8.

BASIC PRINCIPLES OF ORGANIC CHEMISTRY

1. INTRODUCTION

What is organic chemistry?

Organic chemistry is the study of most carbon compounds with the exception of a few (e.g., CO_2 and carbonate salts). While inorganic chemistry deals with the study of all other compounds.

2. PROPERTIES OF ORGANIC COMPOUNDS

In general, organic compounds.

(a) Are far more in number than inorganic compounds. This is due to the catenation property of the C atom. Carbon has the ability to form bonds with almost every other element (Other than the noble gases), forming long chains as well as ring compounds. Moreover, C compounds exist as many isomers.

(b) React more slowly and require higher temperatures for reactions to take place.

(c) Are less stable and sometimes decompose on heating to compounds of lower energy levels.

(d) Undergo more complex reactions and produce more side reaction products.

(e) Are largely insoluble in water.

(f) Have generally lower melting and boiling points.

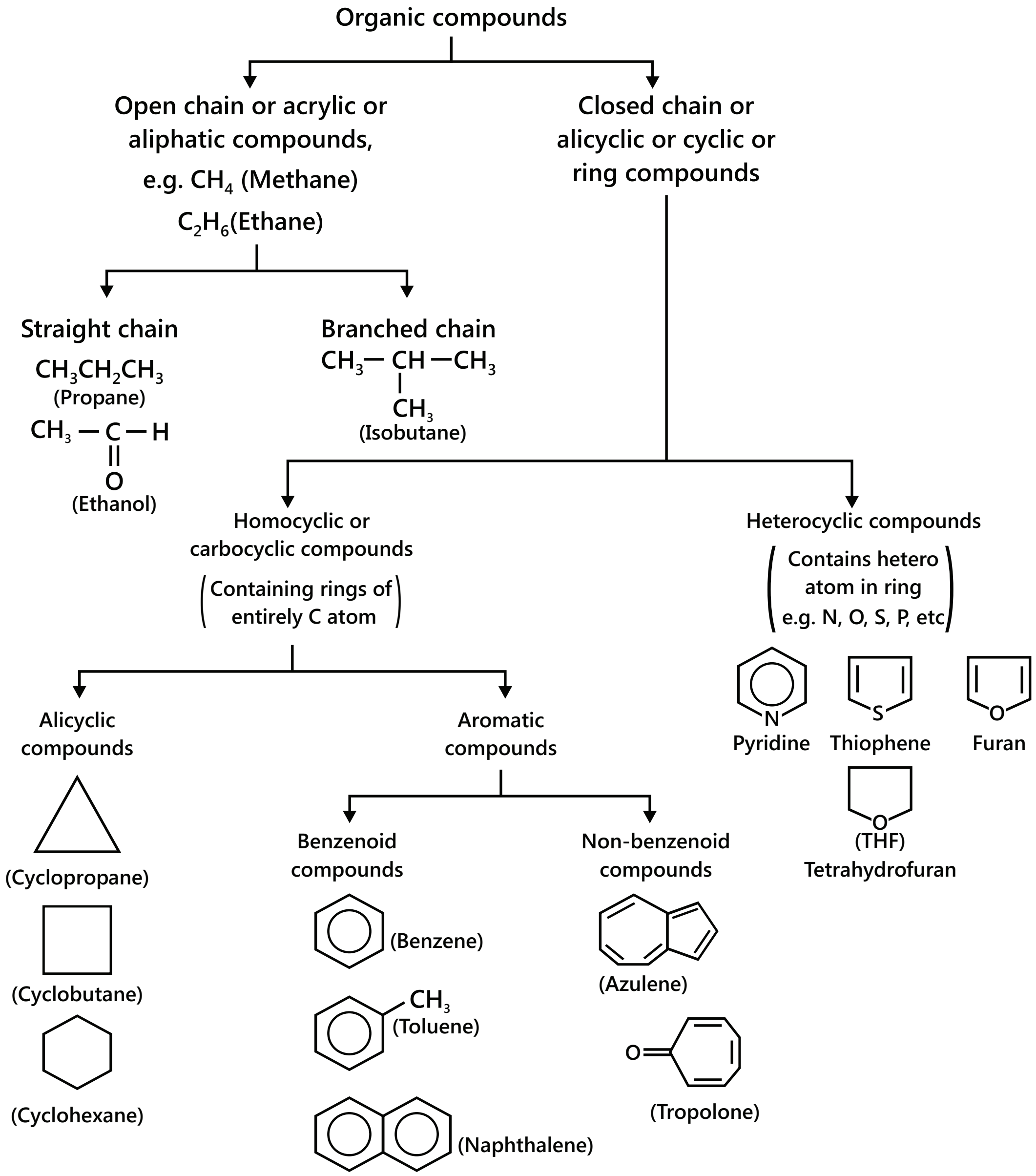
(g) Are classified into families of compounds such as carboxylic acids, which have similar reactive groups and chemical properties.

(h) Are mostly obtained from animals or plants as opposed to the mineral origin of inorganic compounds.

3. CLASSIFICATION OF ORGANIC COMPOUNDS

They are classified follows:

Classification of organic compounds is basically based on the functional group. The chemical properties of compound depends on the properties of the functional group present in it. The rest of the molecule simply affects the physical properties, e.g., m.p., b.p., density etc. and has very little effect on its chemical properties.



Flowchart 8.1: Classification of organic compound

Homologous Series

Organic compounds containing one particular characteristic group or functional group constitute a homologous series, e.g., alkanes, alkenes, haloalkanes, alkanols, alkanals, alkanones, alkanoic acids amines etc.

4. NOMENCLATURE OF ORGANIC COMPOUNDS

4.1 Trivial or Common Names

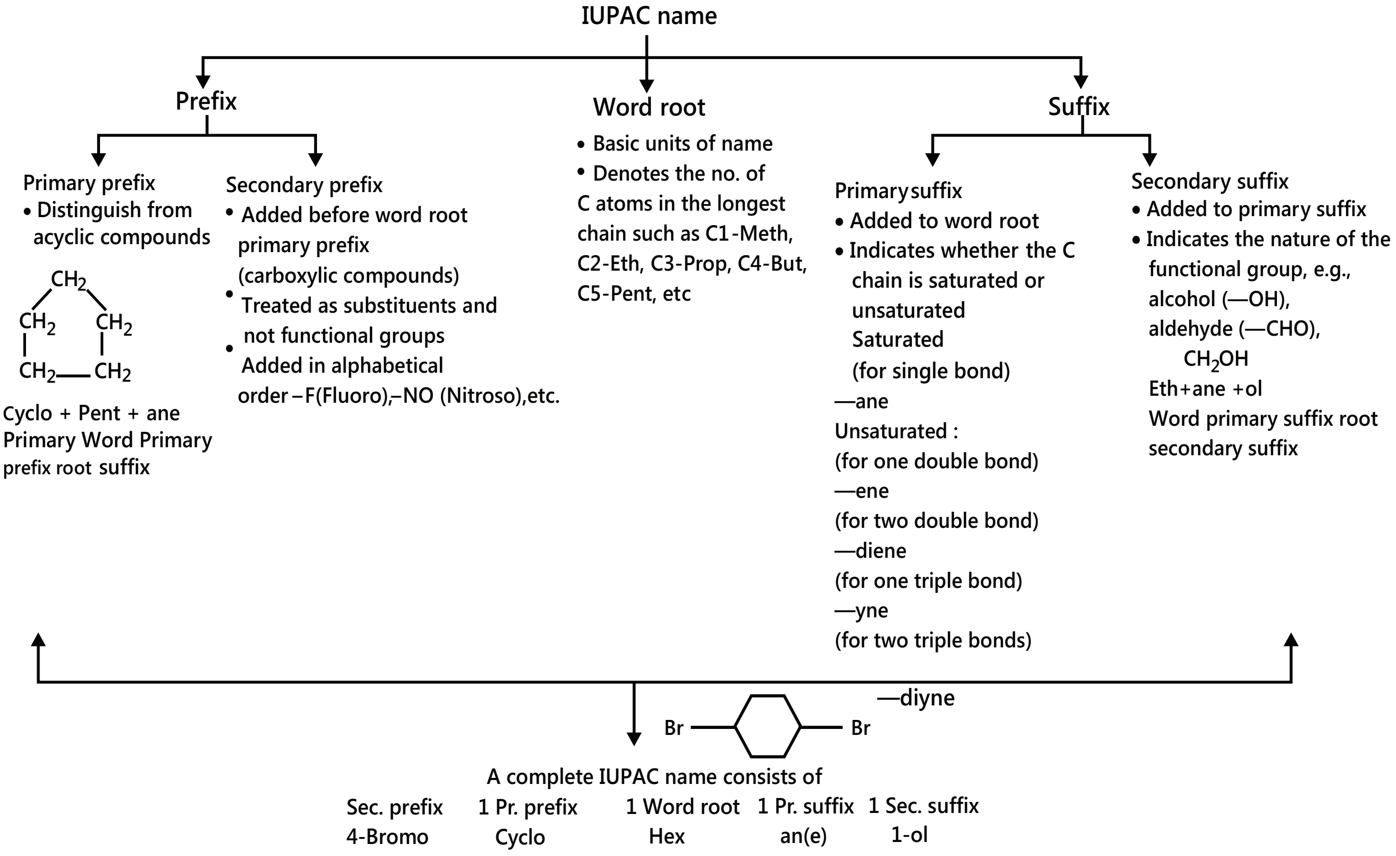
In the earlier days, because of the absence of IUPAC names, the names of the compounds were dependent on the source from which the compound was obtained. Even today, in spite of IUPAC nomenclature some of the common names are still at use. In some case, where the IUPAC name is very tedious we prefer to use common names, for example lactic acid, sucrose etc.

