structure of all resonating structures.

- (iii) The resonance hybrid has lesser energy and hence more stability than any of the resonating structures. The difference between energy of most stable resonating form and that of resonance hybrid is called resonance energy.
- (iv) More the resonance energy more is the stability of molecule w.r.t. most stable canonical structure.
- (v) Similar the resonating forms, more will be resonance energy and hence stability.
- (vi) More stable resonating structures contribute more towards the resonance hybrid.

STABILITY OF RESONATING STRUCTURES

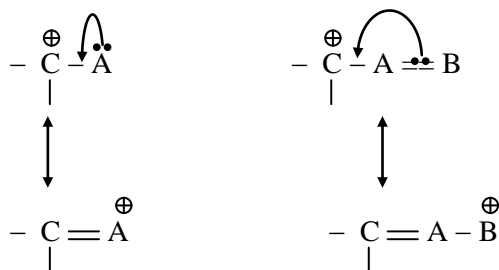
It is not easy to decide relative stabilities of imaginary structures (contributing structures). However, the following logics may be helpful:

- (a) Structures with more covalent bonds are usually more stable than those with lesser covalent bonds. This effect of more bonds generally dominates on other factors.
- (b) Structures with formal charges are less stable than uncharged structures.
- (c) Structures with more than two formal charges usually contribute very little.
- (d) Opposite charges are more stable when nearer to each other while like charges are more stable when away from each other.
- (e) Negative charge is more stable on more electronegative atom while positive charge is more stable on less electronegative atom.
- (f) Structures having more benzenoid rings are more stable.
- (g) Fused benzenoid rings are less stable than separate benzenoid rings.
- (h) Inductive effect also decides the stability of resonating structures. However, resonance must not be considered when comparing stability of various resonating structures.
- (i) More symmetrical structures are more stable.

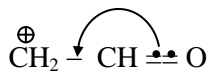
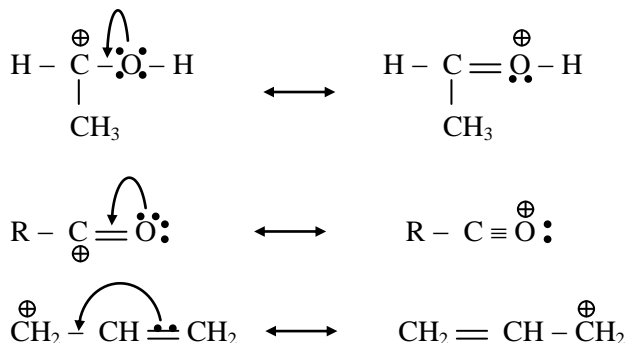
Most of the students face problems while working out various resonating structures. They cannot even predict whether resonance may take place or not for a given species. But actually it is very simple if we apply logics. The simple logic which we must remember is “electron will not go completely away from more electronegative atom.” Although lone pair of highly electronegative atom can become bond pair, as bond pair electrons of an atom are considered with that atom. Electrons go away from negative charge and move towards positive charge.

RESONANCE ON AN ATOM HAVING VACANT ORBITAL

Starting from the atom having vacant orbital, leave one bond and see the next atom. If next atom contains either a lone pair or π electrons, resonance may take place.



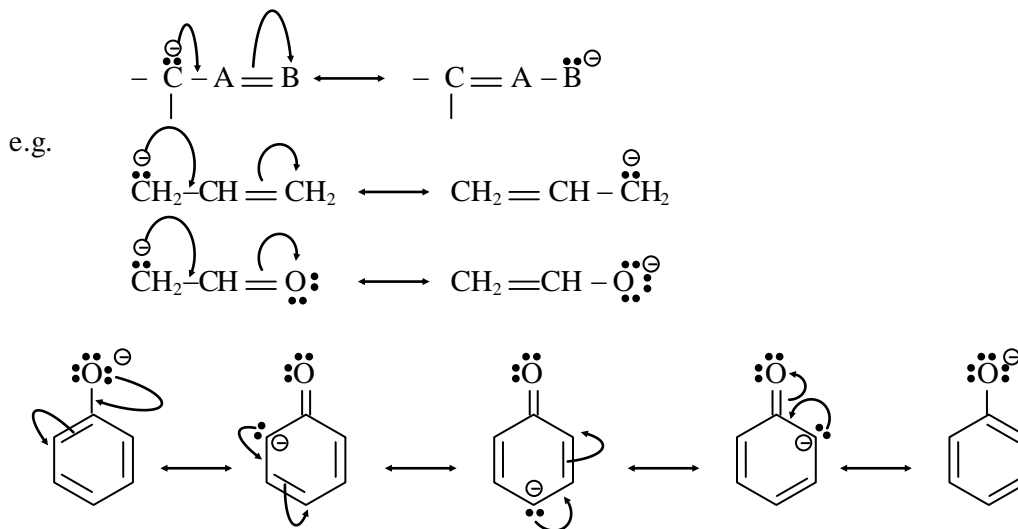
e.g.



Not allowed as electrons are going away from more electronegative atom (oxygen)

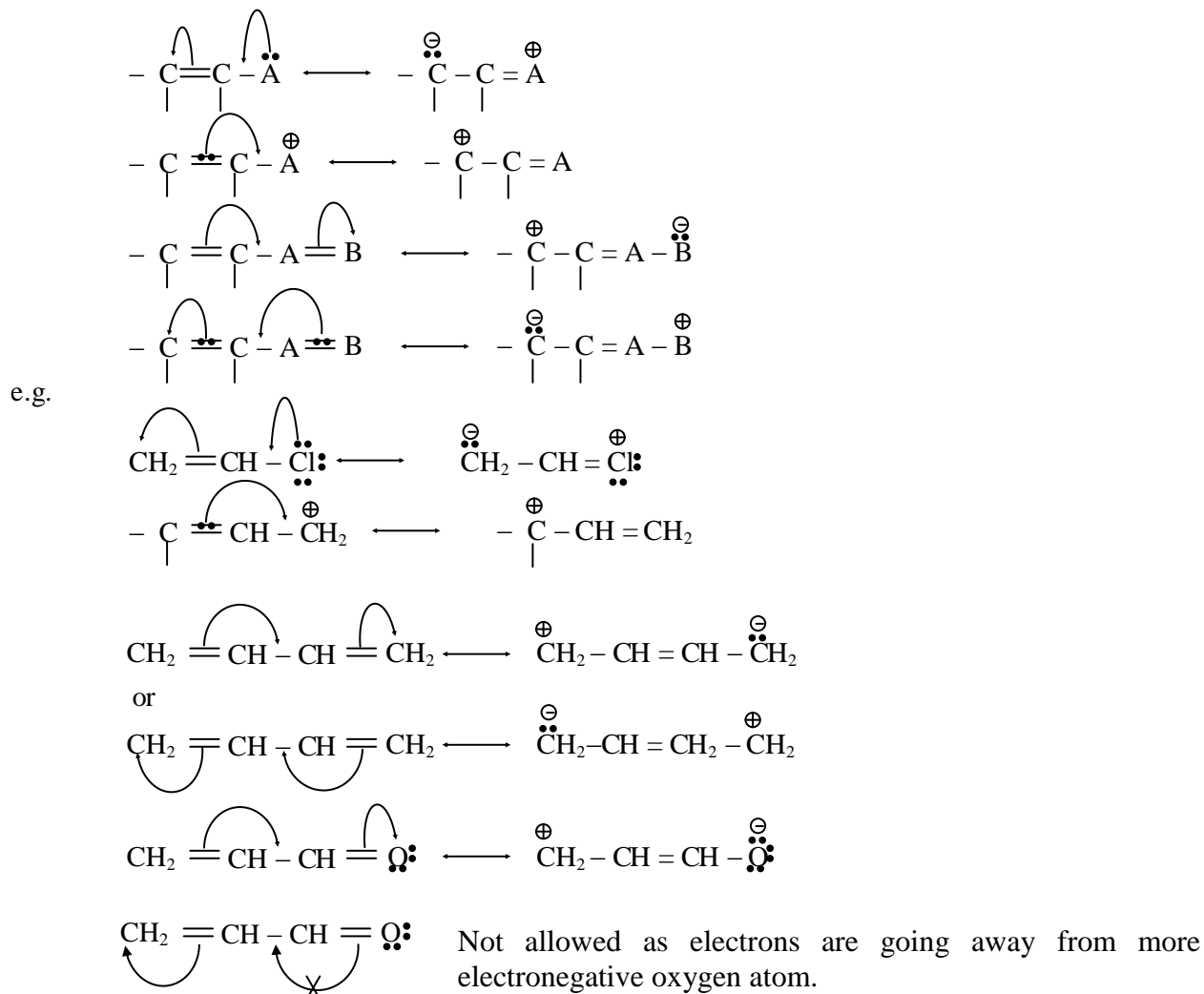
RESONANCE ON AN ATOM HAVING A LONE PAIR OF ELECTRON

Starting from the atom having lone pair, leave one bond and see next atom. If next atom contains vacant orbital (as above) or π electrons, resonance may take place.



