Electronic Effects

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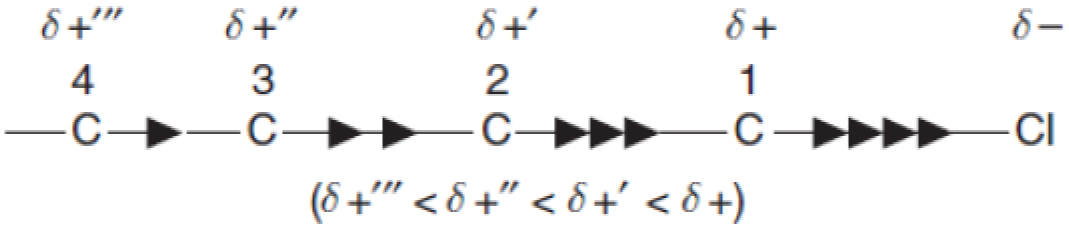
Types of Electronic Effects

Inductive effect

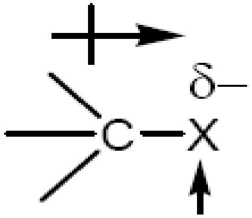
In a covalent bond between two different atoms, the electrons in the $\sigma -$bond are not shared equally. The electrons are attracted towards the most electronegative atom.



The phenomenon of transmission of charge arising due to electronegativity difference in a covalent bond (i.e. dipole) through a chain of carbon atoms linked by sigma bonds is called ***inductive effect.***

When the atom (X) is more electronegative than carbon

electrons attracted to X



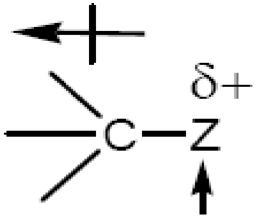
negative inductive effect (–I effect)

–I groups

X=Br, Cl, NO_2, OH, OR, SH, SR, NH_2, NHR, NR_2, CN, CO_2H, CHO, COR

When the atom (Z) is less electronegative than carbon

electrons attracted to carbon



positive inductive effect (+I effect)

+I groups

Z=R(alkyl or aryl), metals (e.g. Li or Mg)

Inductive effect has the following characteristics:

1. It is a permanent effect.
2. It operates through sigma bonds.
3. Its magnitude goes on decreasing with increase in distance from the atom/group responsible for the same. Inductive effect is almost negligible after the third or fourth atom.

-I effect of some groups is in the order

$-H < -C_6H_5 < -OCH_3 < -OH < -I < -Br < -Cl < -F < -COOH < -CN < -NO_2 < -N^+(CH_3)_3$

+I effect of some of the groups is in the following order:

$H- < D- < -CH_3 < -CH_2R < CHR_2 < -CR_3 < -COO^-$

Nature of Group	- I Effect	+ I Effect
Neutral groups	If the first atom of the group is more electronegative than sp^3 hybridised C e.g. O,N,S, Hal, =C (sp^2 C), ≡C (sp C), -C of CCl_3	If the first atom of the group is equal to or lesser electronegative than sp^3 hybridised C e.g. H, Mg, 3°, 2° and 1° alkyl groups (Except $-CCl_3$)
Charged groups	All positively charged groups e.g. $-NH_3^+$, $-CH_2^+$	All negatively charged groups $-O^-$, $-NH^-$, $-CH_2^-$

Electromeric Effect

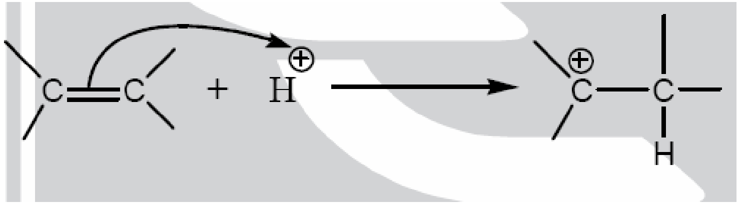
Electromeric effect is defined as the complete transfer of electrons of a multiple bond towards one of the bonded atoms at the demand of an attacking reagent.

a) It is shown by those compounds containing multiple bond

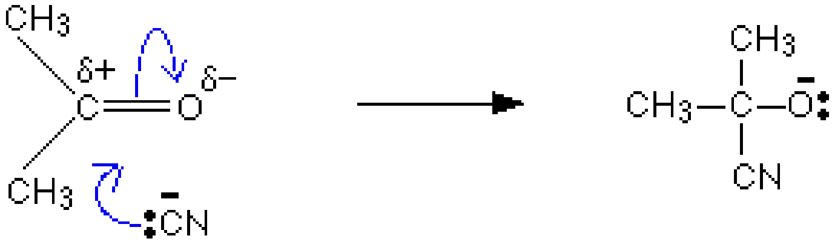
b) It is a purely temporary effect & isbrought into play only at the requirement of attacking agent.

Types of Electromeric Effect

+E effect : When displacement of electrons is away from the atom or group.
e.g : addition of H^+ to alkene.



-E effect : When displacement of electrons is towards the atom or group.
e.g : addition of cyanide ion(CN^-) to the carbonyl group.

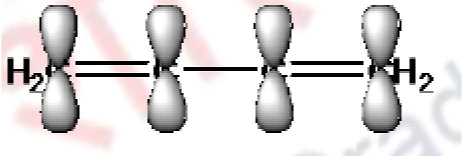


Mesomeric or Resonance Effect

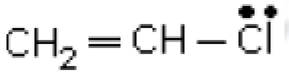
In a normal π bond, the π electrons are localised between the constituent atoms. However, if double and single bonds are present alternately in a molecule, it is called **conjugation**

e.g. in 1,3-butadiene, the double bonds are conjugated

$$CH_2 = CH - CH = CH_2$$



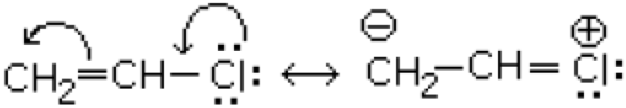
Similarly, if the double, single and a lone pair are present, alternatively, it is also called conjugation e.g. vinyl chloride.


$$CH_2 = CH - \ddot{Cl}$$

The presence of conjugation alters the properties of the compound and there is a difference in the actual and expected properties.

To explain the anomalous properties of such conjugated compounds, Robinson and Ingold gave the concept of **mesomerism**, which was subsequently modified and developed by Pauling as the theory of **resonance**

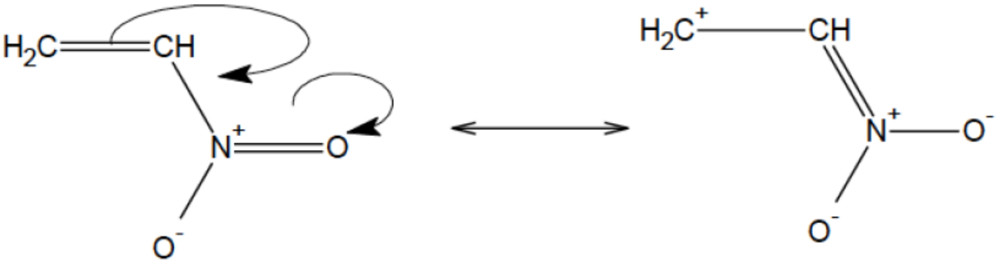
The **theory of resonance** states that when a molecule can be represented by two or more classical structural (or electronic) formula, all of which can explain some but not all the properties, then the molecule has neither of these structures (called contributing or canonical or limiting structures) but is a hybrid of all these contributing structures.



Vinyl chloride

The atoms/groups like Cl in which lone pair(or electrons of negative charge) is in conjugation with double or triple bond are electron donating and gain a formal positive chargein the resonating structure in the process and are known to exert ***+M/+R Effect.***

Consider the case of $-NO_2$ joined to a conjugated system, where the nitro withdraws the conjugated electrons and gives rise to polarization as shown below



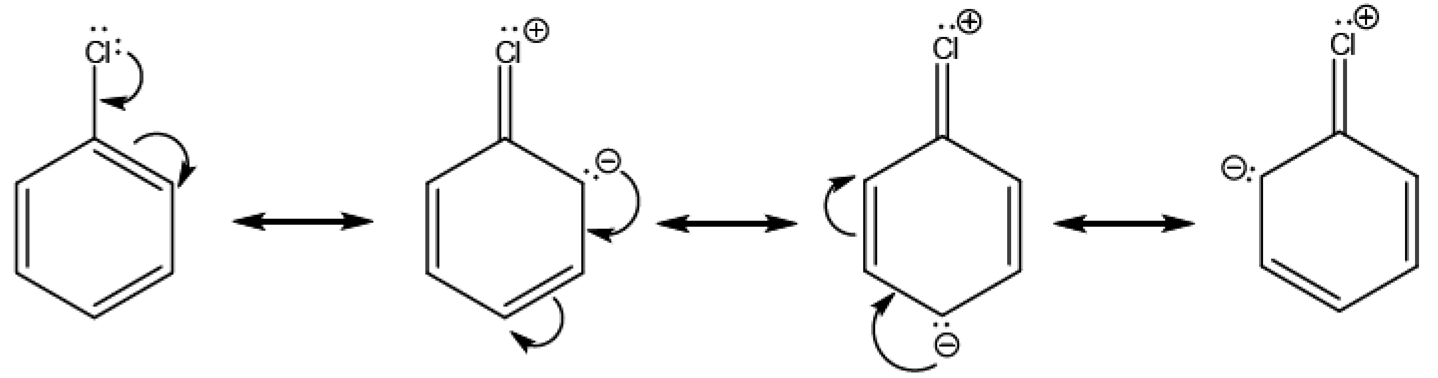
The atoms/groups like $-NO_2$ *which are in conjugation with double or triple bond and are electron withdrawing and gain a formal negative charge in the resonating structure in the process and are known to exert* ***-M/-R Effect.***

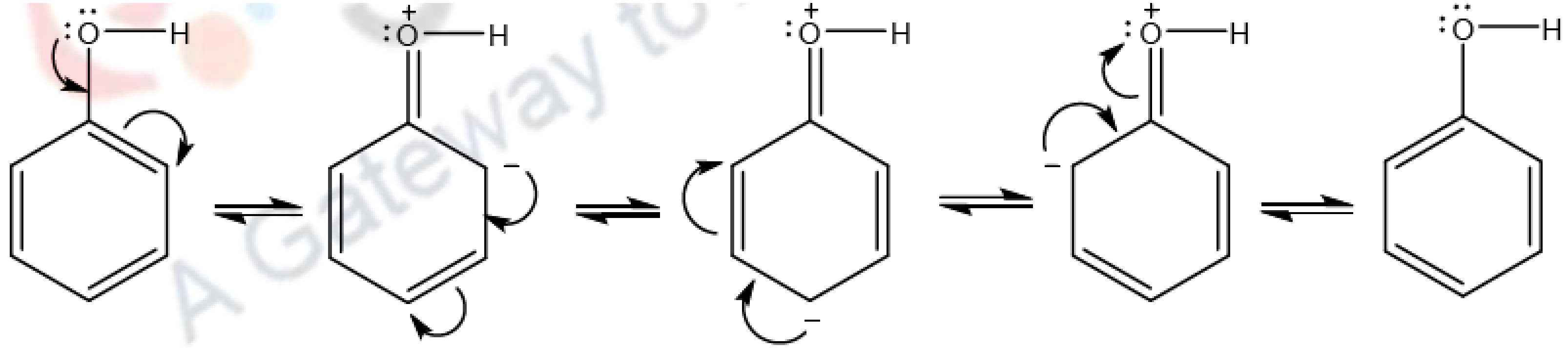
+ M/+R Effect

- 1. If the first atom of the group either has a lone pair or negative charge.
- e.g. – NH_2, -OH, -OCH_3, -$NHCOCH_3$ etc.

- M/+R Effect

- 1. If the first atom of the group has positive charge and after withdrawing a pair of electrons ,it is not violating it's octet.
- e.g. -PH_3^+ and NOT –NH_3^+ (octet of N will be voilated if it withdraws electrons)
- 2. If the first atom of a neutral group has neither a lone pair nor any charge, and is joined to more electronegative atom(s) than itself by double/triple bond.
- e.g. -CHO, -CN, -SO_3H, etc.