Table 8.1: Common names of organic compounds, their sources, and structures

S.No	Common name	Source	Structure
1.	Formic acid	Formica (red ant)	$HCOOH$
2.	Acetic acid	Acetum (vinegar)	$MeCOOH$
3.	Propionic acid	Portopion (first fat)	$MeCH_2COOH$
4.	Butyric acid	Butyrum (butter)	$MeCH_2CH_2COOH$
5.	Valeric acid	Valerian (shrub)	$Me(CH_2)_3COOH$
6.	Caproic acid	Caper (Goat)	$Me(CH_2)_4COOH$
7.	Urea	Urine	NH_2CONH_2
8.	Malic acid	Malum (apple)	CH_2COOH | $CH(OH)COOH$
9.	Methyl alcohol	Methu hule (Mehtu-wine, hule = wood)	$MeOH$

4.2 IUPAC Names

The IUPAC nomenclature of organic compounds is a systematic method of naming organic compounds as recommended by the International Union of Pure and Applied Chemistry (IUPAC). This system uses substitutive nomenclature, which is based on the principal group, and principal chain. The IUPAC rules for the naming of alkanes from the basis of the substitutive nomenclature of most other compounds -



Flowchart 8.2: IUPAC nomenclature of organic compound

4.3 IUPAC and Common Names of Some Functional Groups and Classes of Organic Compounds

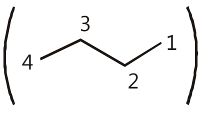
4.3.1 IUPAC Rules for Saturated Hydrocarbons

1. Alkanes: General formula: C_nH_{2n+2} IUPAC group suffix: - ane

E.g. $(H_3\overset{4\,3}{C}CH_2\ \overset{2}{C}H_2\overset{1}{C}H_3)$

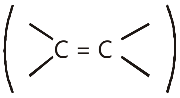
or

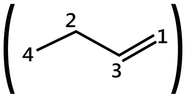
$(Me(CH_2)_2Me)$



Butane (IUPAC name)

2. Alkenes: General Formula: $C_nH_{2n} \Rightarrow \left(\begin{array}{l} \text{suffix} = -\text{ene} \\ \text{Alkane}\dfrac{-\text{ane}}{+\text{ene}}\text{alkene}\end{array}\right)$

Functional group structure: 

E.g. **i.** $(\overset{1}{C}H_2 = \overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3)$ **or** 

But-1-ene (IUPAC)

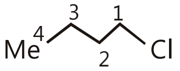
3. Alkyne: General formula: C_nH_{2n-2} $\left(\begin{array}{l} \text{suffix} = -\text{yne} \\ \text{Alkane}\xrightarrow[+\text{yne}]{-\text{ane}}\text{Alkyne}\end{array}\right)$

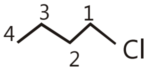
Functional group structure: $(-C \equiv C-)$

E.g. **i.** $HC \equiv CH$ **or** $H - \equiv - H$ $\underset{\text{(IUPAC)}}{\text{Ethyne}}$ $\underset{\text{(Common name)}}{\text{Acetylene}}$

4. Halides: General formula: $C_nH_{2n+1}X$ (X = F, Cl, Br, I) (RX) suffix = Halo

Functional group structure – X

E.g. $\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2Cl$ or 

or 

(1-Chlorobutane)

5. Alcohols: General formula: $C_nH_{2n+1}OH$ (R – OH)

IUPAC suffix: – ol   Common name = Alcohol   IUPAC prefix: -Hydroxy.

$\text{Alkan}\textcircled{e}\xrightarrow[+\text{ol}]{-\text{e}}\text{Alkanol}$

Functional group structure: – OH

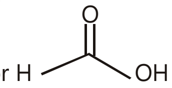
Example	IUPAC name	Common name
i. CH_3OH	Methanol	Methyl alcohol or Carbinol or Zerone

6. Carboxylic acids: General formula: $C_nH_{2n+1}COOH$ (R – COOH)

IUPAC suffix: -oic acid Common name = Acid IUPAC perfix : - Carboxy

$$\text{Alkan}ⓔ \xrightarrow[+\text{oic acid}]{-e} \text{Alkanol}$$

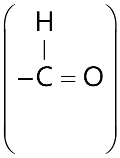
Functional group structure: (–COOH)

Example	**IUPAC name**	**Common name**
HCOOH or 	Methanoic acid	Formic acid

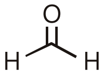
7. Aldehydes: General formula: C_n2_{n+1} . CHO (R – CHO)

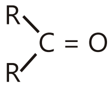
IUPAC suffix: - al Common name = Aldehyde IUPAC prefix: Formyl or oxo-

$$\text{Alkane} \xrightarrow[+\text{al}]{-e} \text{Alkanal}$$

Functional group structure: (–CHO) or 

$$\left(-\overset{\displaystyle H}{\overset{|}{C}}=O\right)$$

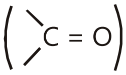
Example	**IUPAC name**	**Common name** (derived from acid)
HCHO or 	Methanal	Formaldehyde

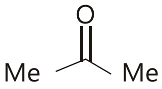
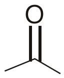
8. Ketones: General formula: 

$$\begin{matrix} R \\ & C = O \\ R \end{matrix}$$

IUPAC suffix: - one Common name; Ketone IUPAC prefix; – oxo,

$$\text{Alkan}ⓔ \xrightarrow[+\text{ one}]{-e} \text{Alkanone}$$

Functional group structure: 

Example	**IUPAC name**	**Common name**
CH_3COCH_3 or  or 	Propan-2-one	Acetone

9. Nitriles: General formula: C_nH_{2n+1} CN (R – C ≡ N)

IUPAC suffix: nitrile Common name: Cyanide IUPAC prefix: Cyano

$$\text{Alkane} \xrightarrow[+\text{nitrile}]{-e} \text{Alkan}ⓔ\text{nitrile}$$

(e is not dropped)

Functional group structure: (– C ≡ N)

Example	IUPAC name	Common name
$\overset{2}{C}H_3\overset{1}{C}N$ or $\overset{2}{Me}-\overset{1}{C}\equiv N$ or $(^{2}-\overset{1}{C}\equiv N)$	Ethane nitrile	Methyl cyanide or Acetonitrile