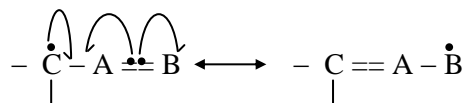
RESONANCE ON UNSATURATION

Starting from the π bond, leave one bond and see next atom. If next atom is electron deficient, or negatively charged (having lone pair), or having π electrons, resonance may take place.

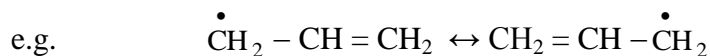


RESONANCE ON FREE RADICALS:

Starting from free radical, leave one bond and see next atom. If next atom contains π electrons, resonance may take place.



Here half arrow (fish arrow) is used for movement of one electron.



RESONANCE EFFECT

Resonance always results in a different distribution of electron density than would be the case if there were no resonance. The effect of resonance on electron density at a part is called resonance or mesomeric effect.

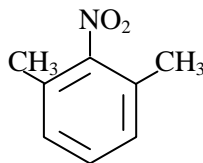
Positive Resonance Effect: When a group or atom gives electron due to resonance, its effect is called positive resonance (+R or +M) effect. E.g. $-\text{NH}_2$ group in aniline.

Negative Resonance Effect: When a group or atom takes electron due to resonance, its effect is called negative resonance (–R) or negative mesomeric (–M) effect. E.g. $-\text{NO}_2$ group in nitrobenzene.

It should be remembered that more electronegative atom has lesser tendency to give electron and more tendency to take electron. However, if π bond is being formed, smaller atoms have more tendencies to form π bonds (this effect of size dominates over effect of electro-negativity in a group)

STERIC INHIBITION OF RESONANCE (Ortho Effect)

The atoms covered by delocalized electrons must lie in a plane or so. Many examples are known where resonance is reduced or prevented because the atoms are sterically forced out of planarity. E.g. Resonance effect of $-\text{NO}_2$ group in the following examples has been diminished by steric factors and the oxygen atoms of $-\text{NO}_2$ group cannot come in the plane of benzene ring.



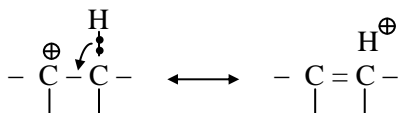
Sometimes, resonance effect of a group with benzene ring (aromatic ring) is diminished due to presence of another group at ortho position (adjacent position). This is called **ortho effect**. This inhibition of resonance occurs because the ortho group repels resonating group out of plane of benzene ring which prevents the resonance. Some groups whose resonance is easily diminished are: $-\text{NO}_2$, $-\text{NR}_2$, $-\text{COOH}$, $-\text{COR}$ etc. *However, resonance of single atom ($-\text{X}$, $-\text{O}^-$), sp hybrid atom ($-\text{C}\equiv\text{N}$), $-\text{AH}$, $-\text{AH}_2$ groups is not generally affected.*

5.3 HYPER CONJUGATION

So far we have discussed delocalization of lone pairs and π electrons only. Another type of delocalization involves σ electrons, and is called hyper conjugation. The most important hyper conjugation is delocalization of $\text{C}-\text{H}$ σ electrons and $\text{C}-\text{X}$ σ electrons. For working out various contributing forms due to hyper conjugation, similar logics (as we have discussed during resonance) are applicable.

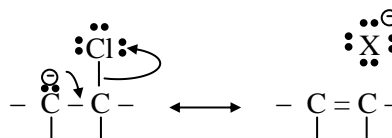
Hyper Conjugation on an Atom Having Six Valence Electrons & Vacant Orbital

Leave one bond see the next σ bond. If next σ bond is C-H bond, hyper conjugation may take place.



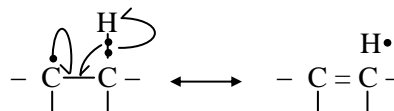
Hyper Conjugation on an Atom Having a Lone Pair of Electrons

Leave one bond and see next σ bond. If next σ bond is C-X bond (X is highly electronegative atom particularly halogen), hyper conjugation may take place.



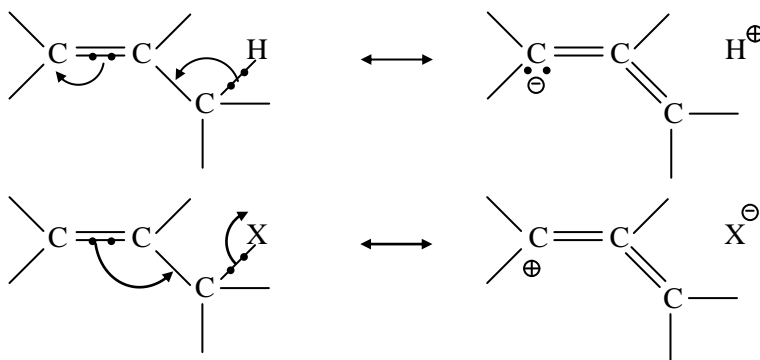
Hyper Conjugation on a Free Radical

Leave one bond and see next bond. If next σ bond is C-H bond, hyper conjugation may take place.

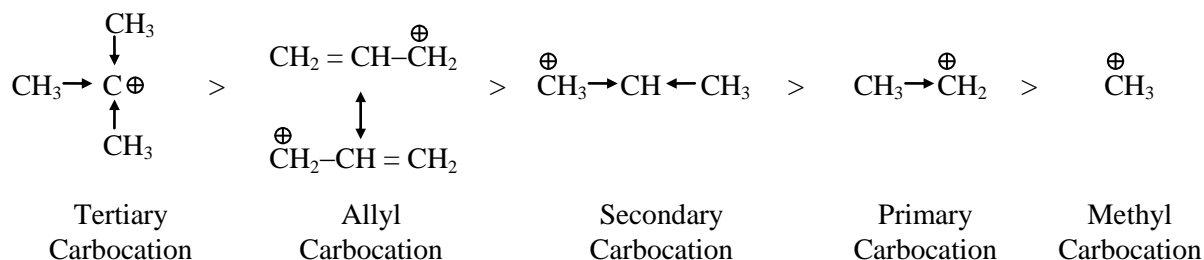


Hyper Conjugation on Unsaturation

Leave one bond and see next bond. If next σ bond is C-H bond or C-X bond, hyper conjugation may take place.



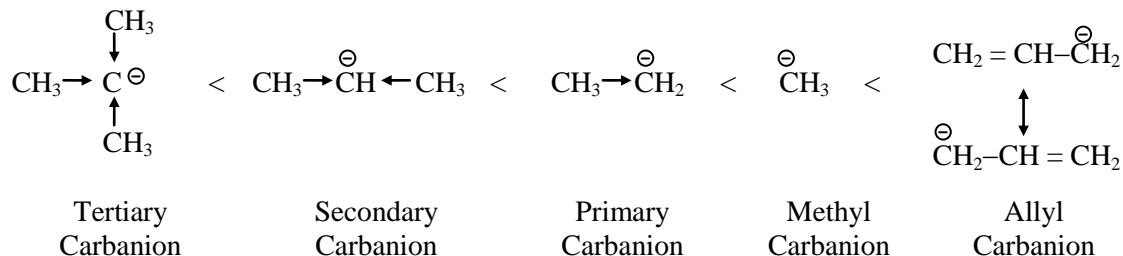
STABILITY OF VARIOUS CARBOCATIONS



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The stability order $3^\circ > 2^\circ > 1^\circ > \text{methyl}$ can be explained due to positive inductive effect of alkyl groups. Alternatively it can also be explained on the basis of hyper conjugation effect with 9, 6, 3 and zero hyper conjugation in above 3° , 2° , 1° and methyl carbocations.