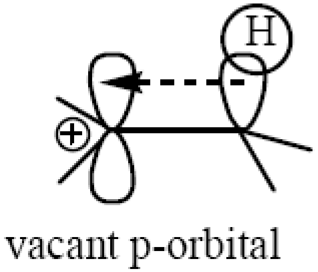


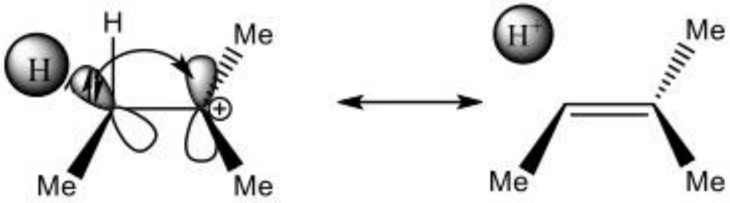
A Gateway to

Positive mesomeric effect in phenol

Hyperconjugation:

Hyperconjugation is the donation of a sigma bond into an adjacent empty or partially filled p orbital, which results in an increased stability of the molecule.



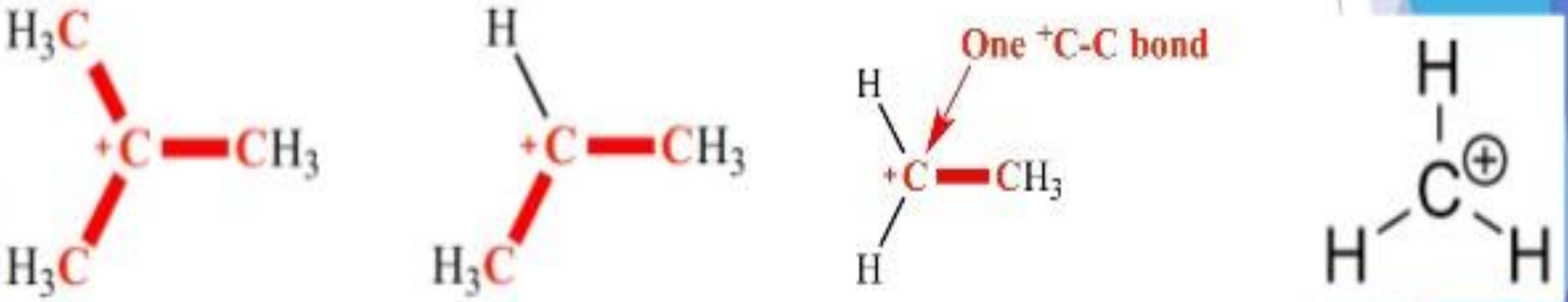


Hyperconjugation was first described by Baker and Nathan in 1935 to describe the "abnormal behavior" of alkyl-substituted compounds.

- The more the number of alkyl groups on the carbocation, more is the number of α C – H σ bonds and hence more are the possibilities for hyperconjugation which makes the carbocation more stable.

- The order of stability of the Carbocations is:

3^0alkyl carbocation > 2^0alkyl carbocation > 1^0alkyl carbocation > methyl carbocation



9 Hyperconjugable H	6 Hyperconjugable H	3 Hyperconjugable H	No Hyperconjugable H

Applications of Inductive effect:

Inductive effect is useful in explaining the strength of some organic acids and bases.

a) Effect of substituent on the acid strength of aliphatic acids.

$HCOOH > CH_3COOH > (CH_3)_2CHCOOH$

Reason : Acidic strength decreases as +I effect of the alkyl group increases.

b) $O_2NCH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH > CH_3COOH$

Reason : Acidic strength decreases as -I effect of the group or halogen decreases.

Relative basic strength of amines

1. All aliphatic amines are more basic than ammonia.
   e.g. Methyl amine is more basic than ammonia.

Reason : Due to +I effect of methyl group.

2. Aniline is weaker base than Ammonia.

Reason : Due to +R effect and –I Effect of phenyl group.

- **Covalent bond cleavage**

- **during the organic reaction, chemical bonds have to be broken in order that new compounds may be formed.**
- **the breaking of chemical bonds is called fission.**
- **When organic compounds react, their bonds can split up in the following ways:**

HOMOLYTIC FISSION (RADICAL CLEAVAGE)

HETEROLYTIC FISSION (IONIC CLEAVAGE)

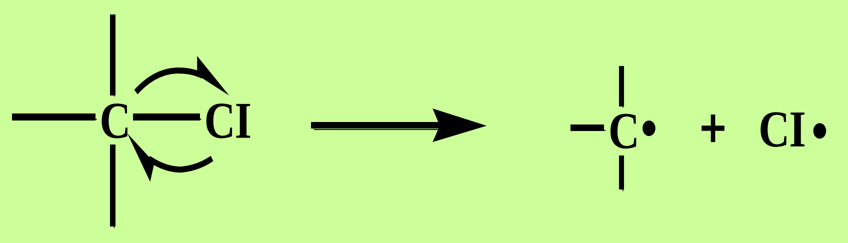
HOMOLYTIC FISSION (RADICAL CLEAVAGE)

- **Homolytic fission: two shared electrons of the covalent bond are split equally between the two atoms joined by the bond.**
- **Also known as homolysis.**
- **One electrons goes to X and the others goes to Y.**
- **The resulting species is called free radicals.**

$$X{:}Y \longrightarrow X\cdot + Y\cdot$$

Free radicals

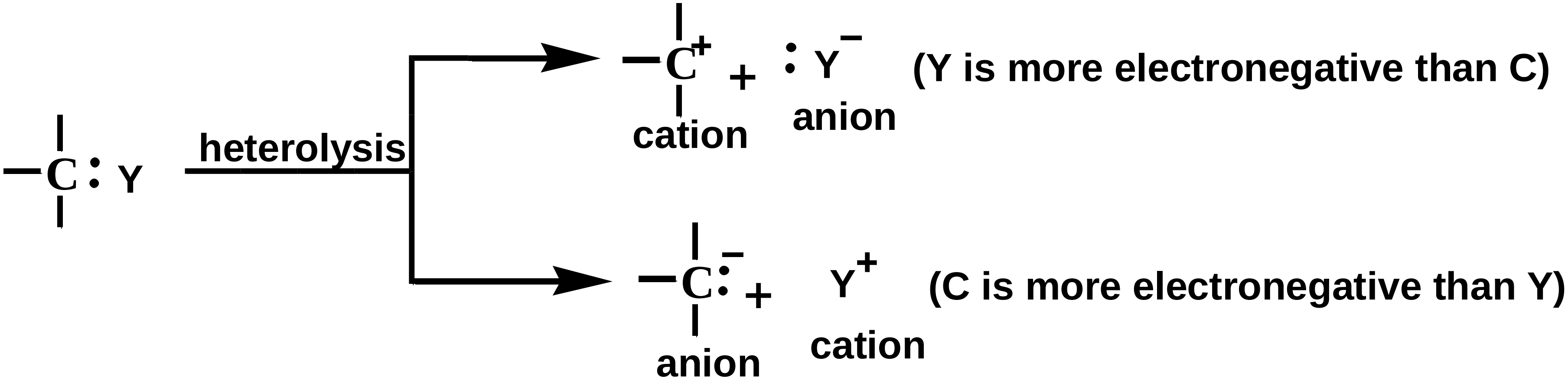
- **Examples of free radicals:**
  i) hydrogen radical, H•
  ii)chlorine radical, Cl•
  iii)methyl radical, •CH_3 or CH_3•
  iv)ethyl radical, •CH_3CH_2 or CH_3CH_2•
- **Free radicals are reaction intermediates.**
- **They are very reactive and many may only exist for a split second.**
- **The movement of a single electron in homolytic fission is shown by a curved half-arrow.**



- **Occurs in reactions which take place in the gas phase or in non-polar solvents.**
- **The reactions are often catalysed by sunlight, ultraviolet light or high temperatures.**

HETEROLYTIC FISSION (IONIC CLEAVAGE)

- **Heterolytic fission**: the breaking of a covalent bond in which both electrons remain on one of the atoms.
- Known as heterolysis.
- Produces positive and negative ions.
- The breaking of the bond (C-Y) can happen in 2 ways, depending on the electronegativities of the carbon atom and the atom Y.



(Y is more electronegative than C)

(C is more electronegative than Y)

- **Carbonium ion or carbocation:**

  - an organic ion which contains a carbon atom with a positive charge (C^+)

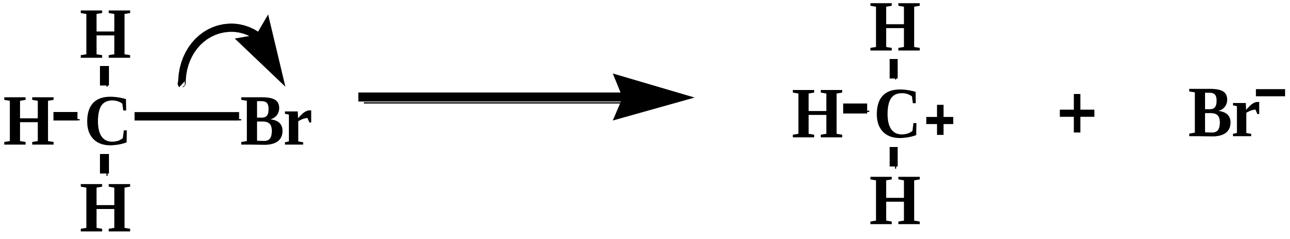
  - electrophiles (lewis acid)

- **Carbanion:**

  - an organic ion which contains a carbon atom with negative charge (C^-)

  - has a lone pair of electrons

- Heterolytic fission is more common where a bond is already polar.
- For example:



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}Br} \longrightarrow \mathrm{H{-}\overset{H}{\underset{H}{C}}{+}} + \mathrm{Br^{-}}$$

methy carbocation

Bromomethane has a polar C-Br bond

Electrophiles :

(Electron loving species) electrophiles are electrons-deficient species and tend to attack the substrate at a site of high electron density. They may be neutral species as examplified by Lewis acid (such as BF_3, $AlCl_3$, $ZnCl_2$), carbene and carbocations.

Classification of electrophiles:

(a) Species having positive charge

Example : H^+, R^+, Cl^+, NO^+, NO_2^+, $C_6H_5-N_2^+$, $CH_3-C^+=O$ etc.

(b) Neutral species having vacant p-orbitals

Example : BF_3, BCl_3, BBr_3, carbene, etc.

Nucleophiles:

(Nucleus-loving species) Nucleophiles are electron donar species. Nucleophilic reagents tend to attack the electron deficient species (electrophiles).

Classification of Nucleophiles:

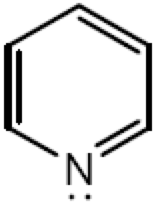
(a) Negative charge species:

$OH^-, OR^-, SH^-, SR^-, R^-, Cl^-, Br^-, I^-$ etc

(b) Organometallic reagent:

R^-MgX, R^-Li, R_2^-CuLi, R_2^-Cd, R_2^-Zn etc

(c) Lone pair containing species:

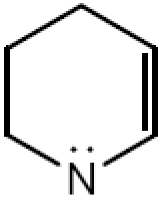
$H_2\ddot{O}:$, $R-\underset{\cdot\cdot}{\ddot{O}}-H$, $\ddot{N}H_3$, $H_2\ddot{S}:$, 

etc

(d) π-bonded molecules:

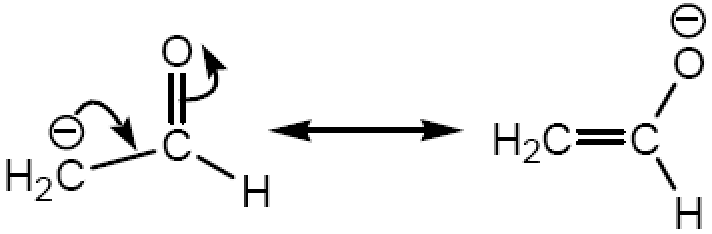
Alkene, Alkyne, Benzene, 

, 

, 

etc

Ambidentated nucleophile : Those nucleophile which posses more than one site for E^+ attack but at the same time only one side is used to form bond with electrophile. It is called ambidented nucleophile, such type of ambidentated nucleophile are regioselective.



REACTION INTERMEDIATES

Carbocations

- An organic species which has a carbon atom bearing only six electrons in its outermost shell and has a positive charge is called **carbocation.**
- The positively charged carbon of the carbocation is sp^2 hybridized.
- The unhybridized p-orbital remains vacant.
- They are highly reactive and act as reaction intermediate.
- They are also called carbonium ion.