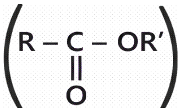
10. Ethers: General formula: (R – O – R′)

IUPAC suffix: -- Common name: (Ether)

IUPAC prefix: alkoxy (smaller chain) alkane (larger chain)

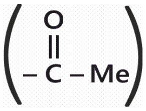
Functional group structure: (R – O – R′)

Example	IUPAC name	Common name
CH_3-O-CH_3 or $(CH_3)_2O$ or Me_2O	Methoxy methane	Dimethyl ether

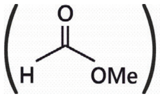
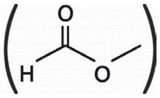
11. Esters: General formula: 

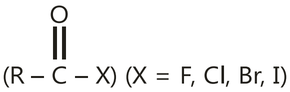
$$\left(R-\underset{\displaystyle O}{\underset{\|}{C}}-OR'\right)$$

IUPAC suffix: -oate IUPAC prefix: alkoxy carbonyl

Functional group structure: (–COOR) or 

$$\left(-\overset{\displaystyle O}{\overset{\|}{C}}-Me\right)$$

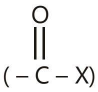
Example	IUPAC name	Common name
HCOOCH$_3$ or  or 	Methyl methanoate	Methyl formate

12. Acyl halides: General formula: 

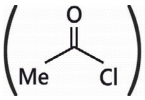
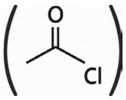
$$(R-\overset{\displaystyle O}{\overset{\|}{C}}-X)\ (X = F, Cl, Br, I)$$

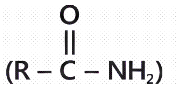
IUPAC suffix: -oyl halide IUPAC prefix: halocarbonyl

$$\text{Alkane}\xrightarrow[\text{oyl halide}]{-e}\text{Alkanoyl halide}$$

Functional group structure: 

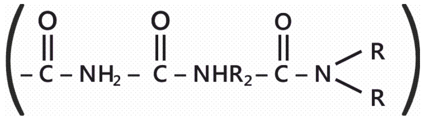
$$(-\overset{\displaystyle O}{\overset{\|}{C}}-X)$$

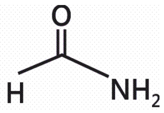
Example	IUPAC name	Common name (derived from acid)
CH$_3$COCl or  or 	Ethanoyl chloride	Formyl chloride

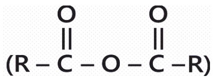
13. Amides: General formula: 
$(R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2)$

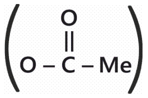
IUPAC suffix: amide IUPAC prefix: Carbamyl

Alkane $\xrightarrow[+\text{ amide}]{-e}$ Alkanomide

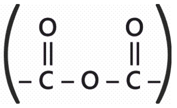
Functional group structure: 
$\left(-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2-\ \overset{\overset{\displaystyle O}{\|}}{C}-NHR_2-\overset{\overset{\displaystyle O}{\|}}{C}-N\begin{smallmatrix}R\\R\end{smallmatrix}\right)$

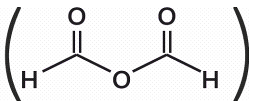
Example	**IUPAC name**	**Common name**
$HCONH_2$ or 	Methanamide	Formamide

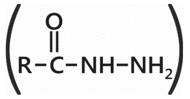
14. Anhydrides: General formula: 
$(R-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R)$

IUPAC suffix: – oic anhydride IUPAC prefix: Acetoxy or acytyloxy or 
$\left(O-\overset{\overset{\displaystyle O}{\|}}{C}-Me\right)$

Alkanoic acid $\xrightarrow[+\text{anhydride}]{-\text{acid}}$ Alkanoic anhydride

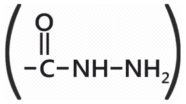
Functional group structure: (–COOCO–) or 
$\left(-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-\right)$

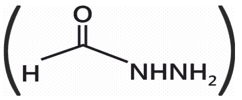
Example	**IUPAC name**	**Common name (derived from acid)**
HCOOCH or (HCO_2) or 	Methanoic anhydride	Formic anhydride

15. Acid hydrazides: General formula: 
$\left(R-\overset{\overset{\displaystyle O}{\|}}{C}-NH-NH_2\right)$

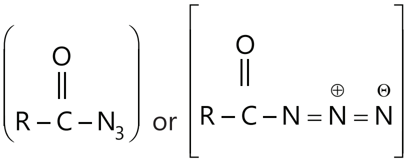
IUPAC suffix – hydrazide IUPAC prefix: --

Alkanoic acid $\xrightarrow[+\text{hydrazide}]{-\text{ic acid}}$ Alkanohydrazide

Functional group structure: $(-CONHNH_2)$ or 
$\left(-\overset{\overset{\displaystyle O}{\|}}{C}-NH-NH_2\right)$

Example	**IUPAC name**	**Common name** (derived from acid)
$HCONHNH_2$ or 	Methanohydrazide	Formyl hydrazide

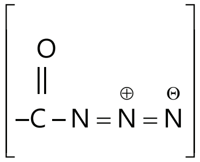
16. Acid azides: General formula:



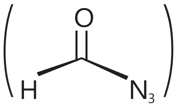
$$\left(R-\overset{\overset{\displaystyle O}{\|}}{C}-N_3\right) \text{ or } \left[R-\overset{\overset{\displaystyle O}{\|}}{C}-N=\overset{\oplus}{N}=\overset{\ominus}{N}\right]$$

IUPAC suffix: azide $\quad$ Alkanoic acid $\xrightarrow[+\text{azide}]{-\text{ic acid}}$ Alkanoazide

Functional group structure: $(-CON_3)$ or



$$\left[-\overset{\overset{\displaystyle O}{\|}}{C}-N=\overset{\oplus}{N}=\overset{\ominus}{N}\right]$$

Example	**IUPAC name**	**Common name**
$HCON_3$ or 	Methanoazide	Formyl azide

17. Thioalcohols or Thiols or Mercaptans: General formula: (RSH)

IUPAC suffix: thiol $\quad$ IUPAC prefix: mercapto

Functional group structure: (–SH) $\quad$ $\text{Alkan}\text{\textcircled{e}} \xrightarrow[+\text{thiol}]{-\text{e}}$ Alkan thiol

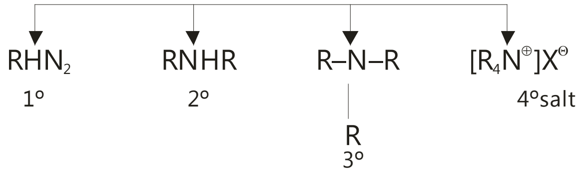
Example	**IUPAC name**	**Common name** (derived from acid)
CH_3SH or MeSH or	Methanthiol	Methyl thioalcohol or Methylmercaptan

18. Thioethers: General formula: (R – S – R)

IUPAC suffix: thioether $\quad$ IUPAC prefix: --

Example	**IUPAC name**	**Common name** (derived from acid)
CH_3SCH_3 ore MeSMe or Me_2S	Methyl thio ether or (Methyl thio) Methane	Dimethyl sulphide

19. Amines: General formula:

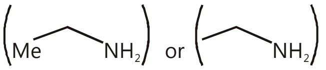


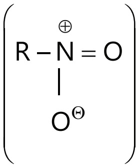
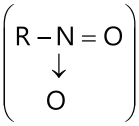
RHN_2 (1°) $\quad$ RNHR (2°) $\quad$ $R-\underset{\displaystyle R}{\underset{|}{N}}-R$ (3°) $\quad$ $[R_4N^{\oplus}]X^{\ominus}$ (4°salt)

IUPAC suffix: amine $\quad$ IUPAC prefix: amino

$\text{Alkan}\text{\textcircled{e}} \xrightarrow[+\text{amine}]{-\text{e}}$ Alkanamine

Functional group structure: $-NH_2$, (1°), $>NH$(2°), $>N-$ (3°)