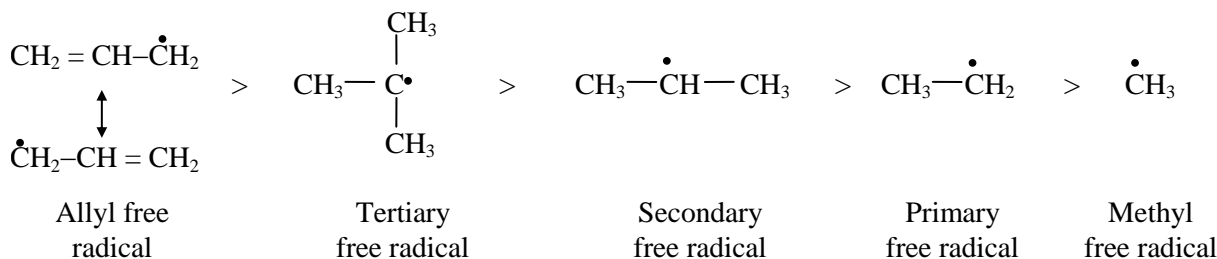
STABILITY OF CARBANIONS



The stability order $3^\circ < 2^\circ < 1^\circ < \text{methyl}$ can be explained on the basis of +I effect of alkyl groups (electron-releasing) which increases -ve charge and decreases stability. The stability of allyl carbanion is due to resonance.

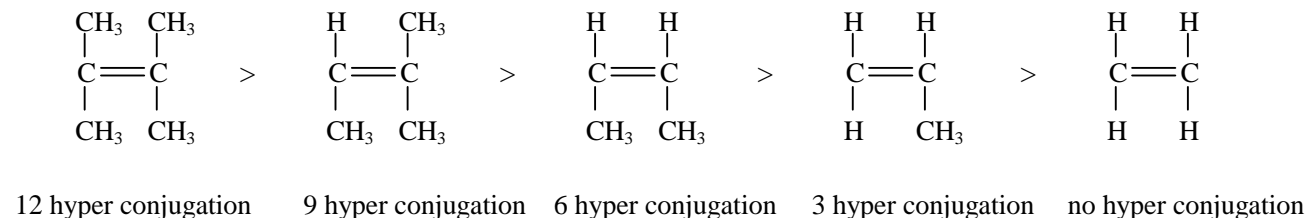
STABILITY OF FREE RADICALS

The stability order of free radicals $3^\circ > 2^\circ > 1^\circ > \text{methyl}$ cannot be explained on the basis of inductive effect. It can, however, be explained on the basis of hyper conjugation effect with 9, 6, 3 and zero hyper conjugation in 3° , 2° , 1° and methyl free radicals. The stability of allyl free radical is due to resonance.

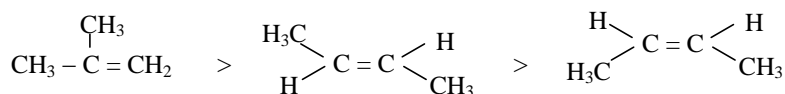


STABILITY OF ALKENES

Alkenes are electron rich (π electrons) species. The stability of alkenes, therefore, is expected to decrease in the presence of alkyl group on doubly bonded carbon because of electron releasing effect of alkyl group. The observation are, however, opposite to above expectations. The stability of alkene is found to be increased in the presence of alkyl group. This can only be explained on the basis of hyper-conjugation. The observed stability of alkenes is given below:



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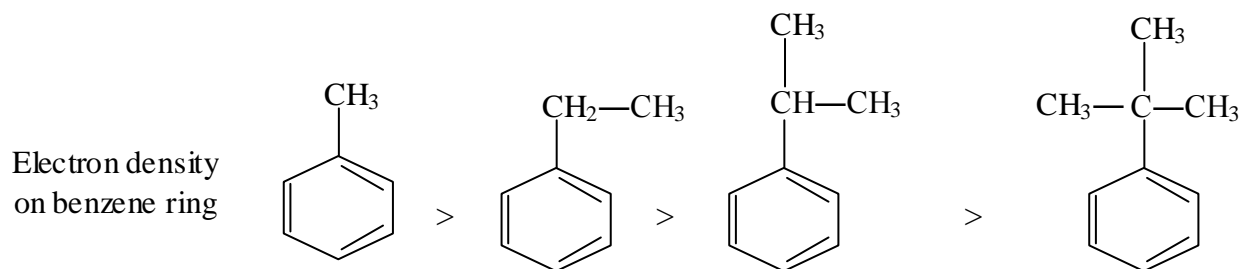


Stability of different isomers of Butene

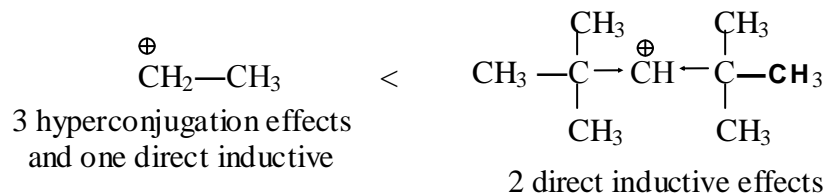
NOTE:

Hyperconjugation effect is much lesser than resonance effect and is comparable to inductive effect. Following points generally help when hyperconjugation and inductive effects contradict each other:

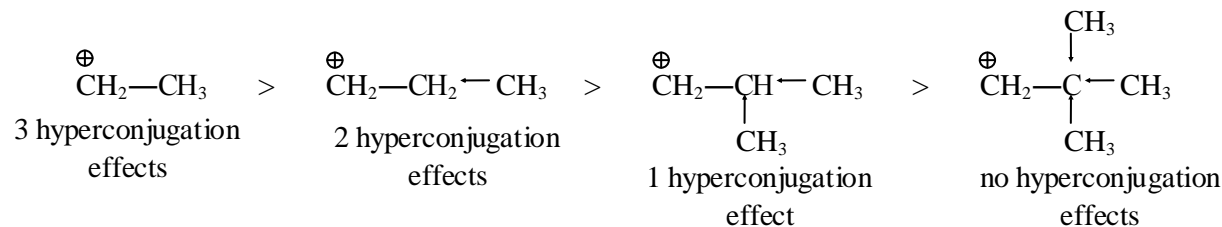
- (i) Hyperconjugation effect dominates over inductive effect in most neutral molecules.



- (ii) Direct inductive effect in ionic species generally dominates over hyperconjugation effect.



- (iii) Hyperconjugation effect generally dominates over indirect inductive effect in ionic species.

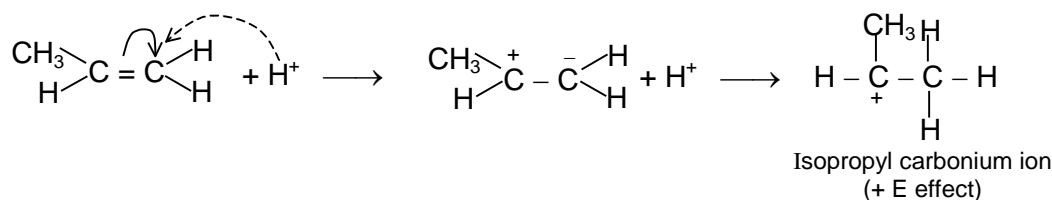


These carbocations have one direct inductive effect but the difference is in the hyperconjugation and indirect inductive effects of additional methyl groups.

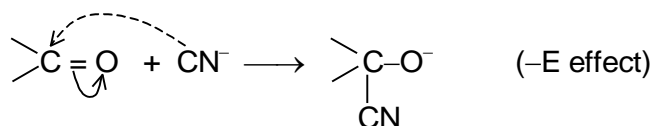
5.4 Electromeric Effect

This is a temporary effect which involves complete transfer of a shared pair of π -electrons towards one of the atoms linked by a multiple bond at the demand of attacking reagent. The atom receiving the electron pair acquires a unit negative charge, while the other atom becomes positively charged. When the electron transfer takes place towards the attacking reagent, it is called + *E effect*.