The heterolytic cleavage in an organic molecule where carbon donates the shared pair of electrons to the leaving group results in the development of positive charge on the carbon atom. Such species where covalency of carbon is three are called carbenium ions or carbocations (e.g. CH_3^+). The carbon atom of carbocation is sp^2 hybridised and it uses the three hybridised orbitals for single bonding to three substituents; the remaining p-orbital is empty. [redacted]

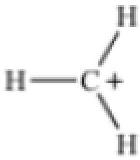
Classification of carbocations

a) **Primary carbocation:** In a primary carbocation the carbon bearing the positive chargeis attached to onecarbon of an alkyl or aryl group.

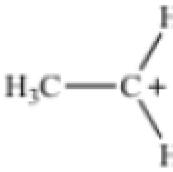
b) **Secondary carbocation:** Here carbon with positive charge is attached to two other carbons.

c) **Tertiary carbocation:** As the name suggest, in this case the positively charged carbon is attached to three carbon atoms.

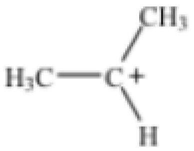
While a carbocation with the carbon bearing a positive charge and attached to only three hydrogen atoms and no carbon is known as methyl carbocation.



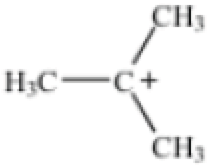
Methyl carbocation



1° Carbocation



2° Carbocation



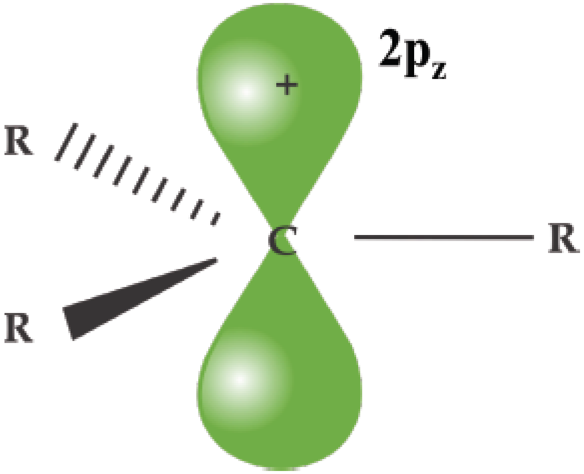
3° Carbocation

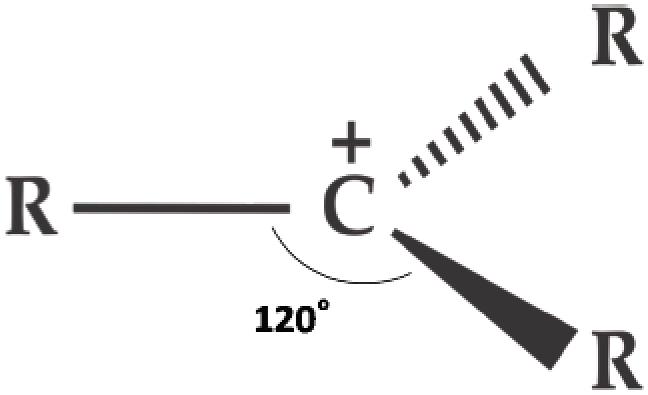
Structure of Carbocation

There are six valance electrons in a carbocation. Therefore they have deficiency of electron and they act as Lewis acids.

Features of a carbocation:

- The carbon bearing positive charge of a carbocation is **sp^2 hybridized** and has vacant unhybridized p orbital.
- It has planar structure having all the three covalent bonds are in plane with the bond angle of 120° between them.
- The positively charged carbon is **trivalent**
- The positive carbon has **sextet of electron** thus it is electron deficient.
- The order of stability of carbocations is **$3^\circ > 2^\circ > 1^\circ >$ methyl** carbocation.

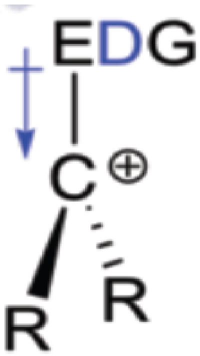




Stability of Carbocation

Inductive effect

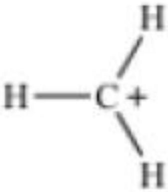
If the groups attached to positively charged carbon are electron releasing they will decrease the intensity of the positive charge on carbon. The electron releasing groups delocalise the positive charge on carbon thereby decreasing its electron deficiency. The alkyl groups are electron releasing in nature (+I effect). More the number of alkyl groups attached more will be the stability of carbocation.



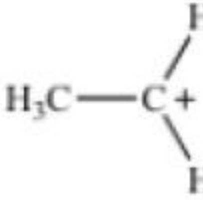
Electron Donating Group:
stabilizes a carbocation

Electron Withdrawing Group:
*de*stabilizes a carbocation

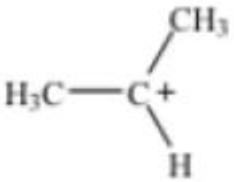
Thus the order of stability of alkyl carbocations is **3°>2°>1°> methyl** carbocation.



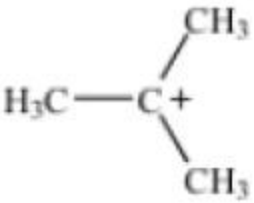
Methyl carbocation



1° Carbocation



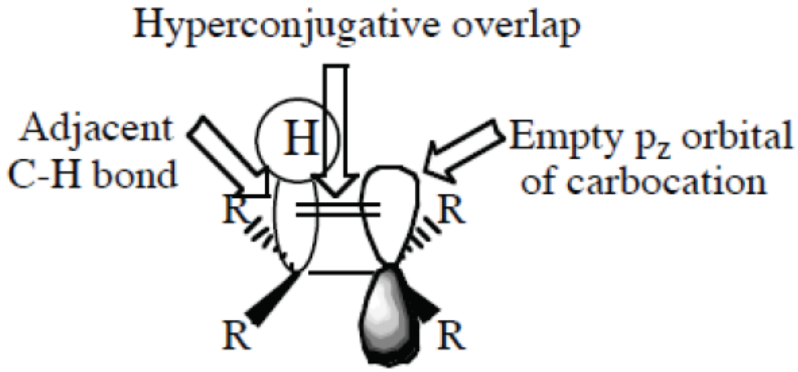
2° Carbocation



3° Carbocation

Thus, +I group increases stability of carbocation and is directly proportional to the +I power of the group.

Hyperconjugation

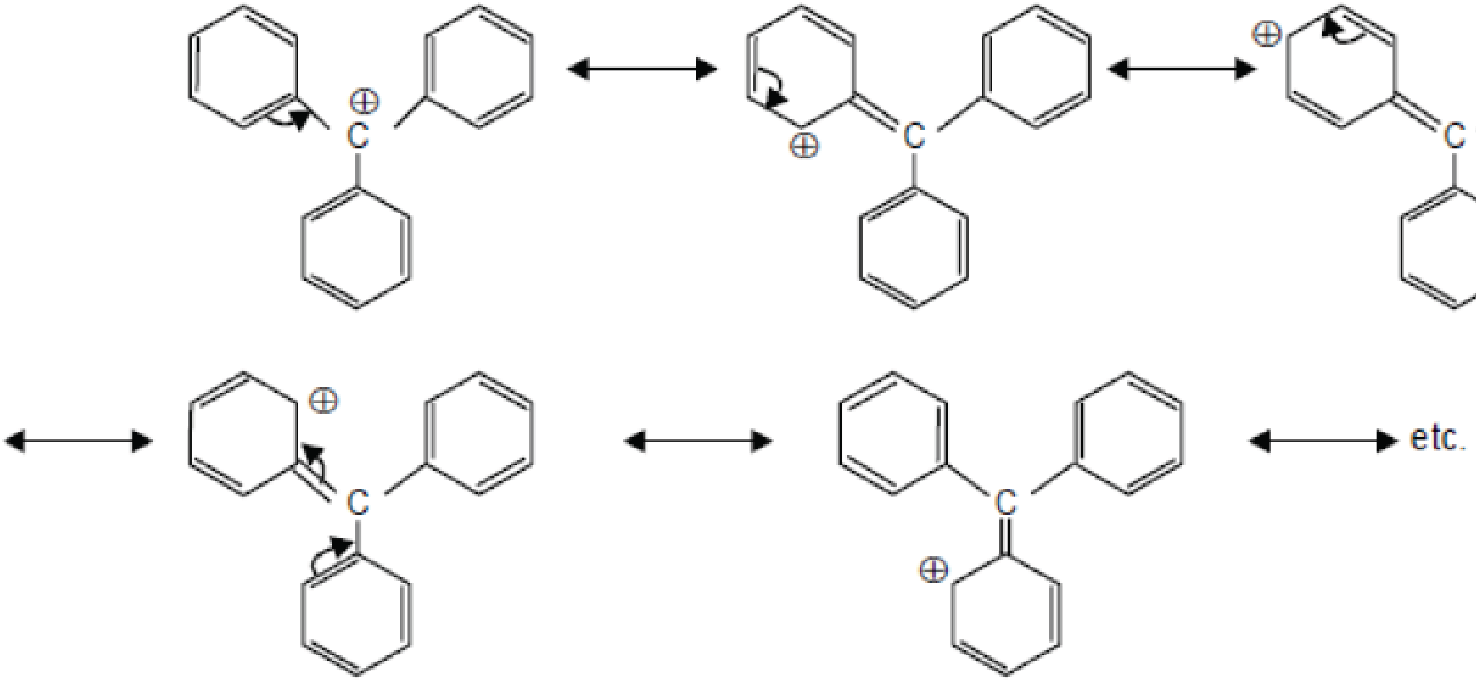


In tert-butyl cation, $(CH_3)_3C^+$ there are nine C-H sigma bonds which participate in delocalisation. In iso-propyl cation, $(CH_3)_2CH^+$six C-H sigma bonds and in ethyl cation, $CH_3CH_2^+$ three C-H bonds are available. Thus $(CH_3)_3C^+$ is more stable than $(CH_3)_2CH^+$ which in turn is more stable than $CH_3CH_2^+$ due to greater number of contributing hyperconjugative structures in former than the latter.

$(CH_3)_3C^{\oplus}$	>	$(CH_3)_2CH^{\oplus}$	>	$CH_3CH_2^{\oplus}$	>	$CH_3^{\oplus}$
t-butyl carbocation		isopropyl carbocation		ethyl carbocation		methyl carbocation

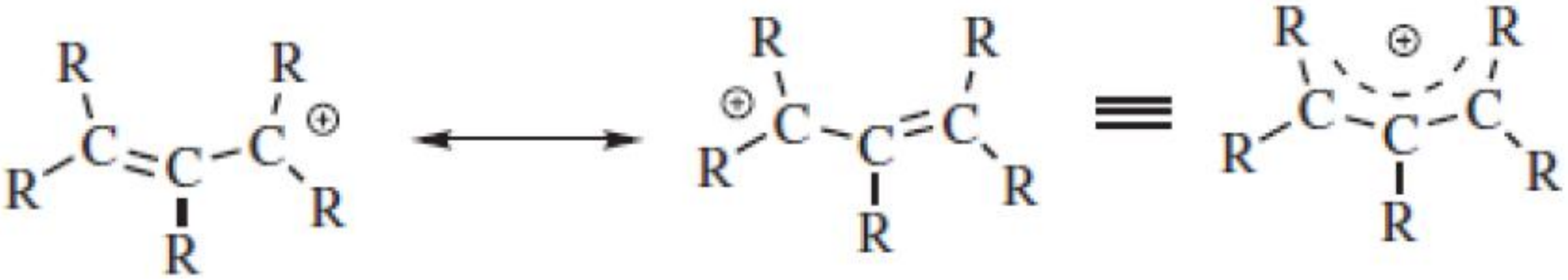
Resonance Effects

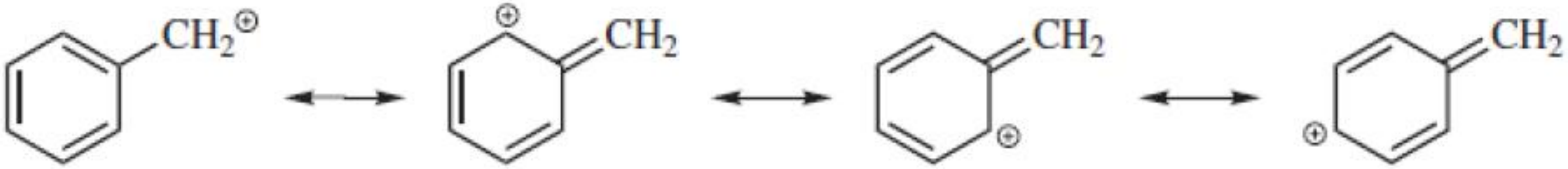
Conjugation with multiple bond or lone pair of electron increases the stability of a carbocation. For example, triphenylmethyl cation is more stable than diphenylmethyl cation which in turn is more stable than phenylmethyl cation. This due to greater delocalization of positive charge in case of triphenylmethyl cation as it has more number of resonating structures. The salt of triphenylmethyl cation with boron fluoride is stable and exists as solid.