Example	**IUPAC name**	**Common name**
$CH_3CH_2NH_2$ or $EtNH_2$ or 	Ethan amine	Ethyl amine

20. Nitro compounds: General formula: (RNO_2) or  or 

$\left(R-\overset{\oplus}{N}=O,\ \text{with } O^{\ominus} \text{ below N}\right)$ or $\left(R-\underset{\underset{O}{\downarrow}}{N}=O\right)$

IUPAC suffix: -- IUPAC prefix: nitro

Functional group structure: ($-NO_2$)

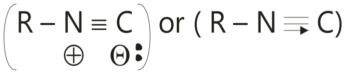
Example	**IUPAC name**
CH_3NO_2	Nitro methane

21. Alkyl nitrites: General formula: (R – O – N = O) IUPAC suffix: nitrite

Functional group structure: (–O–N=O)

Example	**IUPAC Name**
i. CH_3 – ONO or Me – O – N = O	Methyl nitrite
ii. $CH_3CH_2CH_2ONO$ or Pr – O – N = O	Propyl nitrite

22. Alkyl isocyanides or Isonitriles:

General formula: 

$\left(R-\underset{\oplus}{N}\equiv\underset{\ominus:}{C}\right)$ or $(R-N \rightleftarrows C)$

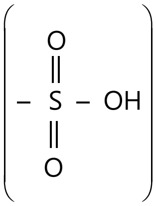
According to an IUPAC recommendation the substituent – NC is termed as carbylamino. Thus, CH_3NC is carbylamino methane and so on. However, this name is not in use.

For naming isocyanides, iso is prefixed to the name of the corresponding cyano/nitrile compound. In another mode the suffix carbylamine is added to the name of the alkyl group.

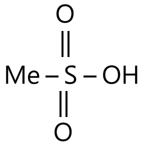
Example	**Common name**
CH_3NC	Methyl isocyanide or Acetoisonitrile or Methyl carbylamine

23. Sulphonic acids: General formula: ($R-SO_3H$)

IUPAC suffix: sulphonic acid IUPAC prefix: sulpho

Functional group structure: ($R-SO_3H$) or 

$\left(-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH\right)$

Example	**IUPAC name**
CH_3SO_3H or  $Me-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$	Methyl sulphonic acid

24. Imines: General formula: RCXH = NH

IUPAC suffix: imine IUPAC prefix: None

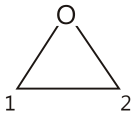
$$\text{Alkane} \xrightarrow[+\text{al imine}]{-\text{e}} \text{Alkanal imine}$$

Functional group structure: (–CH = NH)

Example	**IUPAC name**	**Common name**
HCH = NH	Methanalimine	Formaldimine

25. Cyclic ethers: General formula: O atom ring

IUPAC suffix: -- IUPAC prefix: epoxy

Example	**IUPAC name**	**Common name**
	Oxirane or 1,2-epoxy ethane	Ethylene oxide

4.3.2 IUPAC Rules for Saturated Hydrocarbons

(a) The longest possible chain (parent chain) is selected. The chain should be continuous.

(b) C atoms which are not included in this chain are considered substituents (side chain)

(c) In case of two equal chains having the same length, the one with the larger number of side chains or alkyl groups in selected.

(d) Numbering of C atoms in the parent chain starts from that end where the substituent acquires the lowest position numbers or locant.

(e) Lowest sum rule: In case of two or more substituents, numbering is done is such a way that the sum of position number substituent or location is the lowest

(f) Position and substituent name are separated with a case (-)

(g) In case of more than one substituent, they are prefixed by their respective locants in alphabetical order.

4.3.3 IUPAC Rules for Unsaturated Hydrocarbons

(a) All the rules of alkanes are also applicable there,

(b) The parent or the longest chain is selected irrespective of the = or σ bonds.

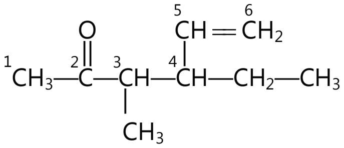
(c) The numbering is done from the end which is nearer to the = bond, and according to the lowest sum of locant rule.

(d) The numbering or sum rule will follow the alphabetical order of the substituent.

4.3.4 IUPAC Rules for Functional Groups

While numbering the longest chain, the function group should acquire the lowest number followed by other substituent and the family of multiple bonds even if it violates the lowest sum rule.

E.g.



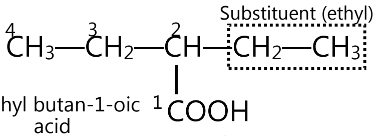
$\overset{1}{C}H_3-\overset{O}{\overset{\|}{\overset{2}{C}}}-\underset{CH_3}{\overset{3}{C}H}-\overset{\overset{5}{C}H=\overset{6}{C}H_2}{\overset{4}{C}H}-CH_2-CH_3$

C = O (Functional group) acquires the lowest number CH_3 (Substituent methyl $CH=CH_2$(= bond)

4.3.5 IUPAC Rules for Chain Terminating Functional Groups (-CHO, -COOH, -$CONH_2$, -COCl)

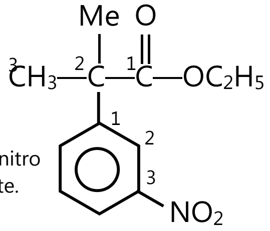
These chain terminating groups are included in the numbering, starting from the end where it acquires the lowest number followed by other substituent's in alphabetical order.

E.g.



$\overset{4}{C}H_3-\overset{3}{C}H_2-\underset{\overset{1}{COOH}}{\overset{2}{C}H}-\boxed{CH_2-CH_3}$

2-Ethyl butan-1-oic acid



Ethyl 2-methyl-2-(3-nitro phenyl) propanoate.

4.3.6 IUPAC Rules for Polyfunctional Compounds

In case of polyfunctional compounds, one of the functional groups is chosen as the principal functional group and the compound is named on that basis. The remaining functional group which are subordinate functional groups, are named as substituents using the appropriate prefixes.

The decreasing order of priority of some functional groups is

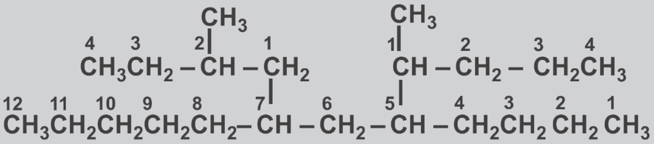
–COOH > – SO_3H > – COOR (ester) > – COCl (acylhalide) > – $CONH_2$ (amide) > – C ≡ N (nitriles) > – CH = O (aldehyde)> $>$ C = O (keto) > – OH (alcohol) > – NH_2 (amine) > $>$ C = C (alkene) > – C ≡ C – (alkyne)

The – R (alkyl group), Ph or C_6H_5 –(phenyl), halogens (F, Cl, Br, I) – NO_2 alkoxy (–OR). Etc., are always prefix substituents. Thus, a compound containing both an alcohol and a keto group is named hydroxyl alkanone since the keto group is preferred to the hydroxyl group.

MASTERJEE CONCEPTS

- When the names of two or more substituents are composed of Identical Words

  The priority of citation is given to the substituent which has the first cited point of difference with in the complex substituent. e.g.



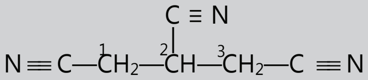
5(1-Methylbutyl) -7-(2-methylbutyl) dodecane

MASTERJEE CONCEPTS

- **Poly-Functional Compounds containing more than two like-functional groups**

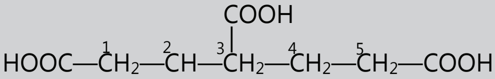
  According to the latest convention (1993 recommendation for IUPAC nomenclature), if an unbranded carbon chain is directly linked to more than two like-functional groups, then the organic compound is named as a derivative of the parent alkane which does not include the carbon atoms of the functional groups.