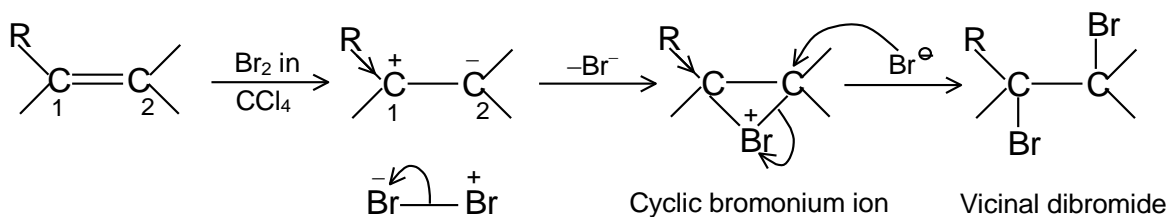
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And when the electron transfer takes place away from the attacking reagent, it is called **– E effect**.



The most common example of the electromeric effect is the reaction of an alkene with bromine in CCl_4 .



In this reaction, when reagent (bromine) approaches alkene, the temporary polarization develops on the alkene with C_2 atom gaining a negative charge and C_1 atom acquiring positive charge (as it can be compensated by the +I effect of R group). The alkenes being electron rich compounds (due to the presence of π -electron cloud) are attacked by the electrophile (Br^+) to give a cyclic bromonium ion. Here, the formation of cyclic bromonium ion as intermediate is possible because bromine has large size and possesses the lone pair, which can be donated to the carbon simultaneously. The cyclic bromonium ion is then attacked by Br^- from the opposite side of the 3-membered cyclic intermediate to give the resultant product.

6 ACIDIC STRENGTH OF ORGANIC ACIDS

6.1 Factors Affecting Acidic Strength

The factors responsible for influencing the acidity of an organic compound, H-X are

(a) *The strength of the H-X bond*: Stronger bond is more difficult to break.

(b) *The electronegativity of X*: More electronegative atom can lose H^+ more easily.

Note: In most of the cases, H-X bond strength and the electronegativity of X oppose each other. However, it has been experienced that the effect of electronegativity dominates in a period while effect of bond strength dominates when X belong to same group but different period.



(c) *Factors stabilizing X^- as compared to HX*: Various factors like inductive effects, resonance effect and hyperconjugation effects. Presence of any electron donating group increases the negative charge on atom X which makes X^- less stable and decreases acidic strength of HX. On the other hand Presence of any electron withdrawing group increases the stability of X^- and increases the acidic strength of HX.

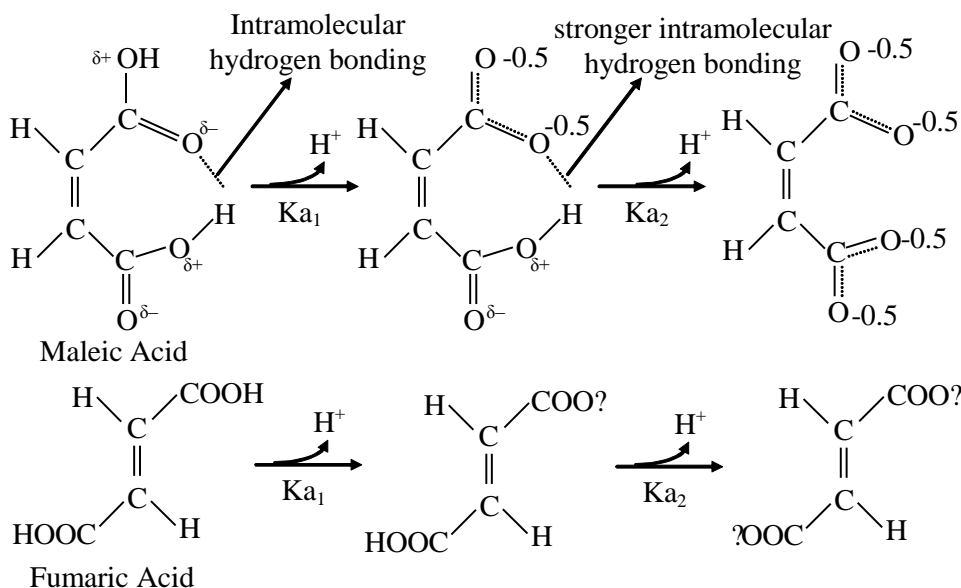
Note: It must be remembered that if H^+ losing atom does not have lone pair, we must convert the acid HX to X^- and then compare electronic effects of other parts. This is because the lone pair of X^- may be involved in resonance and that effect will not be visible if we check electronic effects directly on HX. However, electronic effects can be compared directly on HX or on X^- if H^+ losing atom has lone pair.

(d) The nature of the solvent.

(e) *Intramolecular Hydrogen bonding*: Intramolecular hydrogen bonding can affect acidic strength in two ways as discussed below:

(i) If loss of H^+ increases the already present hydrogen bond, it increases the stability of resultant anion due to increase in the strength of hydrogen bond. Therefore acidic strength is increased due to this increase in the strength of initially present hydrogen bond. Consider higher K_{a1} value of Maleic acid than K_{a1} value of Fumaric acid.

(ii) If H^+ to be lost is itself involved in intramolecular hydrogen bonding, acidic strength is decreased because more energy will have to be given to break this additional bond to lose H^+ . Consider lower K_{a2} value of Maleic acid than K_{a2} value of Fumaric acid.



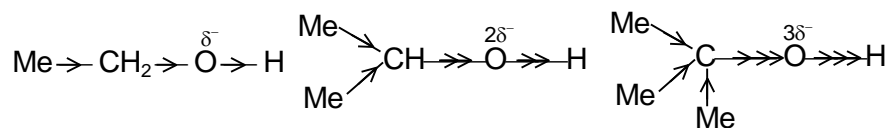
The most important factors among all is (c). However, following points must be remembered while applying electronic effects:

- (i) Resonance effect generally dominates over inductive and hyperconjugation effects.
- (ii) Resonance effect and hyperconjugation effects of a group is very less (indirect) from meta position of benzene ring than that from ortho and para position. Inductive effect can also dominate over resonance effect from meta position.
- (iii) Effect of intramolecular hydrogen bonding can dominate over inductive and hyperconjugation effect but not generally over resonance effect.

6.2 Acidic Strength of Some Organic Compounds.

Acidic Strength of Alcohols

If we were to predict the order of acidic strength of ethanol, iso-propanol and tertiary butanol, we can proceed as



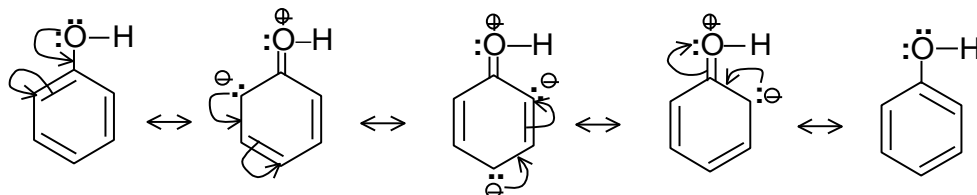
As alkyl groups (methyl group) have a +I effect, the electron density at the oxygen atom will increase. More the number of alkyl groups, more will be the intensity of negative charge on oxygen. The greater the negative charge on the oxygen atom, the closer is the electron pair in the O-H bond driven to the hydrogen atom and consequently separation of a proton becomes increasingly difficult. Thus, the acidic strength of given alcohols will be in the order

Ethanol > iso-propanol > t-butanol

Acidic Strength of Phenols and other derivatives of phenols

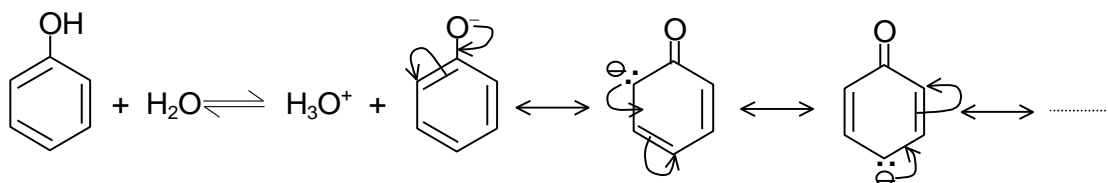
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(a) Because of resonance, the oxygen atom of the OH group acquires a positive charge and so proton release is facilitated.