Which is more stable amongst allyl and benzyl carbocations?

Benzyl cation is more stable than allyl cation. In both the cases the vacant p orbital of carbon bearing positive charge is in conjugation with pi bonds and delocalisation of positive charge occurs through p-pi overlap.In benzyl cation, the number of contributing structures are more as compared to allyl cation.

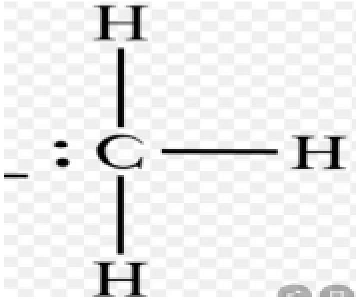




$CH_6H_5CH_2^{\oplus} > CH_2{=}CH{-}CH_2^{\oplus} > CH_3CH_2CH_2^{\oplus}$

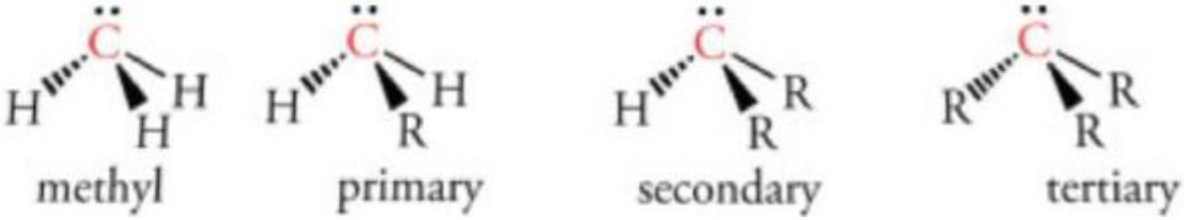
CARBANION

- ANY ORGANIC ION HAVING NEGATIVELY CHARGED CARBON ATOM, CALLED CARBANION. (IN GENERAL, ANIONS WITH UNSHARED PAIR OF ELECTRONS ON A CARBON)
- THEY ARE FORMED BY HETEROLYTIC BOND CLEVAGE OF COVALENT BOND IN WHICH CARBON GAINS BONDING ELECTRON PAIR.



CLASSIFICATION

- CARBANIONS MAY BE CLASSIFIED INTO PRIMARY, SECONDARY AND TERTIARY DEPENDING UPON THE NATURE OF CARBON ATOM BEARING NEGATIVE CHARGE.
- IF ONE CARBON ATOM IS DIRECTLY ATTACHED TO ANIONIC CARBON THEN IT IS CALLED PRIMARY CARBANION.
- IF TWO CARBON ATOMS ARE ATTACHED TO ANIONIC CARBON THEN IT IS CALLED SECONDARY CARBANION.
- IF THREE CARBON ATOMS ARE DIRECTLY ATTACHED TO ANIONIC CARBON THEN IT IS CALLED TERTIARY CARBANION.
- IF NO CARBON ATOM IS ATTACHED TO ANIONIC CARBON THEN IT IS SIMPLY CALLED METHYL CARBANION.

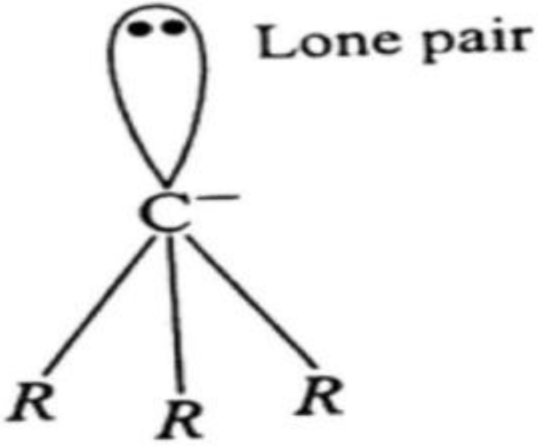


STRUCTURE OF CARBANION

- THE CARBON ATOM OF CARBANION IS **sp3 HYBRIDIZED.**

- **OUT OF FOUR HYBRID ORBITALS THE THREE HYBRID ORBITALS ARE INVOLVED IN FORMATION OF SIGMA BOND, WHEREAS FOURTH HYBRID ORBITAL CONTAINS UNSHARED ELECTRON PAIR, WHICH GIVE NEGATIVE CHARGE TO CARBON ATOM.**

- THEREFORE THE GEOMETRY OF CARBANION WILL BE PYRAMIDAL



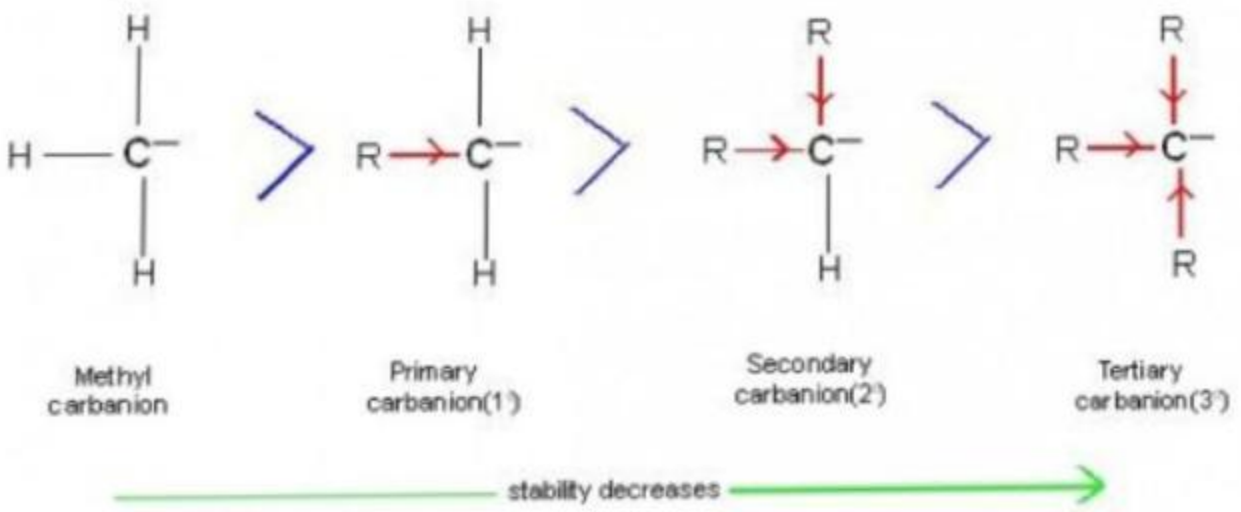
STABILITY OF CARBANIONS

- ANY STRUCTURAL FEATURES WHICH DISPERSE THE NEGATIVE CHARGE OF THE CARBANION WILL INCREASE ITS STABILITY. SOME IMPORTANT FACTORS ARE GIVEN BELOW :

1. BY INDUCTIVE EFFECT
2. BY RESONANCE

BY INDUCTIVE EFFECT

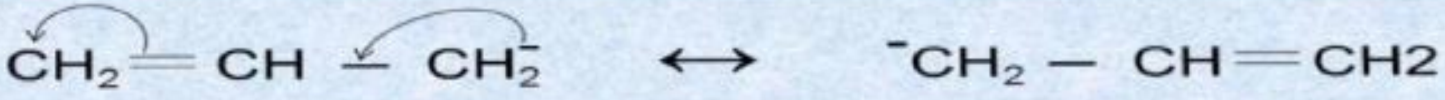
- IF +I EFFECT GROUP ATTACHED TO THE ANIONIC CARBON THEN IT DECREASES ITS STABILITY BECAUSE IT INCREASES THE ELECTRON DENSITY ON ANIONIC CARBON.
- IF – I EFFECT GROUP ATTACHED TO THE ANIONIC CARBON THEN IT INCREASES ITS STABILITY BECAUSE IT DECREASES ELECTRON DENSITY ON ANIONIC CARBON.



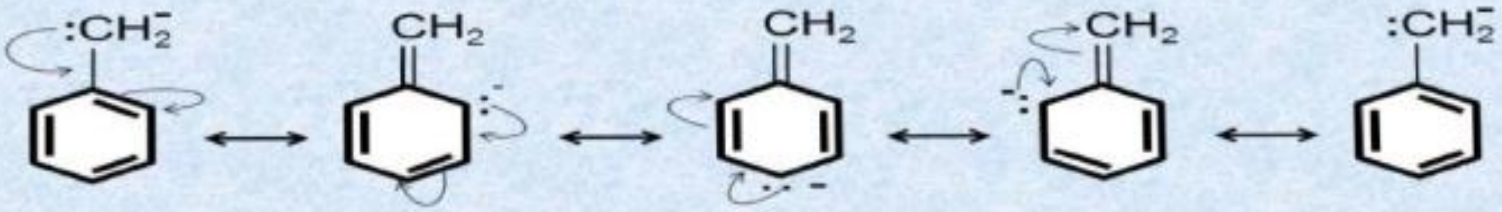
BY RESONANCE EFFECT

- THE UNSATURATED CONJUGATED CARBANIONS ARE STABILISED BY RESONANCE.
- SUCH CARBANIONS ARE MORE STABLE THAN THE SATURATED CARBANIONS.

- MORE THE NUMBER OF RESONATING STRUCTURES MORE WILL BE THE STABILITY OF CARBANION.



(Allyl carbanion is stabilized by resonance)



(Benzyl carbanion is stabilized by resonance)

Free Radicals

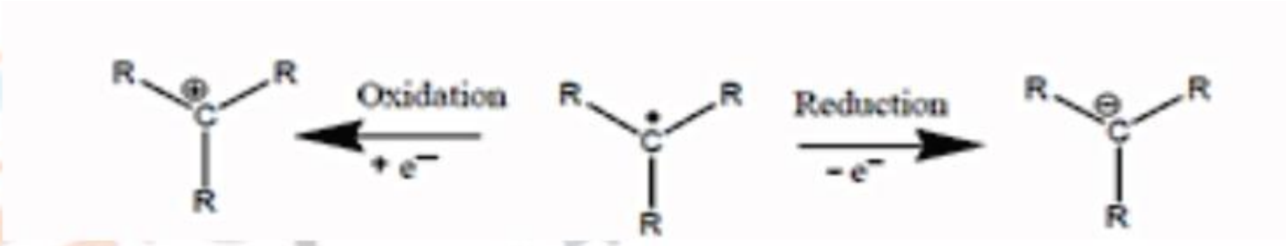
A radical is a reactive intermediate with a single unpaired electron, having very short lifetime .

It is generated by homolysis of a covalent bond.

Radial is represented by atom with one dot.

Electronic movements involving radicals are represented using half headed fishhook arrows.

Carbon radical is a neutral carbon species with three single bonds and one unpaired electron.



Carbocation

carbanion

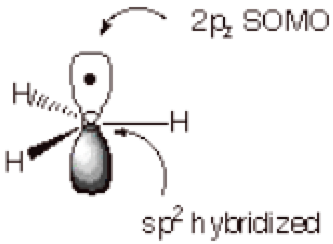
6 valence electron

7 valence electrons

8 valence electrons

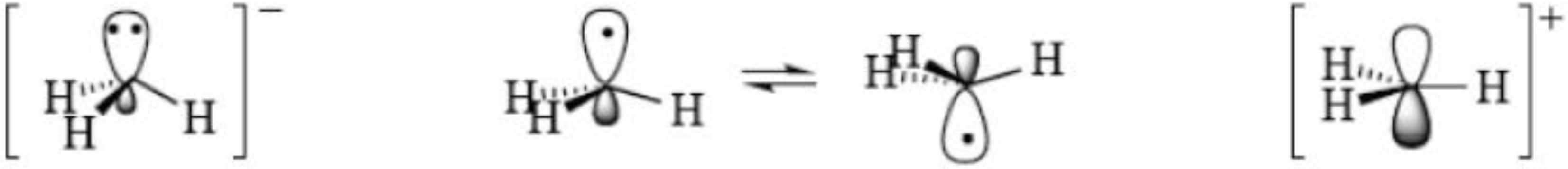
Features of Free Radical

- Free radicals are electron deficient species.
- They are usually uncharged.
- They contain odd number of electrons.
- The alkyl radical ($^{\bullet}CR_3$) has seven electron around the carbon bearing radical character.
- In methyl radical or other alkyl radicals, the radical centre is trivalent and trigonally hybridized.
- The carbon is sp^2 hybridized.
- It has planar structure.