  E.g.

  i. 

  $$N\equiv C-\overset{1}{C}H_2-\overset{\overset{C\equiv N}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-C\equiv N$$

  Propane-1,2,3-tricarbonitrile
  (Not 3-cyanopentane-1, 5-dinitrilic)

  ii. 

  $$HOOC-\overset{1}{C}H_2-\overset{2}{C}H-\overset{\overset{COOH}{|}}{\overset{3}{C}H_2}-\overset{4}{C}H_2-\overset{5}{C}H_2-COOH$$

  Pentane-1,3,5-tricarboxylic acid
  (Not 4-carboxyheptane-1,7-dioic acid)

- **When both double and triple Bonds are present in the compound**

  In such cases, their locants are written immediately before their respective suffixes and the terminal 'e' from the suffix 'ene' is dropped while writing their complete names. It may be emphasized here that such unsaturated compounds are always named as derivatives of alkyne rather than alkene.

  E.g.

  i. $\overset{5}{C}H_3-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}\equiv\overset{1}{C}H$

  Pent+3-en(e)+1-yne
  = Pent-3-en-1-yne
  (Formerly 3-Penten-1-yne)

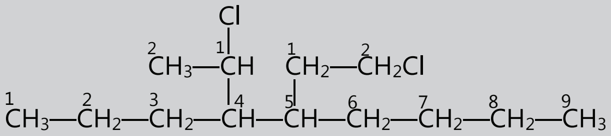
  ii. $H\overset{5}{C}\equiv\overset{4}{C}-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$

  Pent-1-en(e) + 4-yne
  = Pent 1-en-4-yne
  (Formerly 1-Penten-4-yne)

- **When two or more prefixes consist of identical Roman letters (words):**

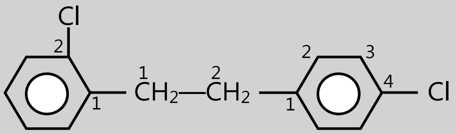
  The priority for citation is given to that group which contains the lowest locant at the first point of difference.

  e.g.

  i. 

  $$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{\overset{\overset{2}{C}H_3-\overset{\overset{Cl}{|}}{\overset{1}{C}H}}{|}}{\overset{4}{C}H}-\overset{\overset{\overset{1}{C}H_2-\overset{2}{C}H_2Cl}{|}}{\overset{5}{C}H}-\overset{6}{C}H_2-\overset{7}{C}H_2-\overset{8}{C}H_2-\overset{9}{C}H_3$$

  4-(1-chloroethyl)-5-(2-chloroethyl) nonane

  ii. 

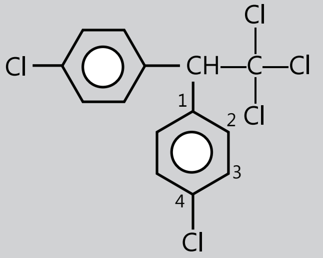
  1-(2-chlorophenyl)-2-(4-chlorophenyl) ethane

MASTERJEE CONCEPTS

- **When the Organic molecular contains more than one similar complex substituents**

  In such case, the numerical prefixes, such as di, tri, tetra etc,. are replaced by bis, tris, tetrakis, etc., respectively.

  E.g.



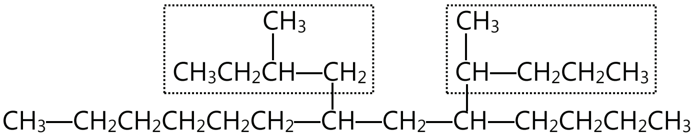
1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane

- **When all the three like groups are not directly linked to the unbranched carbon chain**

  The two like groups are included in the parent chain while the third group which forms the side chain is considered a substituent group.

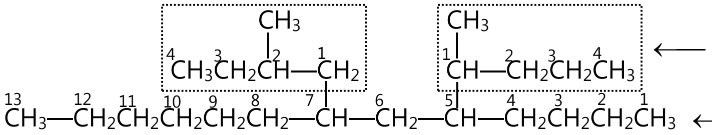
Vaibhav Krishnan (JEE 2010, AIR 44)

Illustration 1: Write the IUPAC name of the following compound: **(JEE ADVANCED)**



$$CH_3-CH_2CH_2CH_2CH_2CH_2-\overset{\boxed{\overset{\overset{CH_3}{|}}{CH_3CH_2CH-CH_2}}}{\overset{|}{CH}}-CH_2-\overset{\boxed{\overset{\overset{CH_3}{|}}{CH-CH_2CH_2CH_3}}}{\overset{|}{CH}}-CH_2CH_2CH_2CH_3$$

Sol: In case of a complex substituent and other substituents, the complex substituent begins with the first letter of its complete name. In case of two same complex substituents, one with the lowest positional number or locant is named first. This called priority citation.



$$\overset{13}{CH_3}-\overset{12}{C}H_2\overset{11}{C}H_2\overset{10}{C}H_2\overset{9}{C}H_2\overset{8}{C}H_2-\overset{\boxed{\overset{\overset{CH_3}{|}}{\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H-\overset{1}{C}H_2}}}{\overset{|}{\overset{7}{C}H}}-\overset{6}{C}H_2-\overset{\boxed{\overset{\overset{CH_3}{|}}{\overset{1}{C}H-\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_3}}}{\overset{|}{\overset{5}{C}H}}-\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_3$$

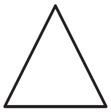
⟵ Lowest locant number

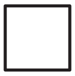
Lowest locant number
⟵ (Numbering should be from this end and not from the other end)

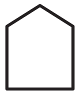
The IUPAC name of this compound is 5-(1-methyl butyl)-7-(2-methyl butyl) tridecane Priority of citation (5 < 7, 1 < 2); Locant 1 comes before 2.

4.3.7 IUPAC Rules for Alicyclic Compounds

1. IUPAC suffix: ane, ene, yne IUPAC prefix: cyclo

I. 

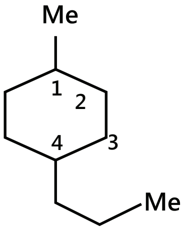
II. 

III. 

Two or more alkyl groups or other substituent's are present in the ring, their positions are indicated, e.g., 1,2,3 …., etc. The substituent which comes first in the alphabetical order is give n the lowest number, as per the lowest sum rule, e.g.

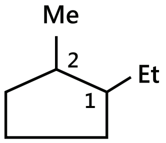
2. **(a)** If the ring contains equal or more number of C atoms than the alkyl groups attached to it, is named as an alkyl cycloalkane.

(I)



1- Methyl-4-propylcyloexane

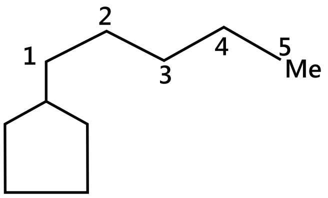
(II)



1- Ethyl-2-2methyl
cyclopentane

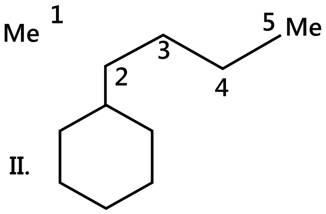
(b) If the ring contains lesser number of C atoms than the alkyl groups attached to it, is named cycloalkyl alkane, e.g.,

I.



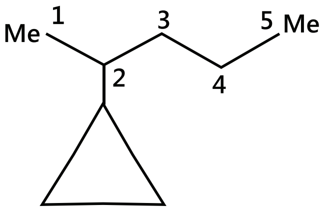
(Same number of C atoms in ring and side chain)
Pentyl cylopentane
(Alkly cylcloalkane)

II.



(Ring contains more C atoms than side chain)
2-Cyclopropyl pentane
(Cycloalkyl alkane)

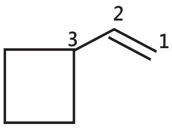
III.



(Ring contains less C atoms than side chain)
2-Pemtyl cyclohexane
(Alkly cylcloalkane)

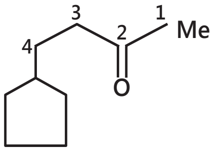
(c) If the side chain constrains a functional group or a multiple bond, then the alicyclic ring is considered substituent irrespective of the size of the ring, e.g.,

I.



3-Cyclobutyl
prop-1-ene

II.