It might be noted that since the carbon atom of C–OH group is sp^2 hybridised, it is more electron-attracting than an sp^3 carbon atom (as in alcohols) and therefore there is an increased –I effect which facilitates proton release. But this inductive effect alone is not large enough to explain the increased acid strength of phenols as compared with alcohols.

(b) When phenol ionizes, the phenoxide ion is also a resonance hybrid, but it is more stabilised by resonance than is the unionized phenol molecule because of spreading of negative charge only. In the unionized molecule, unlike charges are spread and so is less stable.



Phenols are stronger acids than alcohols. This is attributed to the fact that in phenoxide anion (obtained by the loss of proton from phenol), there is possibility of the delocalization of its negative charge through interaction with the π -orbitals of the aromatic nucleus while alkoxide cannot be stabilized by such effect. Thus phenoxide is a weaker base than alkoxide. Consequently, the phenol would be stronger acid than alcohol.

The effect of a ring substituent on the acid strength of phenol depends on whether the group is electron attracting or releasing, its ability to enter into resonance with the hydroxyl group, and its position. Effects in the o-position are similar to those in the p-position, but there are added complications due to the steric effect and to hydrogen bonding (when this is possible). Effects from meta position are altogether different from ortho and para position. In general, the presence of electron withdrawing groups in phenol increases its acidity while the presence of electron releasing groups decreases the acidity of phenol.

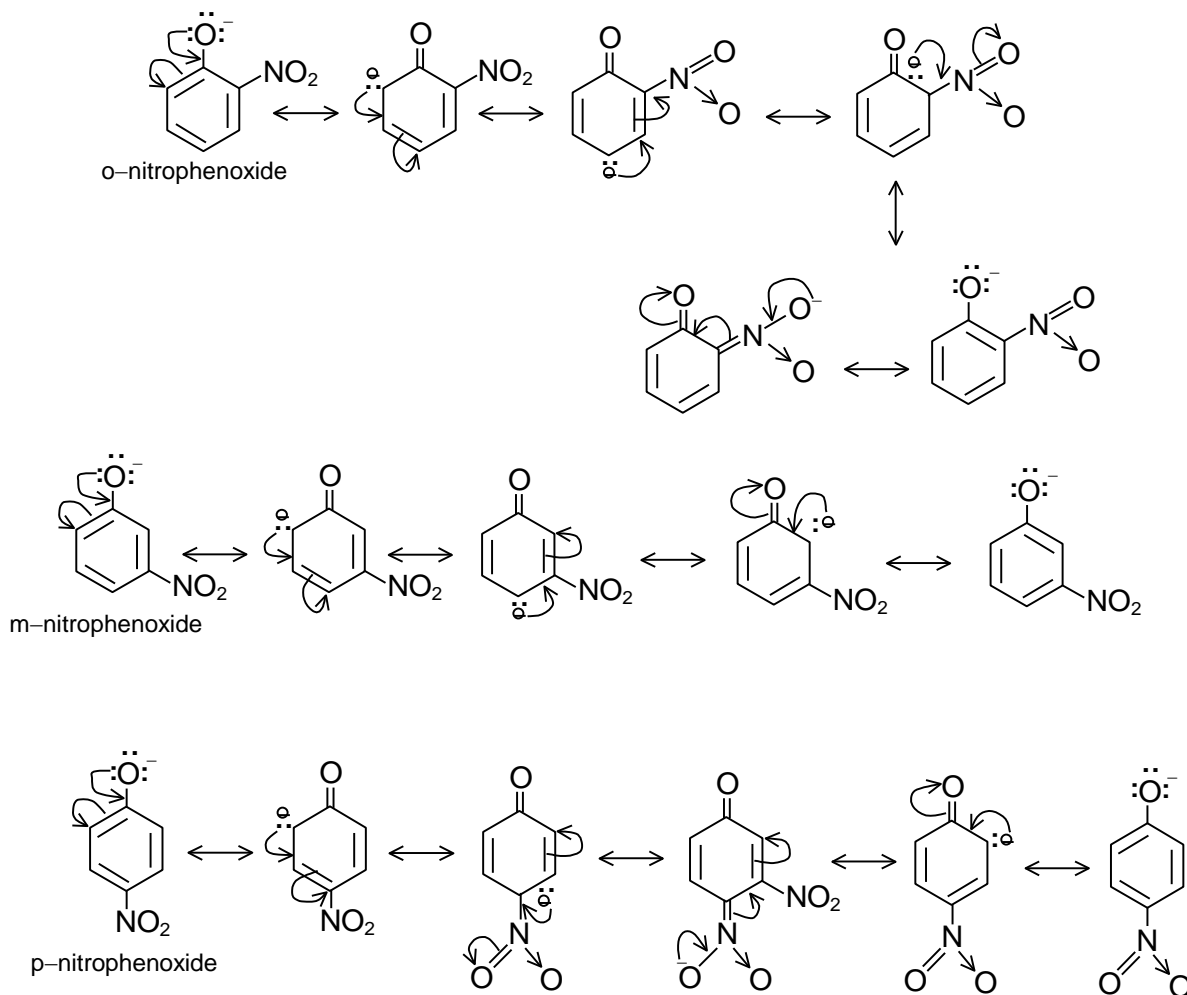
The resonance effect of a group from meta position is not experienced by the lone pairs of oxygen directly as these groups are not conjugated with the lone pairs of oxygen. However the resonance effect of these groups will increase or decrease electron density on benzene ring which will affect the –R effect of benzene ring on the lone pairs of oxygen. Therefore, resonance effect of any group at meta position will also affect the acidic strength but the magnitude of the effect is very less (sometimes inductive effect dominates over resonance effect from meta position).

The methyl group decreases the acid strength of phenol from all ring positions. The methyl group is electron releasing and so release of a lone pair from oxygen (of the OH group in

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the unionized phenol or from the O^- in the phenoxide ion) into the ring is opposed. This results in diminished resonance in the contributing structures and consequently the phenoxide ion is more resonance stabilized with respect to phenol than is the methylphenoxide ion with respect to methylphenol. Hence, phenol is a stronger acid than all methylphenols. The order of acidity of methyl phenols is phenol > m-methyl phenol > p-methylphenol > o-methyl phenol.

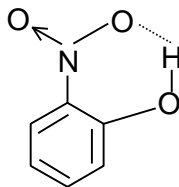
Now, let us compare the acidic strength of o-, m- and p- nitrophenols. The corresponding phenoxide ions obtained from the three nitrophenols would be stabilized by delocalization as



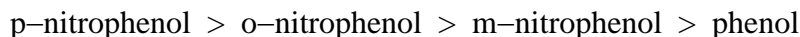
From the structures of phenoxide ions, it is evident that o- and p-nitrophenoxides are more extensively stabilized with respect to m-nitro phenoxide (as additional contributing structure is obtained by the dispersal of negative charge over oxygen atom of NO_2 group also in o- and p-nitrophenoxide but not in m-nitrophenoxide). Thus corresponding o- and p-nitrophenols are much stronger acids than m-nitrophenol. A meta-nitro group cannot enter into resonance with the hydroxyl group but can exert $-I$ effect and indirect $-R$ effect for this position. Hence, meta-nitrophenol is also stronger acid than phenol. Out of o- and p-nitrophenols, p-nitrophenol is slightly stronger than o-isomer as

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o-isomer is a bit stabilized by intramolecular hydrogen bonding, thus having a reduced tendency to release proton.



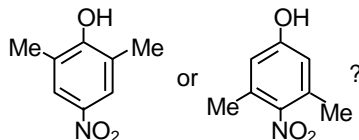
The order of acidic strength of the nitrophenols is



The cumulative effect of three nitro groups in the 2,4,6 positions is shown by the fact that 2,4,6-trinitrophenols (picric acid) is a very strong acid.