- The unpaired electron occupies a 2p atomic orbital of carbon. This singly occupied orbital is often referred as singly occupied molecular orbital (SOMO).

- The alkyl radical have shallow pyramid geometry i.e., between sp^2 and sp^3 hybridization. But the energy required to invert the pyramid is very small. Practically speaking alkyl radicals are considered sp^2 hybridized.



carbanion pyramidal

alkyl radical shallow pyramid

carbocation trigonal planar

Stability of Free Radical

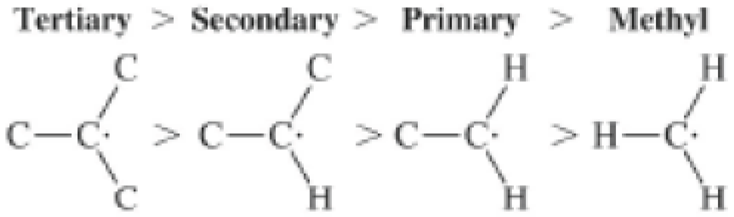
The order of stability of alkyl radicals is 3° > 2° > 1°.

- Inductive effect
- Hyperconjugative effect
- Resonance effect

Inductive effect

Greater the number of alkyl groups attached to the free radical carbon centre more will be the stability of the radical. This is due to the electron donating inductive effect of the alkyl groups which decrease the electron deficiency of the radical.

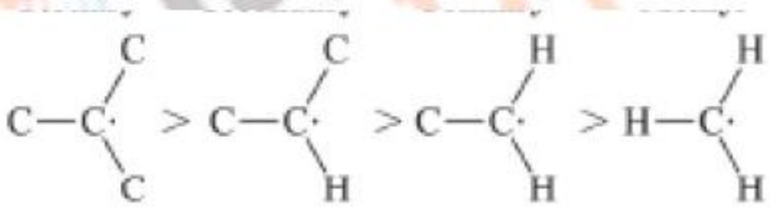
Thus, the order of stability is 3°>2°>1°

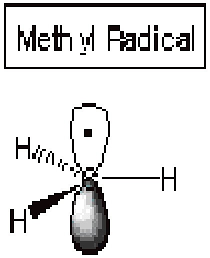


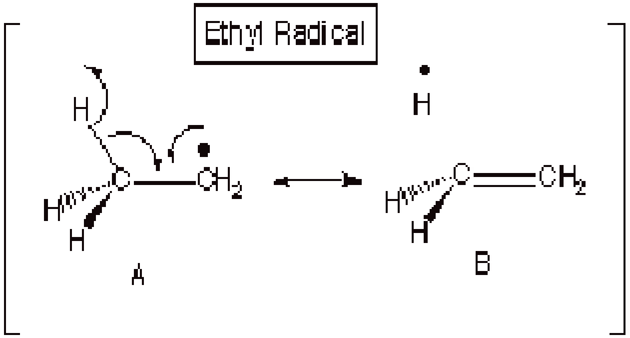
Hyperconjugation

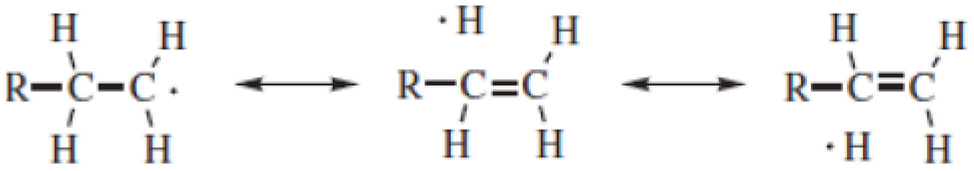
Hyperconjugative effect also give stability to free radicals as in the case of carbocations. The stability order of alkyl free radicals is tertiary >secondary > primary > CH_3. This stability order can be explained by hyperconjugation. The odd electron in the alkyl radical is delocalized onto the β-hydrogens, through hyperconjugation, which confers stability to the radical. Thus, tert-butyl radical is more stable than sec-butyl radical which in turn more stable than n-butyl radical. As tert-butyl radical has three methyl groups or nine beta hydrogens which give it nine hyperconjugative structures. sec-butylradical has six and n-butyl radical has three hyperconjugative structures. Greater the number of hyperconjugative structures more will be the stability of the radical.

Therefore the order of stability is:





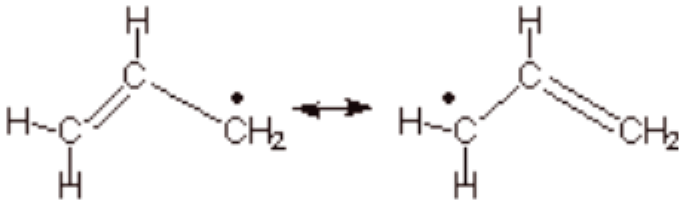




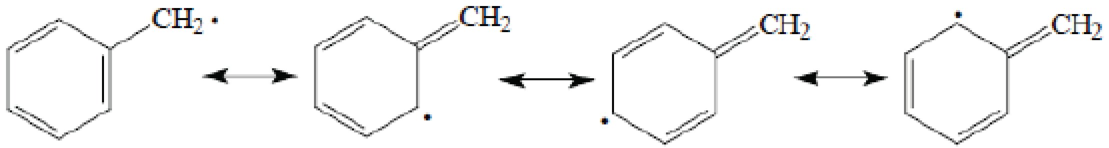
Resonance Effect

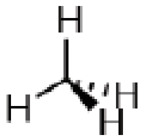
In the free radicals where the carbon centre is in conjugation to a double bond, the resonance effect leads to stabilisation of these molecules. The stabilising effects of vinyl groups (in allyl radicals) and phenyl groups (in benzyl radicals) are very significant and can be satisfactorily explained by resonance. Allyl and benzyl free radicals are more stable than alkyl free radicals but still have only a transient existence under ordinary conditions.

Resonance in allyl free radical



Resonance in benzyl free radical

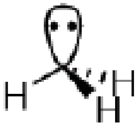




Methane

CH_4

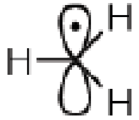
sp^3



Methyl anion

CH_3^-

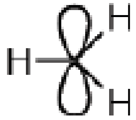
sp^3



Methyl radical

$CH_3^\bullet$

sp^2



Methyl cation

CH_3^+

sp^2

Carbenes

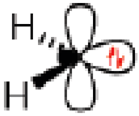
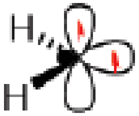
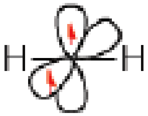
Carbenes are neutral intermediates having bivalent carbon, in which a carbon atom is covalently bonded to two other groups and has two valency electrons distributed between two non bonding orbitals.

$$:CR_2$$

Classification

When the two electrons are spin paired the carbene is a singlet,
if the spins of the electrons are parallel it is a triplet.

Structure

Structure			
Hybridization	*sp^2*	*sp^2*	*sp*
Geometry	Bent	Bent	Linear (not observed)
State	Singlet	Triplet	Triplet

A singlet carbene is thought to possess a bent sp2 hybrid structure in which the paired electrons occupy the vacant sp2 orbital. A triplet carbene can be either bent sp2 hybrid with an electron in each unoccupied orbital, or a linear sp hybrid with an electron in each of the unoccupied p-orbital. It has however, been shown that several carbenes are in a non-linear triplet ground state.

Reactivity of carbenes:

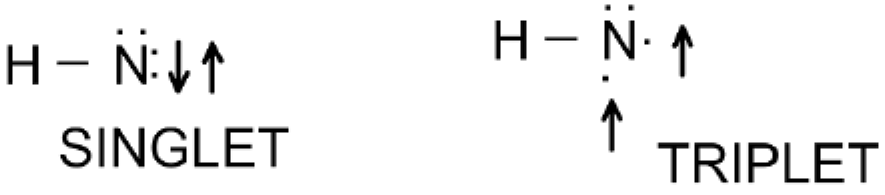
Carbenes being electron deficient molecules are generally electrophilic. Singlet carbene is more like an electrophilic species (R_3C^+, CO and isocyanides). Triplet carbenes should behave like a radical.

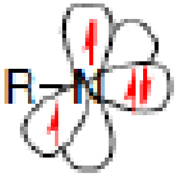
Both singlet and triplet carbenes are very reactive. Most of them are generated *in situ.*

Nitrenes

Nitrenes (R-N), are the nitrogen analogues of carbenes, and most of the comments about carbenes also applies to them. Nitrenes are too reactive for isolation under ordinary conditions, although ab initio calculations show that nitrenes are more stable than carbenes with an enthalpy difference of 25–26 kcal mol^{-1} (104.7–108.8 kJ mol^{-1}).

Nitrenes differ from carbenes in terms of electronic states





Organic acids and bases

An **organic acid** is an **organic compound** with **acidic** properties. The most common organic acids are the **carboxylic acids**, whose acidity is associated with their **carboxyl group** –COOH. **Sulfonic acids**, containing the group $-SO_2OH$, are relatively stronger acids. Alcohols, with **–OH**, can act as acids but they are usually very weak.

Acording to Bronsted acids are proton donors and according to Lewis acids are electron pair acceptors. As well as: Bronsted base = proton acceptor, Lewis base = electron pair donor.

An acid HB is ionizes by following

$$\mathrm{HB} \rightleftharpoons \mathrm{H}^{\oplus} + \mathrm{B}\!:^{\ominus} \qquad K_a = \frac{[\mathrm{H}^{\oplus}]\,[\mathrm{B}\!:^{\ominus}]}{[\mathrm{HB}]} \qquad pKa = -\log K_a$$

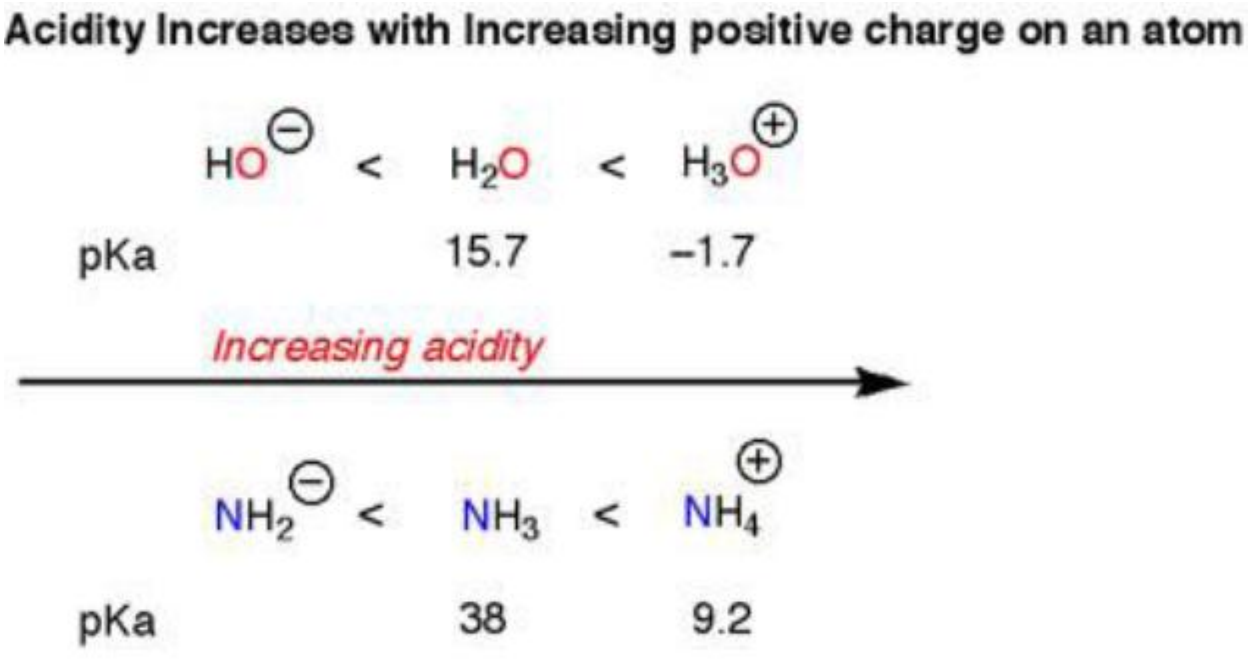
A conjugate base is obtain when remove a proton (H+) from a compound. For instance, HO^- is the conjugate base of water. O^{2-} is the conjugate base of HO^-. Conversely, conjugate acids are what you obtain when you add a proton to a compound. The conjugate acid of water is H_3O^+.