4-Cyclopentyl but
-3-en-2-one

4.3.8 IUPAC Names of Bicyclo Compounds

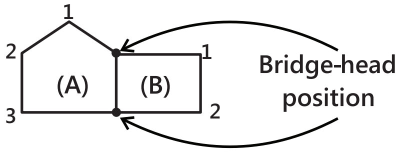
Compounds with two fused cycloalkane rings are called bicyclo compounds. They are cyclo alkanes having two or more atoms in common.

The prefix bicycle is followed by the name of the alkane whose number of C atoms is equal to number of C atoms in the two rings.

The bracketed numbers show the number of C atoms (except bridge-head position C atoms) in each bridge and they are cited in decreasing order.

E.g.

(a)

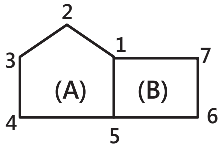


(i) Number of C atoms in ring A = 3

(ii) Number of C atoms in ring B = 2

(iii) Number of C atoms between bridge-head position = 0

(iv) Total C atoms = 3 (in ring A) + 2(in ring B) + 2 (Bridge-head position) = 7

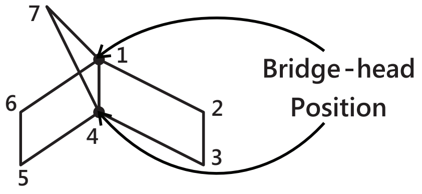


(Numbering starts from the bridgehead to the larger ring and then back to the smaller ring.)

4.3.9 IUPAC Names of Tricyclo Compounds

Compounds with three fused rings are called tricyclo compounds. The prefix tricyclo is followed by the name of alkane whose number of C atoms is equal to the number of C atoms in the rings.

E.g.



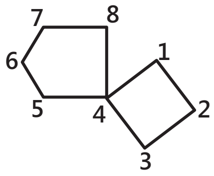
Tricyclo [2.2.1.0] heptane

The bracketed numbers show the number of C atoms (except the bridge-head position) in each bridge and they are cited in decreasing order.

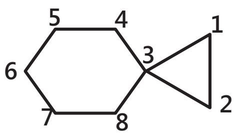
4.3.10 IUPAC Names of Spiranes

Spiranes are polycyclics that share only one C atom. In substituted spiranes, the numbering is started next to the fused C atom in the lower-member ring.

E.g.



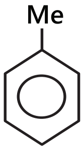
Spiro [3, 4] octane



Spiro [2.5] octane

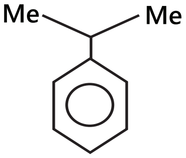
4.3.11 IUPAC Name of Aromatic Compounds

(a) No specific rules are required to name aromatic compounds. However, they are named substituted benzene, e.g.

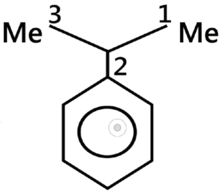


Methyl beznene
(Toluene)

(b) When larger and complex groups are attached to the benzene ring, the molecule is named as an alkane, alkene, etc., and benzene as side chain derivatives, abbreviated as, Ph –, or C_6H_5 – Ph – or ϕ. When the benzene ring contains some substituent's, it is abbreviated as Ar – .



Isoperopylbenznen or
2-Phenyl propane or



2-Phenyl propanoic
acid

4.4 Writing the Structural Formula from the Given IUPAC Name

The IUPAC name of an organic compound consists of the following parts:

a. Root word b. 1° suffix c. 2° suffix d. 1° prefix e. 2° prefix

(a) Root word indicates the longest chain thus, first locate the longest chain from the root word. Write the number of C atoms in a straight chain or in zigzag manner (for bond line structure) and then number them from any end.

(b) 1° suffix (-ane, -ene, or -yne) indicates the nature of the chain. Put the multiple bonds at proper places in the chain.

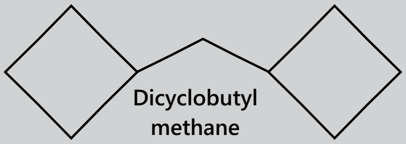
(c) 2° suffix indicates the principal functional group. Put it at a proper place in the chain.

(d) Prefixes are the substituents or secondary functional groups. Put them at a proper place with the help of locants.

(e) Add H atoms to satisfy valences of each C atom if stick formula is used. If the structure is written bond line, then there is no need of adding H atoms.

MASTERJEE CONCEPTS

- If more than one alicyclic ring is attached to a single chain, then the compound is named as cycloalkyl alkane (i.e., derivative of alkane) irrespective of the number of C atoms in the ring or the chain, e.g.,

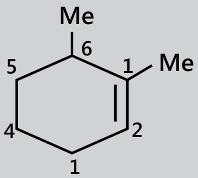


Dicyclobutyl
methane

MASTERJEE CONCEPTS

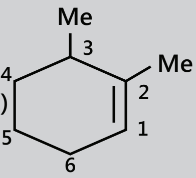
- If double or triple (multiple) bonds and some other substituents are present in the ring. The numbering is done in such a way that the multiple bond gets the lowest number, e.g.

(I)



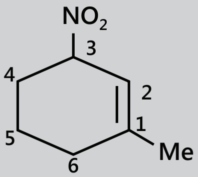
1,6-Dimethyl cyclohex-1-en
(correct)

(not)



2,3-Dimethyl cyclohex-1-ene
(incorrect)

(II)

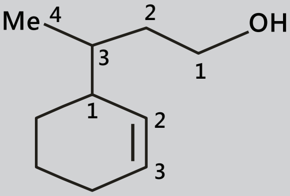


1-Methyl-3-nitro
cyclohex-1-ene

[Lowest number for Me substituent and also for double bond. although it violates lowest sum rule]

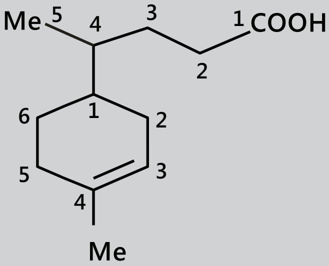
- If the ring contains a multiple bond and the side chain contains functional group, then the ring is considered the substituent and the compound is named a derivative of the side chain, e.g.,

I.



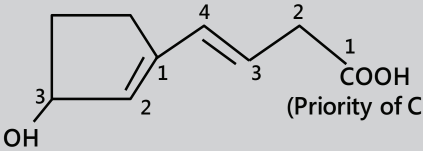
3–(Cyclohex-2-enyl)
butan-1-ol

I.



4-(4-Methyl cyclohex-3-enyl)
Pentanoic acid

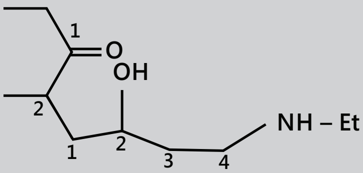
- If the ring and side chain both contain functional groups, then
  - **(i)** If the side chain constrains higher priority of of functional group then the compound is named the derivative of the side chain



(Priority of COOH>OH)

4-(3-Hydroxy cyclopent-1-enyl) but-3-en-1-oic acid

  - **(ii)** If the ring contains higher priority of functional group, then the compound is named the derivative of the alicyclic ring, e.g.,

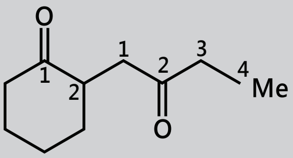


2-(4-Amino ethyl-2-hydroxy butlyl)

MASTERJEE CONCEPTS

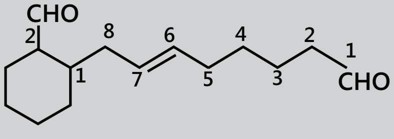
- If both the side chain and the alicyclic ring contain the same functional group, then it is of two types.