All the halophenols are stronger acids than phenol and so it follows that the $-I$ effect of halogen atom is greater than its $+R$ effect. Thus, the order of acidity of halophenols is $o\text{-halophenol} > m\text{-halophenol} > p\text{-halophenol} > \text{phenol}$.

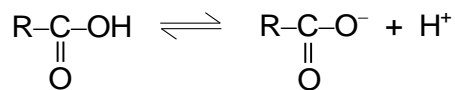
Question 1: Which phenol is more acidic,



Solution: The former is stronger acid than the latter because the NO_2 of latter is forced out of plane of benzene ring due to steric repulsion by CH_3 group which causes steric inhibition of resonance.

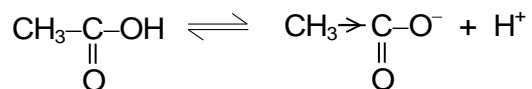
Acidic Strength of Aliphatic carboxylic acids

The aliphatic carboxylic acids are much stronger acids than phenols and alcohols. This is attributed to the fact that the carboxylate ion (obtained by the loss of proton from carboxylic acid) is relatively more stabilized by delocalization than the phenoxide and alkoxide ions with respect to their undissociated molecules.

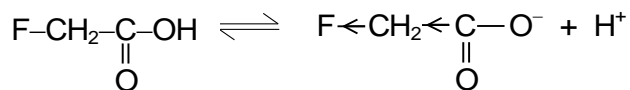


The delocalization of the negative charge in the carboxylate anion involves structures of identical energy content (as the negative charge resides on more electronegative atom, oxygen) while in phenoxide anion, the negative charge also resides on the less electronegative atom (carbon) making these structures of high energy content with respect to those structures in which the negative charge is on oxygen.

The presence of electron-withdrawing substituents in simple aliphatic acids increases their acidity while the electron-releasing substituents have reverse effect. For instance, let us compare the acidic strength of fluoroacetic acid and acetic acid.

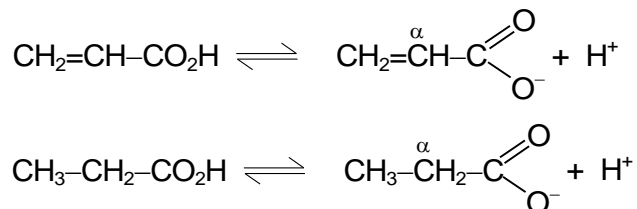


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The fluoro acetate ion is stabilized more due to strong $-I$ effect of fluorine, with respect to acetate ion. Hence, fluoro acetate ion is less basic than acetate ion, thereby making fluoroacetic acid stronger than acetic acid.

If there is a doubly bonded carbon atom adjacent to the carboxyl group, the acid strength is increased. This will be evident if we compare the acid strength of propanoic acid and propenoic (acrylic) acid.

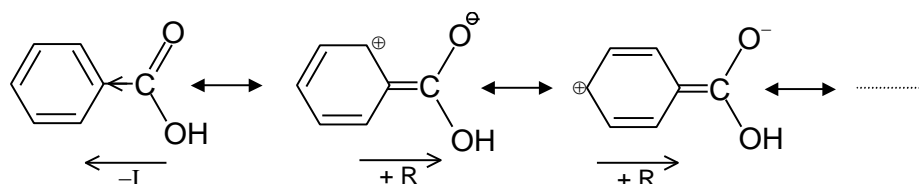


As we know that unsaturated α -carbon atom in propenoate ion is sp^2 hybridised, which means that electrons are drawn closer to the carbon nucleus than in a saturated, sp^3 hybridised α -carbon atom, due to greater s-contribution in the sp^2 hybrid orbital. The result is that sp^2 hybridised carbon atoms are less electron-donating than saturated hybridised ones, thus, propanoate ion will be comparatively less stabilized than propenoate ion, thereby making propenoic acid stronger than propanoic acid (but propanoic will still be weaker than methanoic acid).

If there is a triple bonded carbon atom adjacent to carboxyl group, the acid strength is more with respect to the presence of a doubly bonded carbon atom adjacent to $-\text{CO}_2\text{H}$ group. This is attributed to the fact that sp hybridized carbon atoms are less electron-releasing than sp^2 hybridized carbon atoms.

Acidic Strength of Aromatic carboxylic acids

It has been pointed out that replacement of the hydrogen atom in formic acid by an alkyl group weakens the strength of the acid and the greater the $+I$ effect of the R group, the weaker is the acid. Phenylacetic acid, $\text{PhCH}_2\text{CO}_2\text{H}$ is stronger than acetic acid and therefore the phenyl group has an overall $-I$ effect. On the other hand, benzoic acid is weaker than formic acid. In this case, the phenyl group has an overall releasing effect (*which is smaller than that of methyl group*). These apparently contradictory results may be explained as follows. When the carboxyl group is directly attached to the nucleus, the resonance effect ($+R$) overcomes $-I$ effect (in phenylacetic acid the phenyl group is insulated from the carboxyl group by a CH_2 group and so the $+R$ effect is not possible):

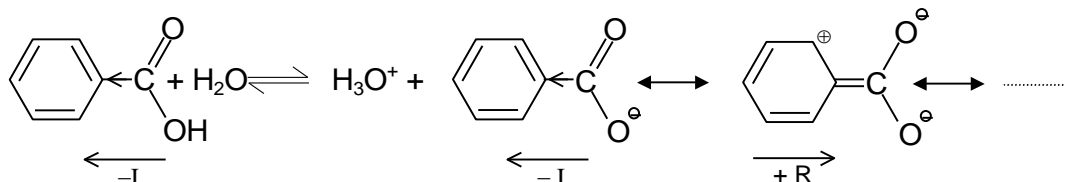


This prevents to a large extent, the lone pair on the O atom of the OH group from entering into resonance with the CO group. The result is a smaller positive charge on the O atom

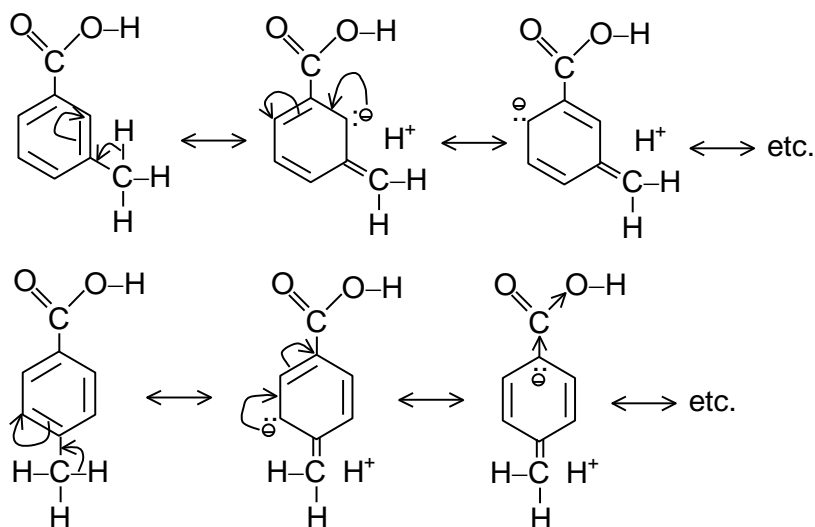
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of the OH group and so proton release is more difficult than in formic acid. The fact that benzoic acid is stronger than acetic acid means that $[-I + (+R)] < +I$ of the methyl group.

The same arguments may be applied to ionized benzoic acid.