According to this, **anything which stabilizes the conjugate base will increase the acidity.** Therefore pKa is also a measure of how stable the conjugate base is. Put another way, strong acids have weak conjugate bases, and vice versa.

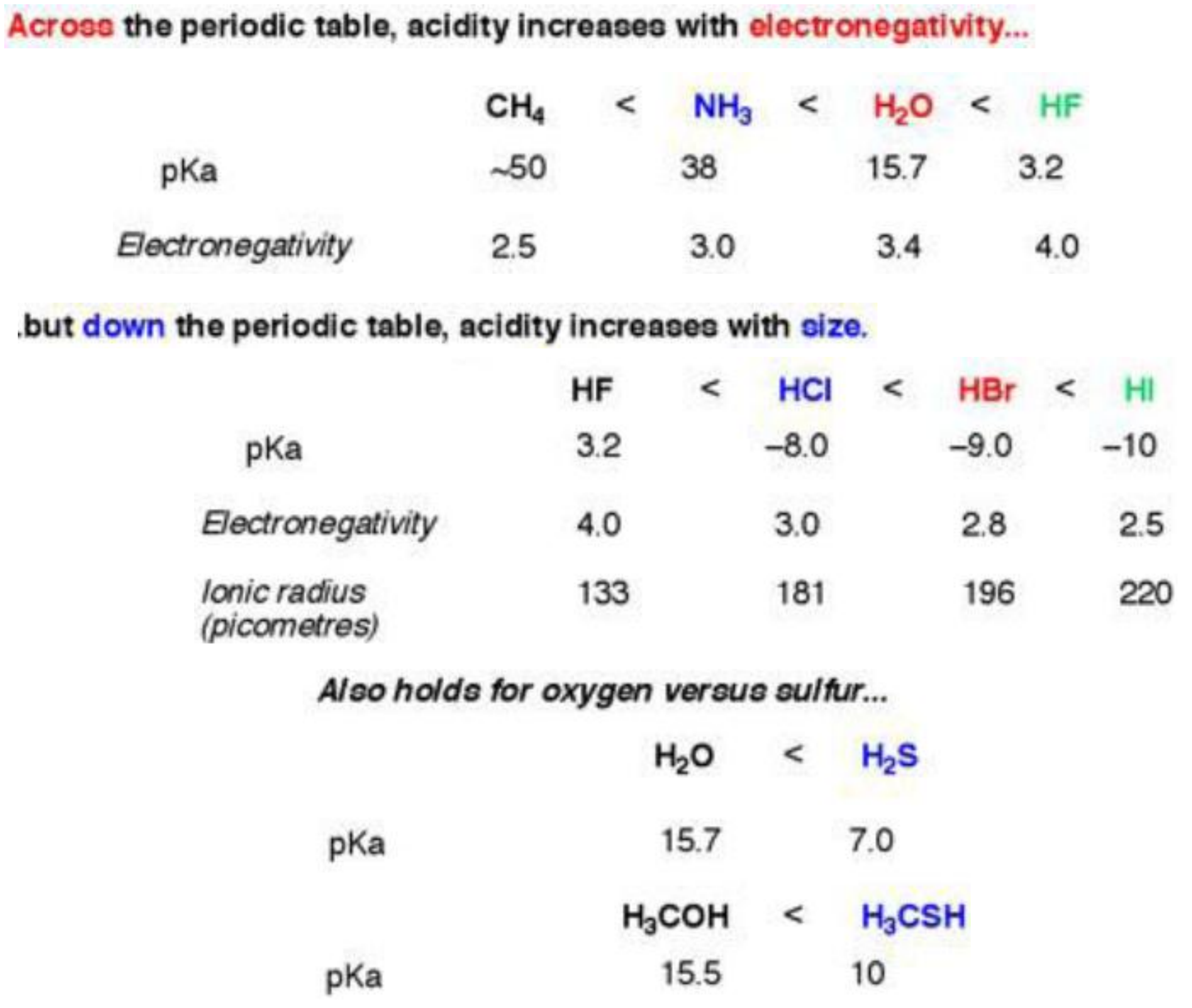
Factors Affecting the Acidity of Organic Compounds

(1) Charge

Removal of a proton, H+ , decreases the formal charge on an atom or molecule by one unit. This is, of course, easiest to do when an atom bears a charge of +1 in the first place, and becomes progressively more difficult as the overall charge becomes negative. The acidity trends reflect this:



(2)The Role of the Atom



Across the periodic table, acidity increases with electronegativity...

$CH_4 < NH_3 < H_2O < HF$

	CH_4	NH_3	H_2O	HF
pKa	~50	38	15.7	3.2
Electronegativity	2.5	3.0	3.4	4.0

.but **down** the periodic table, acidity increases with **size.**

$HF < HCl < HBr < HI$

	HF	HCl	HBr	HI
pKa	3.2	–8.0	–9.0	–10
Electronegativity	4.0	3.0	2.8	2.5
Ionic radius (picometres)	133	181	196	220

Also holds for oxygen versus sulfur...

$H_2O < H_2S$

	H_2O	H_2S
pKa	15.7	7.0

$H_3COH < H_3CSH$

	H_3COH	H_3CSH
pKa	15.5	10

The first reason has to do with the shorter (and stronger) H-F bond as compared to the larger hydrogen halides. The second has to do with the *stability of the conjugate base.* The fluoride anion, F(–) is a tiny and vicious little beast, with the smallest ionic radius of any other ion bearing a single negative charge. Its charge is therefore spread over a smaller volume than those of the larger halides, which is energetically unfavorable: for one thing, F(–) begs for solvation, which will lead to a lower entropy term in the ΔG.

(3) Resonance

A huge stabilizing factor for a conjugate base is if the negative charge can be delocalized through resonance.

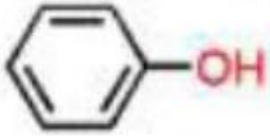
Remember, **any structural feature that increases the stability of the conjugate base will increase acidity.**

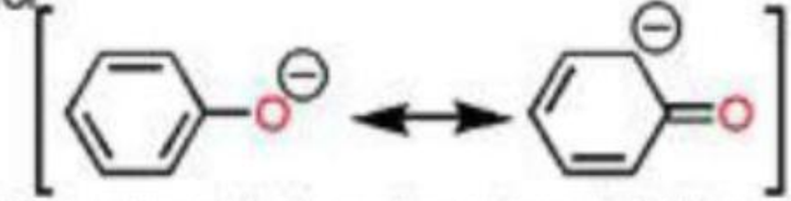
Key question: can the lone pair of the conjugate base participate in resonance with an adjacent π bond?

Resonance will increase the stability of the conjugate base (therefore increasing acidity) because the negative charge can be delocalized.

Example 1 - contrast methanol versus phenol:

CH_3OH





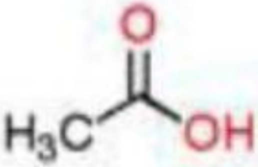
The anion of phenol can be stabilized through resonance

pKa 15 < **10**

more acidic

Example 2 - alcohols (e.g. methanol) versus carboxylic acids

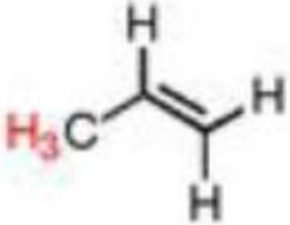
CH_3OH

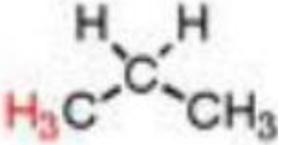


pKa 15 < **4**

more acidic

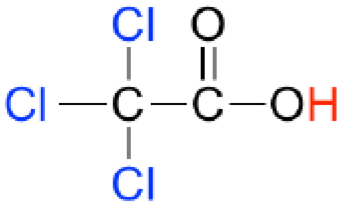
Question: Which proton (in red) would you expect to be more acidic?





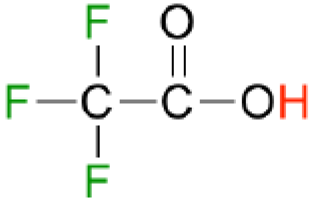
(4) Inductive effects

Electronegative atoms can draw negative charge toward themselves, which can lead to considerable stabilization of conjugate bases. Check out these examples:



trichloroacetic acid

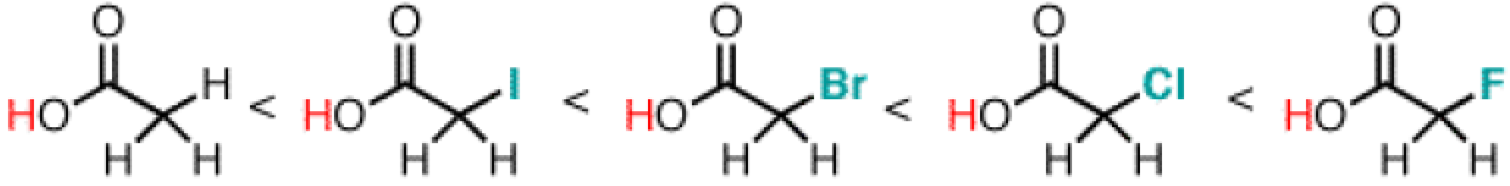
pK_a = 0.64



trifluoroacetic acid

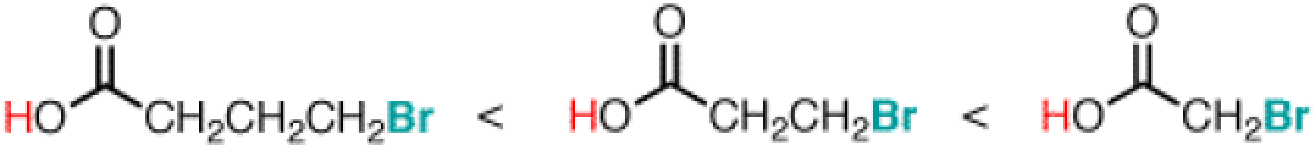
pK_a = -0.25

Electronegativity increases in the order F > Cl > Br > I :