  (i) If the number of C atoms of the alicyclic ring is equal or greater than that of the side chain, then it is named the derivative of the alicyclic ring. e.g.,



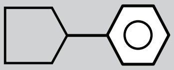
2-(2-Oxobutyl)cyclohexan-1-one

  (ii) If the number of C atoms of the side chain is greater than that of the alicyclic ring, then it is named the derivative of the side chain. e.g.,

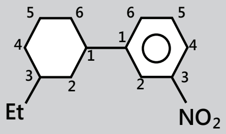


8-(2-Formyl cyclohexyl) oct-6-en-1-al

- If an alicyclic ring is directly attached to the benzene ring, it is named the derivative of benzene. e.g.,



Cyclopentyl benzene

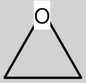


1-(3-Ethyl cyclohexyl)-
3-nitro benzene

- Naming of cyclic ethers

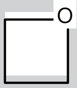
  The IUPAC names for cyclic ether $(CH_2)_nO$, where n = 2,3,4,5 and 6.

a.



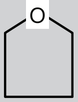
Oxirane

b.



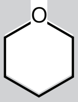
Oxetane

c.



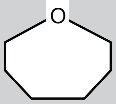
Oxolane

d.



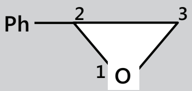
Oxane

e.



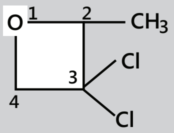
Oxepane

f.



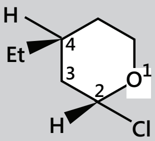
Phenyloxirane

g.



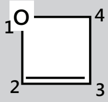
3,3-Dichloro-2-methyl
oxetane

h.



trans-2-chloro-4-ethyloxane

i.



Oxetane

- Mono-substituted benzene compounds :

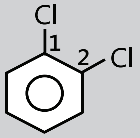
  According to IUPAC nomenclature, the substituent is placed as prefix and benzene as suffix.

  However, common names (written in bracket) of many substituted compound are commonly used, e.g- Toluene, Phenol etc.

MASTERJEE CONCEPTS

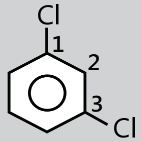
- If the benzene ring is disubstituted, the substituents are located at the lowest number. In the trivial system of nomenclature, the terms ortho (o), meta (m) and para (p) are used as prefixes to indicate the relative positions 1,2 - ; 1,3 -, and 1,4- respectively, e.g.

I.



1,2-Dichloro benzene
(o-Dichloro benzene)

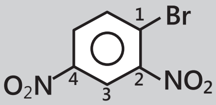
II.



1,3-Dichloro benzene
(m-Dichloro benzene)

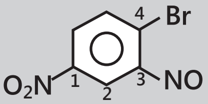
- If the benzene ring is tri- or higher substituted, then the compounds are named by identifying the substituent position on the ring by following the lowest locant sum rule. The substituent of the base compound is given the number 1 and then the direction of the numbering is selected such that the next substituent gets the lowest number. The substituent's are written in the name in alphabetical order, e.g.,

I.



(1-Bromo-2,4-dinitro benzne)
(not 4- Bromo- 1,3 -dinitro benzne)

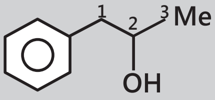
not



(Lowest sum = 1 + 2 + 4 =7)
(Highest sum = 4 + 1 + 3 = 8)

- When a benzene ring is attached to an alkane with a functional group, it is considered as a substituent instead of a parent. The name for benzene as substituent is phenyl (C_6H_5–) also abbreviated as Ph, e.g.,

I.

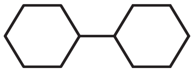


1-Phenyl propan-2-ol

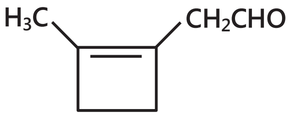
Nikhil Khandelwal (JEE 2010, AIR 443)

Illustration 2: Give the IUPAC name of the following compounds: **(JEE MAIN)**

I.

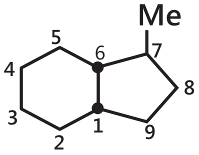


II.

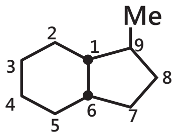


Sol: i. Cyclohexylcyclohexane ii. 2-(2-Methylcylobut-1-enyl) ethanal

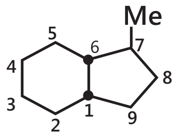
Illustration 3: Write the IUPAC Name for **(JEE MAIN)**



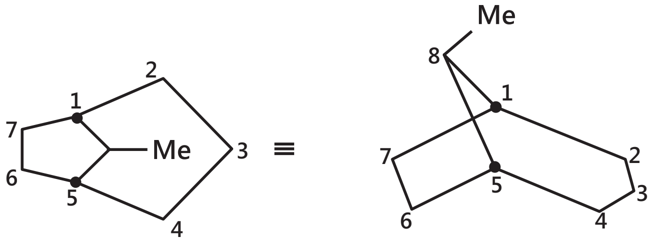
Sol:



Wrong numbering
since the position
of the substituent is at C-9



Correct numbering
since the position
of the substituent is at
the lowest number ,i.e .,
at C-7

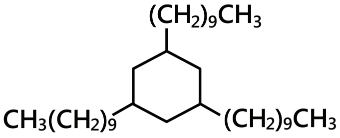


IUPAC name: 7-Methyl bicycle [4.3.0] nonane

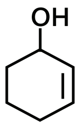
Numbering from the longest bridge-head (i.e., from the larger ring) to the next longest bridge-head (i.e., to the smaller ring.)

Illustration 4: Write the IUPAC name: **(JEE ADVANCED)**

I.



II.



Sol: (i) 1,3,5-Tris(decyl)cyclohexane ; (ii) Cyclohex-2-en-1-ol

5. GENERAL ORGANIC CHEMISTRY

5.1 Basics of GOC

5.1.1 Theory of Development of Quantum Mechanics

The Quantum theory was developed by Erwin Schrödinger. He worked on a mathematical model for the motion of electrons based on wave functions. This whole model was based on the fact that electron have a dual nature i.e., they show properties of both particles as well as waves. This theory led to the idea of atomic orbitals.

Atomic orbital: Due to the dual nature of electrons, the Schrodinger wave equation came up. However, the wave equation fails to tell us exactly where the electron is at any particular moment, or the speed with which it is moving. All it tells us is the probability of finding the electron at any particular place. The region in space where the electron is most likely to be, is known as an orbital. These orbitals are of different kinds, and are hence dispersed about the nucleus in specific ways. The particular shape of orbital that an electron occupies, depends: upon the energy of the electron.

By knowing the shapes of these orbitals and there dispositions with respect to each other, we can be more precise in conveniently explaining the arrangement in the space of the atoms forming the nucleus and as a result, determine its physical and chemical behaviors.

5.1.2 Covalent Bonding

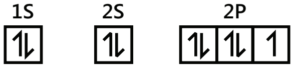
Covalent bonds, make up compounds of carbon. This bond is of chief importance in the study of organic chemistry.

Overlap Theory: According to this theory, for a covalent bond to the formed, the atoms must be located sufficiently close together so that an orbital of one atom overlaps with the other. Each orbital must contain single (unpaired) electrons. When this happens, single bond orbitals are occupied by both electrons. The two electrons that occupy the orbital must have opposite spins i.e. it must be paired.

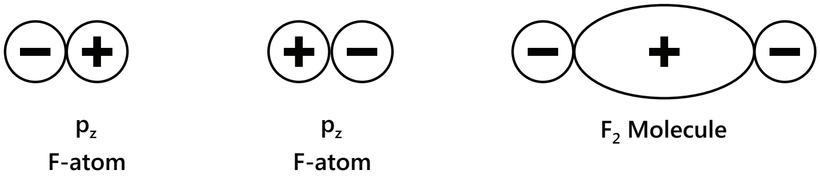
This arrangement contains less energy and hence is more stable.

E.g. F atom

Valence shell contains 7 electrons



The two F-atom some together and overlap through their p-orbital

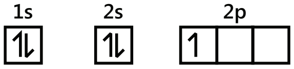


$BeCl_2$ molecule

$BeCl_2$: The electronic configuration of Be atom can be represented as

Be atom in order to take part in covalent bonding must have single electron orbitals.