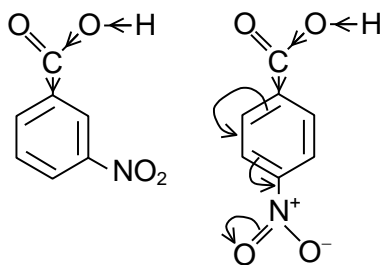


Now let us consider substituted benzoic acids. At this point, we will consider the effect of substituents from m- and p-positions only. First let us take methyl substituted benzoic acids. As the methyl group has $+I$ effect, so the net result will be to increase the $+R$ effect in the m- or p-tolyl group. Since, the inductive effect decreases with distance, so the $+I$ effect of CH_3 from para position would be less than the $+I$ effect of CH_3 group from meta position. Thus, the electron-density in the O-H bond of m-methyl benzoic acid would be greater than that in p-methyl benzoic acid. Accordingly, the p-isomer should be more acidic than the m-isomer. But in real practice, the order is reverse. Actually, we have ignored the hyperconjugation effect of CH_3 group. Due to hyperconjugation effect of CH_3 in p-isomer, the electron density in the O-H bond would be increased greatly with respect to that in m-isomer, the electron density in the O-H bond would be increased greatly with respect to that in m-isomer.



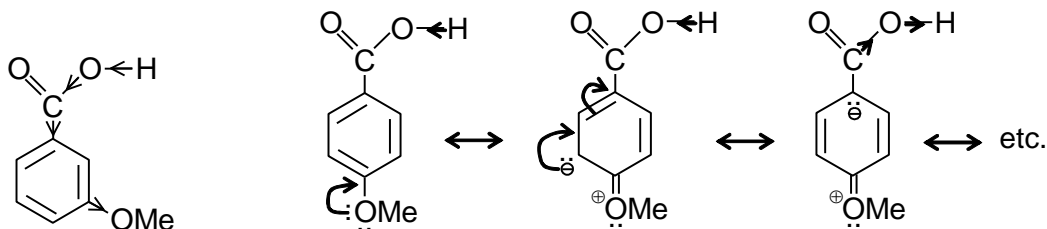
Thus, the release of proton is facilitated easily in m-isomer than in p-isomer.

Secondly, let us take nitro substituted benzoic acids. As the $-\text{NO}_2$ group exerts $-I$ and $-R$ effect (both reinforcing each other), the electron-density from the O-H bond would be withdrawn, thus destabilizing the O-H bond and making m- and p- nitro benzoic acids stronger than benzoic acid.



As it is clear that NO_2 group exerts its electron withdrawing resonance effect more from the p-position and lesser from m-position, thus withdrawal of electron density from the O–H bond is greater in p-nitro benzoic acid than m-nitro benzoic acid. Thus, p-isomer is stronger acid than m-nitro benzoic acid.

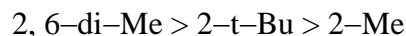
Thirdly, we compare the acid strength of m- and p- methoxy benzoic acid. OMe group exerts $-\text{I}$ and $+\text{R}$ effects. The electron-releasing resonance effect ($+\text{R}$) is more operative in p-methoxy benzoic acid and lesser in m-methoxy benzoic acid while $-\text{I}$ effect is operative lesser in p-methoxy benzoic acid and more in m-methoxy benzoic acid. Thus, the electron density is greatly increased in the O–H bond in p-isomer than in m-isomer, thereby making m-isomer stronger acid than p-isomer.



The ortho-effect

This is a special effect that is shown by o-substituents, but is not necessarily just a steric effect. Examination shows that, irrespective of the polar type, nearly all o-substituted benzoic acids are stronger than benzoic acid.

As we have seen that benzoic acid is a resonance hybrid and so the carboxyl group is coplanar with the ring. An o-substituent tends to prevent this coplanarity. Thus, resonance is diminished (or prevented) and so the O atom of the OH group has a greater positive charge, resulting in increased acid strength. It follows from this that greater the steric inhibition of resonance, the stronger is the acid. Support for this is the following order of strengths of substituted benzoic acids.

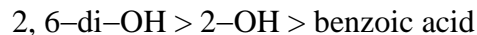


Here again, if we consider the stability of the anion, steric inhibition of resonance prevents the $+\text{R}$ effect of the ring coming into operation and since this weakens acid strength, its absence results in increased acid strength.

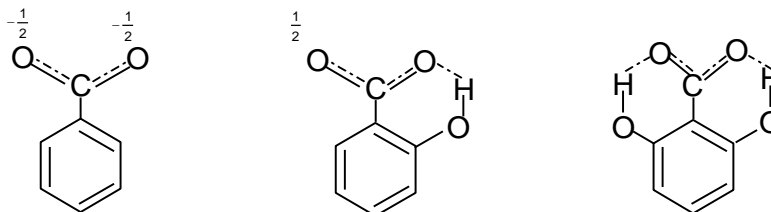
o-Hydroxybenzoic acid (salicylic acid) is far stronger than the corresponding m- and p-isomers. Steric inhibition of resonance cannot explain this very large increase, since the corresponding methoxybenzoic acids all have similar strengths. The explanation offered is

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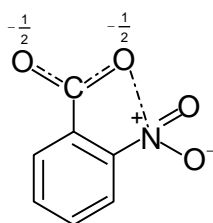
hydrogen bonding; H of the OH group can form a hydrogen bond with the carboxyl group, whereas the Me of OMe cannot. The carboxylate ions of o-hydroxybenzoic acids are stabilized by intramolecular hydrogen bonding and support for this is given by the following order of acid strength,



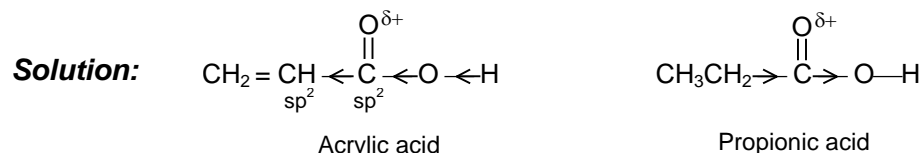
It can be seen that two hydrogen bonds would be expected to bring about more stabilization than one hydrogen bond.



The much greater strength of o-nitrobenzoic acid as compared with that of its m- and p- isomers may also be explained in a similar manner.



Question 2: Explain why acrylic acid is stronger acid than propionic acid?



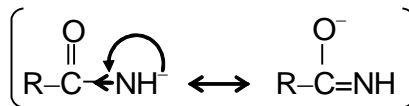
If we look at these two acids, electron withdrawing effect of sp^2 carbon adjacent to carbonyl group in acrylic acid is observed and consequent strong polarization of O-H bond in $\text{-C}(=\text{O})\text{OH}$ form takes place. Ethyl group in propionic acid has +I effect to the carboxyl group reducing the partial positive character of C atom in $\text{-C}(=\text{O})\text{OH}$ group. Therefore, less polarization of O-H takes place.

Question 3: Account for the fact that salicylic acid, o-HOC₆H₄CO₂H is a stronger acid than o-CH₃OC₆H₄CO₂H.

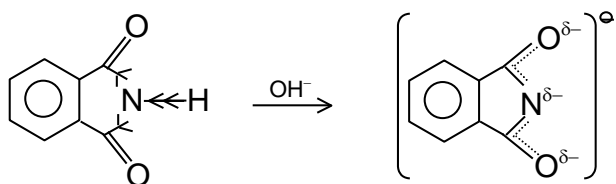
Solution: The hydrogen to be lost is itself involved in intramolecular hydrogen bonding in o-CH₃OC₆H₄CO₂H while loss of H⁺ increases the strength of intramolecular hydrogen bonding in o-HOC₆H₄CO₂H.

Acidic Strength of Amides

The amides are also found to be fairly acidic in water (though less acidic than H_2O), because of $-I$ and $-R$ effect of RCO group which makes the negative charge on nitrogen atom more stable.



If two $\text{C}=\text{O}$ groups are present the resultant imides often become sufficiently acidic to form alkali metal salts. For example, benzene-1,2-dicarboxamide is not basic but is acidic in nature because of the presence of two electron-withdrawing CO groups.