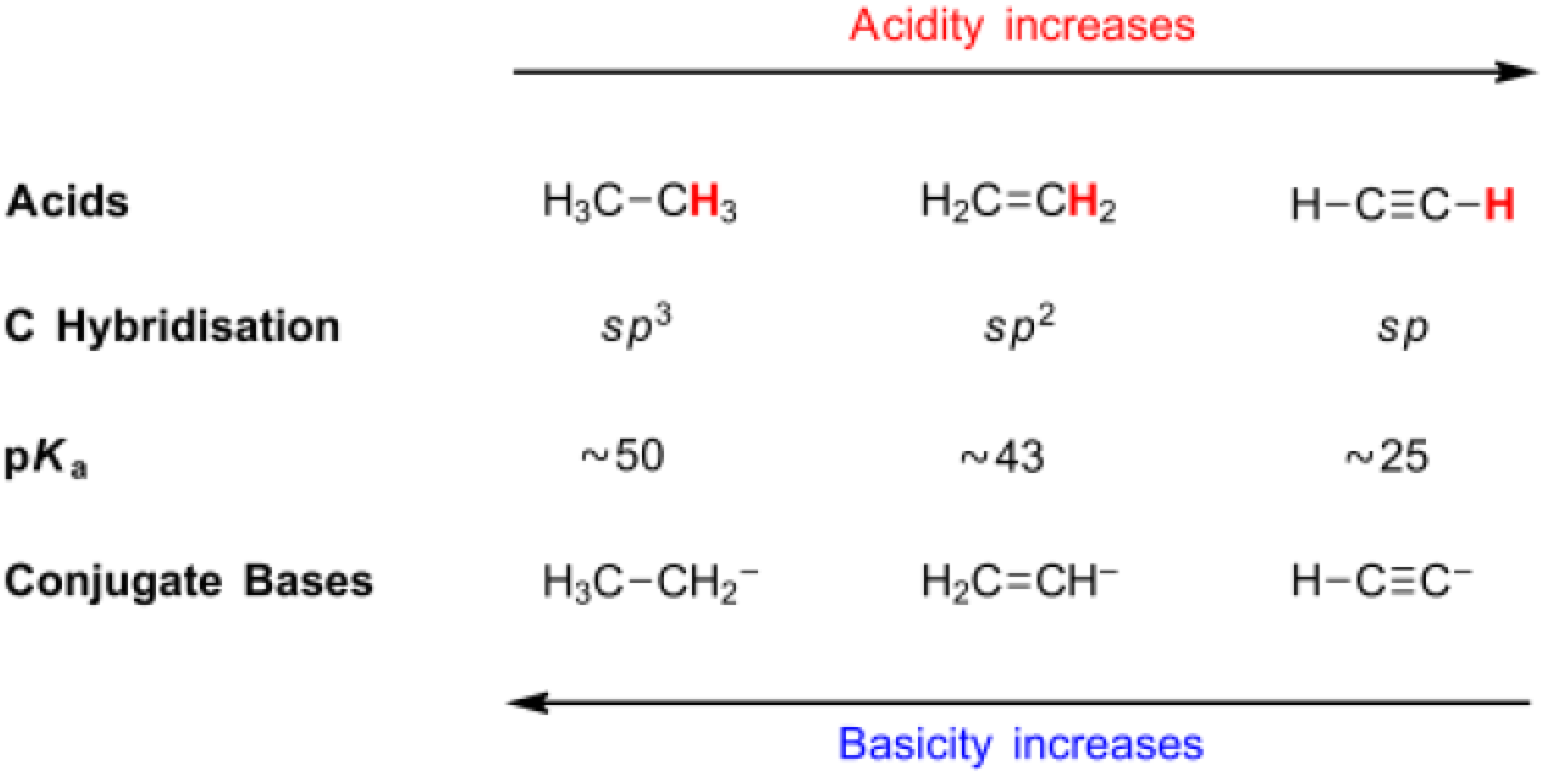
pKa 4.76 3.15 2.86 2.81 2.66

More acidic



pKa 4.59 4.01 2.86

5. Hybridisation: Higher the s-character, higher the electronegativity and higher Will be the acidity

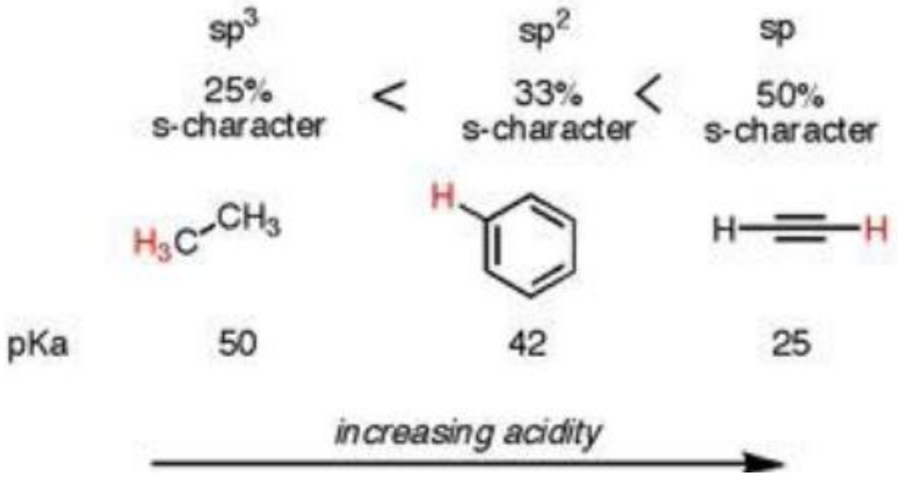


Acidity increases

Acids	H_3C-CH_3	$H_2C=CH_2$	$H-C\equiv C-H$
C Hybridisation	sp^3	sp^2	sp
pK_a	~50	~43	~25
Conjugate Bases	$H_3C-CH_2^-$	$H_2C=CH^-$	$H-C\equiv C^-$

Basicity increases

The higher the *s*-character of a bond to hydrogen, the more acidic it will be.



Organic Bases

Organic bases are usually Lewis bases that can donate lone pair of electron.

Factors affecting strength of organic bases

(1) **Charge:** A postive formal charge on the electron donating atom will DECREASE its electron density, making it less likely to form a bond with a hydrogen proton. A NEGATIVE formal charge on the electron donating atom will INCREASE its electron density, making it more likely to form a bond with a hydrogen proton

(2) **Electronegativity:** When an atom has greater electronegativity, this means that the atom is greedier for electrons.If the atom donating electrons to the proton has a high electronegativity, then the molecule containing that atom has a lower basicity.

Ex: NH3 vs F- The electron donating atoms are N and F-. Because F has a higher electronegativity than N, it is less willing to donate electrons to the proton. This reduces the likelihood that F will form bonds with H, meaning that F is the less basic out of the two.

(3) **Hybridisation:** The order of basicity is $SP^3 > SP^2 > SP$. Higher the S character higher the electronegativity and lower will be basicity.

(4) **Atomic size:** Atoms with smaller atomic radius's will have greater electron density, increasing basicity. Atoms with larger atomic radius's will have less electron density, reducing basicity. F- has a greater electron density than BrTherefore, Br- is less basic than F-.

(5) **Inductive effect:** Inductive effect is when other atoms within the molecule can take or give electrons from the atom donating electrons to a proton. …Atoms that do not donate electrons to protons can influence basicity as well.

(6) **Resonance:** Resonance usually DELOCALIZES electrons from the atom, thus REDUCING electron density. This causes the molecule to have lower basicity. If a basic atom is not involved in resonance, then resonance has no impact on the molecule's basicity! This is because the atom's electron density is not delocalized.

HARD AND SOFT ACIDS AND BASES (HSAB)

The HSAB (Hard Soft Acid Base) theory categorizes chemical species as acids or bases and as "hard", "soft", or "borderline". It explains that soft acids or bases tend to be large and very polarizable, while hard acids or bases are small and non-polarizable. Since these categories are not absolute, there are species that are considered borderline, which lie in between hard and soft.

Generally, we could characterize hard acids and bases as having:

Hard **Acceptor atoms are marked by:**	**Soft** **Acceptor atoms are marked by:**
1) Small size	1) Large size
2) High positive oxidation state.	2) Zero or low positive oxidation state
3) Absence of any outer electrons Which are easily excited to higher States.	3) Presence of several excitable valence shell electrons.
4) Absence of d-electrons.	4) With nearly full d-electrons.

5) Usually light metal ions.	5) Mostly heavy metal ions.
6) Know as Lewis acids which Are not easily polarizable Prefer to coordinate with hard	6) Known as Lewis acids and are easily polarizable. Prefer to coordinate with soft bases.

Hard	Borderline	Soft
$H^{+,}$ Li^{+} ,Na^{+}, K^{+}	Fe^{2+} Co^{2+} Ni^{2+}	Cu^{+},Ag^{+},Au^{+},TI^{+}
Be2+,Mg2+,Ca2+	Cu^{2+} ,Zn^{2+},Pb^{2+}	Hg^{+},Pd^{2+},Cd^{2+},
Cr^{2+},$Cr^{3+,}$$Al^{3+}$	SO_2,BBr_3	Pt^{2+},Hg^{2+},BH_3,Br_2
SO_3,BF_3,BCl_3		Br^{+},
HX(H-bonding)		M^0 (metal atoms) and bulk metals

Hard	Soft
1) High electronegativity.	1) Low electronegativity
2) Low polarisability.	2) High Polarisability.
3) Presence of filled orbits ; empty orbitals may exist at high energy level.	3) Partially filled orbitals, empty orbitals are low- lying.
4) These are anions or neutral molecule known as Lewis bases or ligands, prefer to co-ordinate with hard acids.	4) these are anions or neutral molecules called similarly as Lewis bases or ligands, prefer to bind with soft acids.

Hard	Borderline	Soft
F^-,OH^-,H_2O,NH_3	NO_2,SO_3,Br^-	H^-,R^-,CN^-,CO,I^-,
CO_3^{2-},NO_3^-,O^{2-},	N_3^-,N_2,C_6H_5N,	SCN^-,R_3P,C_6H_6,
SO_4^{2-}, $PO_4^{3-}ClO_4^-$,(Cl^-)	SCN^-	R_2S.

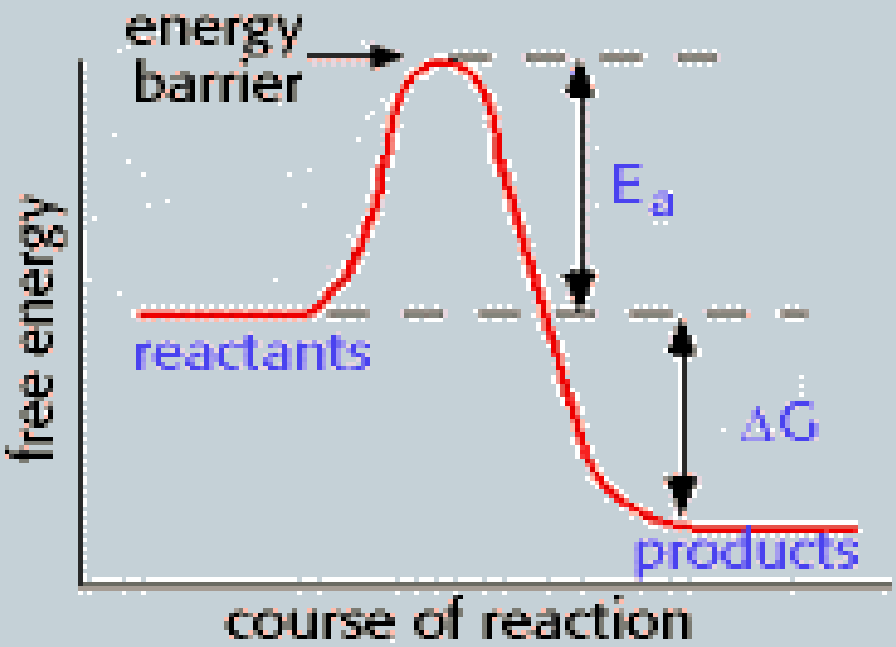
PEARSON’S CONCEPT

Pearson suggested a simple rule (Sometimes called Pearson’s principle) for predicting the stability of complexes formed between hard and soft acids and bases.

“Hard acids prefer to bind (co-ordinate) with hard bases and soft acids prefer to bind with soft bases and gives stable complex compound ”.

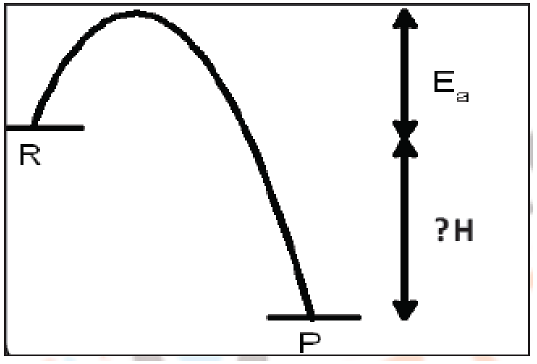
Energy Of Reactions

- **Activation Energy:** The minimum amount of energy needed to start a reaction.

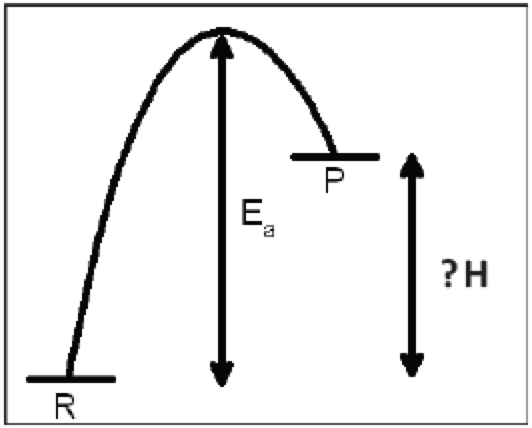


Energy Profile Diagrams

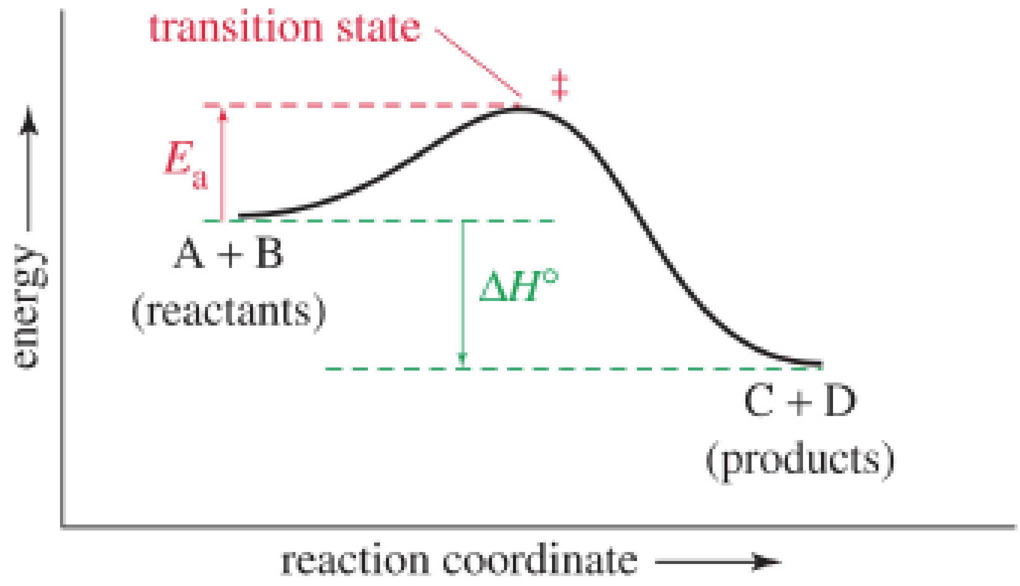
Exothermic Reactions: If the bonds that are formed in a reaction are stronger than the bonds that are broken, more energy will be released as a result of bond formation than will be consumed in the bond-breaking process and **ΔH** will be negative. Therefore, **exothermic reaction** is a reaction with a negative **ΔH**



Endothermic Reactions: If the bonds that are formed are weaker than those that are broken, ΔH will be positive. Therefore, endothermic reaction is a reaction with a positive ΔH.

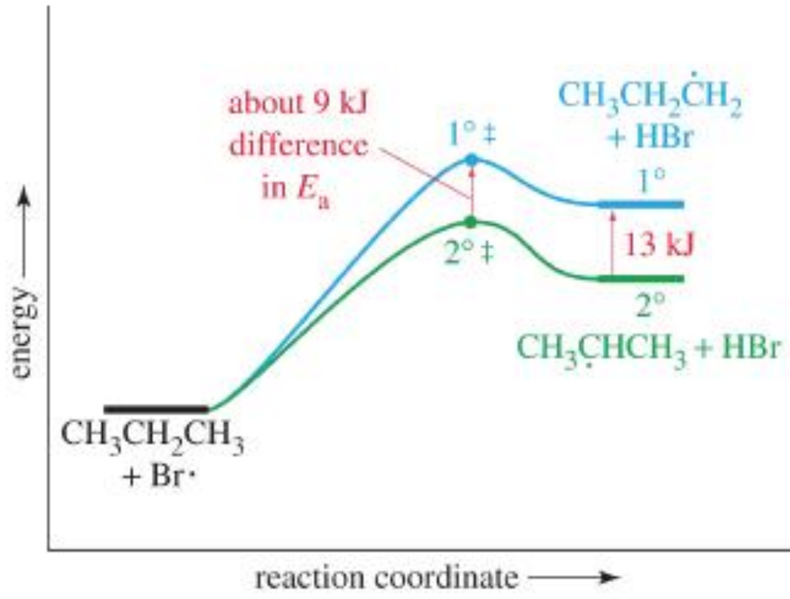


Energy Diagram of One-Step Exothermic Reaction

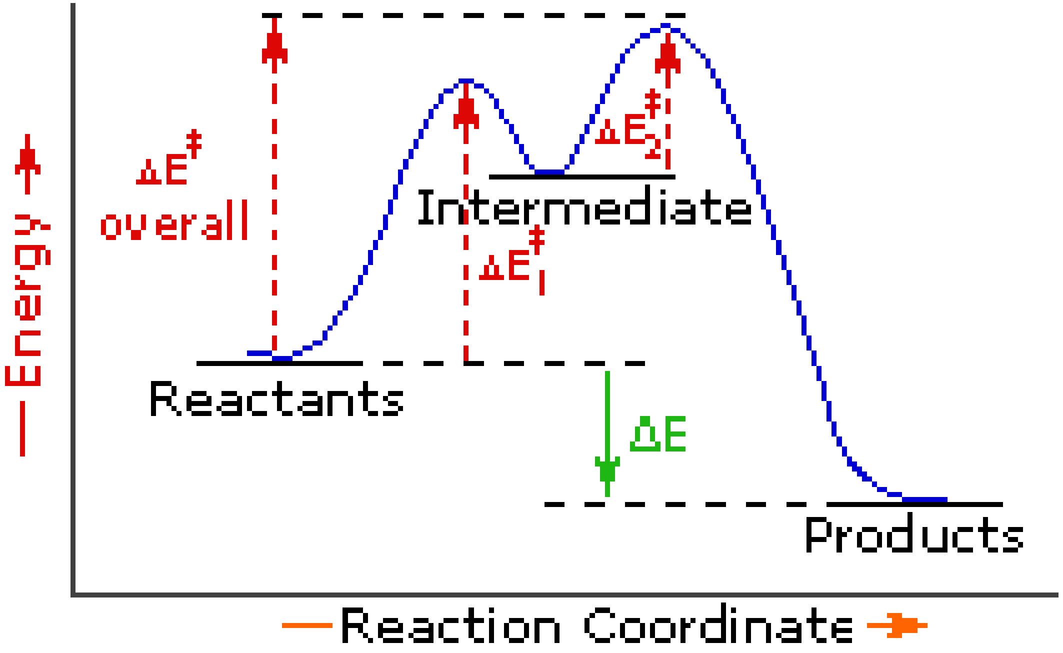


- The **vertical** axis in this graph represents the **potential energy**.
- The **transition state** is the highest point on the graph, and the **activation energy** is the energy difference between the reactants and the transition state.

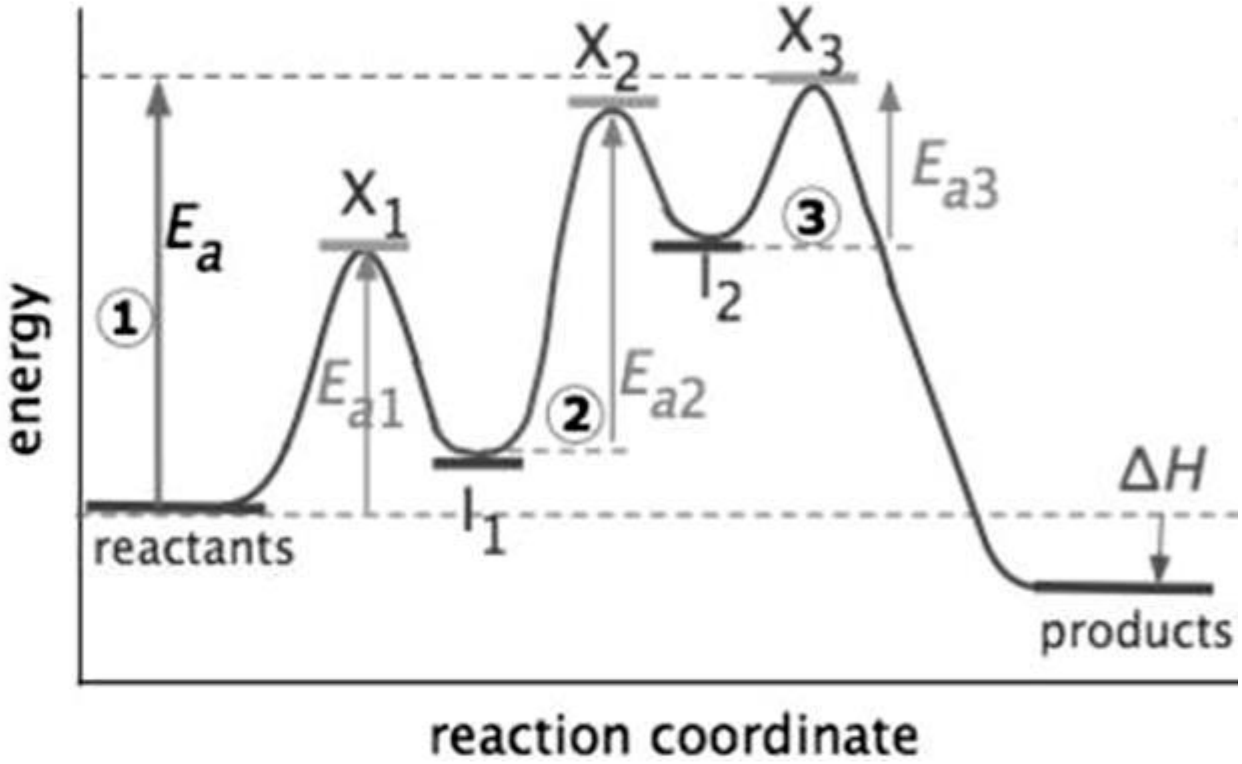
Energy Diagram of Endothermic Reaction



Energy profile diagram for a two step reaction



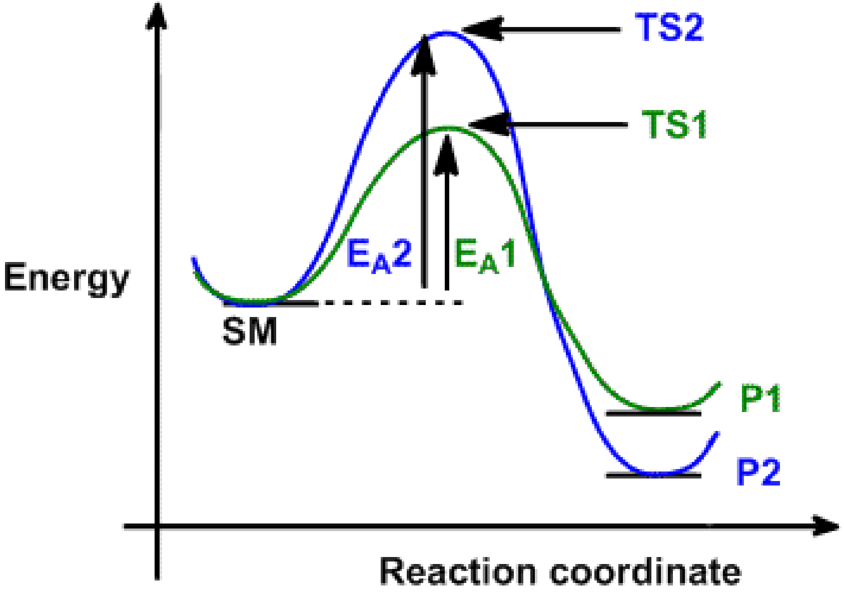
Energy profile diagram for a three step reaction



Kinetic and Thermodynamic Control

The potential outcome of a reaction is usually influenced by two factors:
the relative stability of the products (*i.e. thermodynamic factors)*
the rate of product formation (*i.e. kinetic factors)*

The following simple reaction coordinate diagram provides a basis for the key issues about kinetic and thermodynamic control:



Consider the case where a starting material, **SM**, can react in a similar manner to give two different products, **P1** and **P2** via different (competing) pathways represented by **green** and **blue** curves.

Reaction 1 via pathway 1 (**green**) generates product 1 (**P1**) via transition state 1 (**TS1**). This will be the *faster reaction* since it has a lower energy (more stable) transition state, and therefore a lower activation barrier. Therefore, product 1, **P1** is the **kinetic product** (the product that forms the fastest).

Reaction 2 via pathway 2 (**blue**) generates product 2 (**P2**) via transition state 2 (**TS2**). **P2** is the more stable product since **P2** is at a lower energy than **P1**. Therefore, **P2** is the **thermodynamic product** (the more stable product).

We now need to consider how the outcome of this situation changes with the competing reactions of the starting material as we alter the reaction temperature and therefore the *average* energy of the molecules changes.

1. At low temperature, the average energy of the molecules is low and more molecules have enough sufficient energy cross activation energy E_A1 than E_A2. Therefore the reaction preferentially proceeds along the green path to **P1**. The reaction is not reversible since the molecules lack sufficient energy to reverse to **SM**, *i.e. it is irreversible*, so the product ratio of the reaction is dictated by *the rates of formation of* **P1** and **P2**, $k_1 : k_2$.

2. At some slightly higher temperature, reaction 1 will become reversible when sufficient molecules have enough energy to cross the reverse reaction barrier for reaction 1, while reaction 2 remains irreversible. So although **P1** may form initially, over time it will revert to **SM** and react to give the more stable **P2**.

3. At high temperature, both reaction 1 and 2 are reversible and the product ratio of the reaction is dictated by the *equilibrium constants for* **P1** and **P2**, $K_1 : K_2$.

Summary

At low temperature, the reaction is under **kinetic control** (rate, irreversible conditions) and the major product is that from the fastest reaction.

At high temperature, the reaction is under **thermodynamic control** (equilibrium, reversible conditions) and the major product is the more stable system