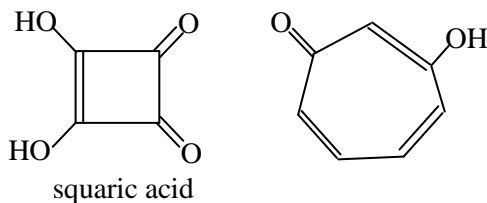


The following overall order of acidic strength must be remembered

$\text{Ar}-\text{SO}_3\text{H} > \text{R}-\text{SO}_3\text{H} > \text{HCOOH} > \text{Ar}-\text{COOH} > \text{RCOOH} > \text{H}_2\text{CO}_3 > \text{PhOH} > \text{H}_2\text{O} > \text{ROH} > \text{R}-\text{C}\equiv\text{CH} > \text{NH}_3 > \text{Alkene} > \text{RH (alkane)}$

Bicarbonate Test

When any compound more acidic than H_2CO_3 is treated by HCO_3^- , that acid loses its proton to HCO_3^- to generate weaker acid H_2CO_3 that is unstable and dissociate to give CO_2 and H_2O immediately causing effervescence of CO_2 . Therefore, mineral acids like H_2SO_4 , HX , HNO_3 etc., sulphonic acids and carboxylic acids give bicarbonate test. Dinitro phenols and some other compounds like squaric acids etc. also give bicarbonate test.



7. BASIC STRENGTH OF ORGANIC BASES

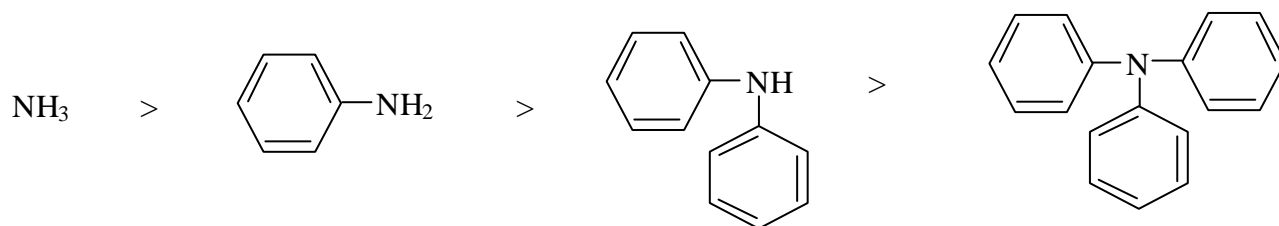
7.1 Factors Affecting Basic strength of Amines

Basic strength of amines depends on following factors:

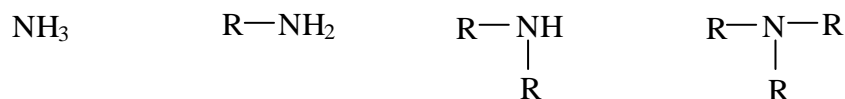
- More the electron density on nitrogen more will be basic strength.
- More the steric hindrance (crowding) around nitrogen, lesser is basic strength.
- More the hydration more is basic strength in aqueous solution.

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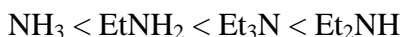
Consider the order of basic strength of following molecules:



Presence of phenyl group on nitrogen decreases electron density by $-ve$ I and $-ve$ M effect, increases steric hindrance and decreases hydration. All these factors indicate decrease in basic strength as shown above.



Presence of alkyl group on nitrogen increases electron density by $+ve$ I effect which should increase the basic strength. However, presence of alkyl group increases steric hindrance and decreases hydration (due to lesser hydrogen bonds with water). These two factors favour decrease in basic strength. Now if the reference acid is H^+ steric hindrance will be negligible, however, decrease in hydration will still favour decrease in basic strength in aqueous medium. The experimental order of basic strength in aqueous medium is $\text{NH}_3 < \text{RNH}_2 < \text{R}_2\text{NH} > \text{R}_3\text{N}$ i.e. tertiary alkyl amines are weaker bases than secondary alkyl amines. The increasing order of basic strength was found to be different for different alkyl groups.

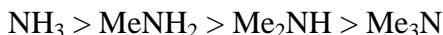


In above cases effect of hydration is maximum in tertiary amine that is found to be lesser basic than secondary amine which must be remembered.

However the order of basic strength in gas phase when reference acid is H^+ is shown below which is decided by electron density alone as hydration will not occur. Same order will be observed in solvents like n-hexane where every alkyl group will increase the solvation also which favours increase in basic strength.



However, if reference acid is bulky, the order of basic strength can be different depending on the amount of steric hindrance. If the reference acid is $(t\text{-Bu})_3\text{B}$, steric hindrance will be very large and will dominate over inductive effect also resulting in following order of basic strength:



Introduction of alkyl group (like Me) on the nitrogen atom of aniline results in small increase in the basic strength.

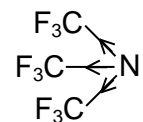


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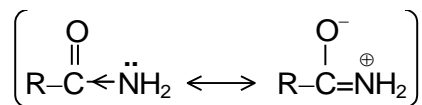
Unlike such introduction in aliphatic amines, this small increase in basic strength is progressive, indicating that cation stabilization through hydrogen-bonded solvation, here has less influence on the overall basic strength.

Tetraalkylammonium salts, e.g. $R_4N^+I^-$ on treatment with moist silver oxide ($AgOH$) react to yield basic solutions comparable in strength with the mineral alkalis. This is readily understandable as $R_4N^+OH^-$ formed is completely ionized to give R_4N^+ and free OH^- .

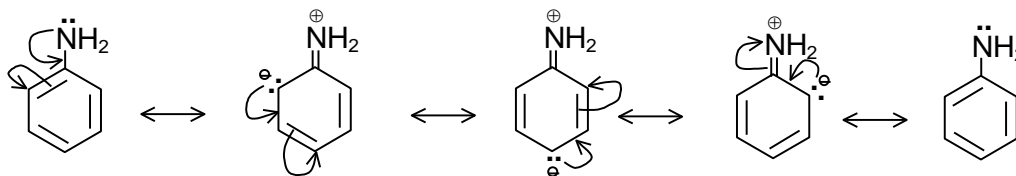
The effect of introducing electron-withdrawing groups, e.g. Cl , NO_2 , close to a basic centre decreases the basicity, due to their electron-withdrawing inductive effect. Thus the amine Tris(trifluoromethyl)amine is found to be virtually non-basic due to the presence of three powerful electron-withdrawing CF_3 groups.



The amides are also found to be only very weakly basic in water [pK_a for ethanamide(acetamide) is ≈ 0.5], because of the $-I$ and $-R$ effect of RCO group which makes the electron pair very slightly available on nitrogen atom.



In aniline, owing to resonance, the lone pair of electrons on the nitrogen atom is less available for coordinating with a proton and at the same time, small positive charge on the nitrogen atom would tend to repel a proton. Alternatively, since there are more resonating structures possible for aniline itself than for the cation $C_6H_5^+NH_3$, the former will be stabilized with respect to the latter.



Aniline is a weaker base than ammonia or cyclohexylamine. It is because of the fact that the electron pair on nitrogen is involved in delocalization, making it less available for donation.



Diphenylamine is even a weaker base than aniline due to the presence of another phenyl group and triphenylamine (Ph_3N) is not basic at all by ordinary standards.

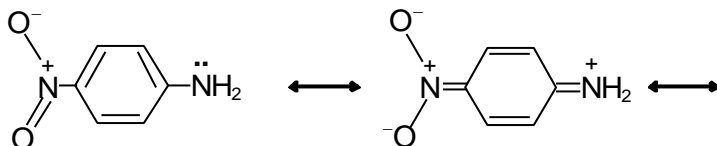
The effect of a ring substituent on basic strength depends on whether the substituent is electron attracting or releasing, its ability to enter into resonance with the amino-group and its

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position. All the nitroanilines are weaker bases than aniline. The nitro-group has a strong $-R$ effect and o - and p - nitroaniline are therefore, more resonance stabilized than aniline itself.

It must be further noted that the basic strength of aniline is decreased by any group when attached to ortho position. This is because this ortho group though does not affect the resonance of NH_2 group but causes the steric inhibition to hydration.

However, the basic strength of N,N -Dialkylaniline is increased by any group when attached to ortho position. This is because this ortho group causes steric inhibition of resonance by forcing NR_2 group out of plane of benzene ring.



A m -nitro group cannot enter into direct resonance with the amino-group, but nevertheless m -nitroaniline is a much weaker base than aniline. In this case, nitro-group has a strong $-I$ effect and indirect $-R$ effect. This $-ve$ effect tends to draw into the ring the lone pair of N , thus decreasing its basicity. Thus, the order of basicity of nitroanilines is