Electronic Configuration of Be atoms just about to get bonded to chlorine atoms.

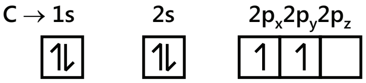


This leads to the idea that Be forms two different kinds of overlaps with every chlorine atom i.e. one Be-Cl bond s-p overlap and other Be-Cl bond p-p overlap which would result in two different types of Be-Cl bonds having different bond energies and bond lengths.

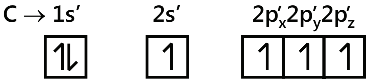
But experiments have shown that both the Be-Cl bonds in $BeCl_2$ are identical. So the theory of overlap is not applicable everywhere

Even if you consider the molecule of CH_4 . Here, the central atom is carbon. The electronic configuration of carbon is

$$C \rightarrow 1s^2 \quad 2s^2 \quad 2p_x^1 \ 2p_y^1$$



Just before combining with the 4H–atoms the electronic configuration of carbon becomes

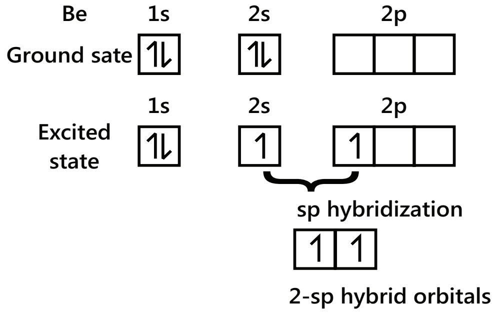


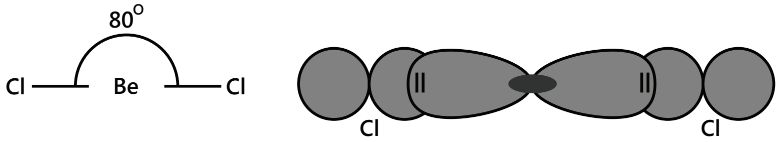
Here again we will find that according to the theory of overlap, there are 3 p-s overlaps and one s-s overlap meaning that the bonds are not identical, but experiments have shown beyond doubt that the 4 C–H bonds are all equivalent.

Hence we apply the concept of hybridization.

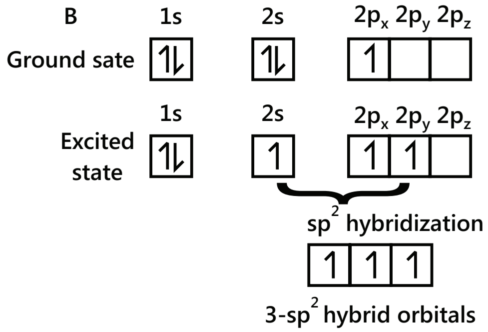
Hybridization: It is the process of mixing up of non-degenerate atomic orbitals of the atom to form degenerate orbitals called hybrid orbitals each having the greatest degree of directionality.

Hybrid orbitals: sp

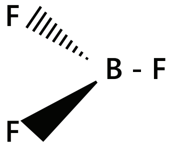




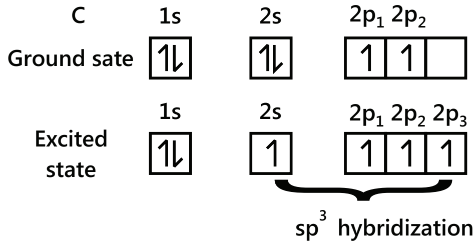
Hybrid orbitals: Sp²



BF_3 is trigonal planar



Hybrid Orbital –sp³



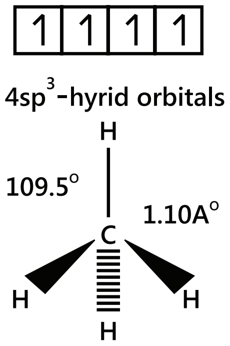
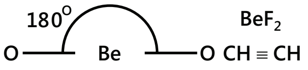
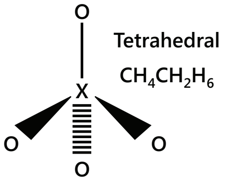
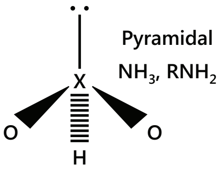
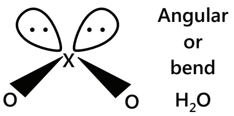


Table 8.2: Shape and geometry of the compound depending upon the hybridization

S. No.	Hybridization	Number of lone pair	Geometry	Shape and example
1.	sp BeF_2	0	Linear	
2.	sp^3	0	Trigonal Planar	Angular or bond BF_3, $CH_2{=}CH_2$
3.	sp^3	0	Tetrahedral	
4.	sp^3	1	Tetrahedral	
5.	sp^3	2	Tetrahedral	

5.1.3 Polarity in Molecule

Each time a covalent bonds is formed between the same atoms, then the electrons are shared equally between the two atoms forming the bond e.g. F_2, H_2, etc. However, when the covalent bond is formed between two dissimilar atoms then there is an unequal sharing of electrons resulting in the electron of the covalent bond being drawn closer to the more electronegative atom, resulting in a bond dipole. e.g. HCl, HBr etc.

The polarized covalent bond due to the difference of electro negativity may be shown as

$\overset{\delta^+}{H}-\overset{\delta-}{F} \quad \underset{H-F}{+\!\!\!\longrightarrow} \quad \overset{\delta^+}{H}-\overset{\delta-}{Cl} \quad \underset{H-Cl}{+\!\!\!\longrightarrow}$

The polarity in a bond arises from the difference in electronegativity of the atoms participating in the bond formation.

The greater the difference in the electronegativity between the atoms bonded, the greater will be the polarity of the bond. Electronegativity order of some elements is below:

F > O > Cl ~ N > Br > C ~ S > I > P ~ H > Si > Al > Mg > Li > Na > K

4.0 3.5 3.0 3.0 2.8 2.5 2.5 2.4 2.1 2.1 1.8 1.5 1.2 1.0 0.9 0.8

Electronegativity of carbon and hydrogen are close enough, hence C-H bonds do not have much polarity.

H – O
H – F
H – Cl
H – N

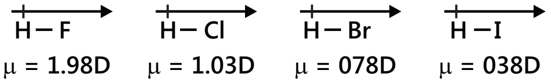
Even C – X, C – O and C – N bonds are also polar

Dipole moment = charge × distance

Bond polarity contributes greatly to the physical and chemical properties of molecules.

Dipole Moments of Covalent Molecules

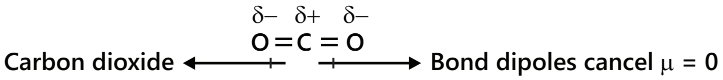
(a) For a distant molecule with different atoms, the level dipole is also the dipole moment.

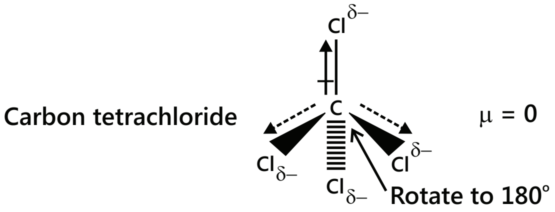


(b) For diatomic molecules with the same atoms there is no bond dipole e.g., H—H and I — I

(c) The overall dipole moment of a molecule containing more than two atoms is the vector sum of the individual bond dipole moments.

A molecule may contain polar bonds but has no overall dipole moment if the shape of the molecule is such that the individual bond moments cancel out.





5.1.4 Molecular Interactions

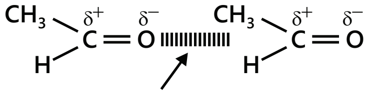
It is found that covalent compounds exist as solids, liquids and gases. So what forces hold neutral molecules together?

Like interionic forces, these forces seem to be, electrostatic in nature, involving the attraction of +ve charge for negative charge (a) Dipole-Dipole interactions (b) Vander waal's forces.

Dipole-Dipole Interactions

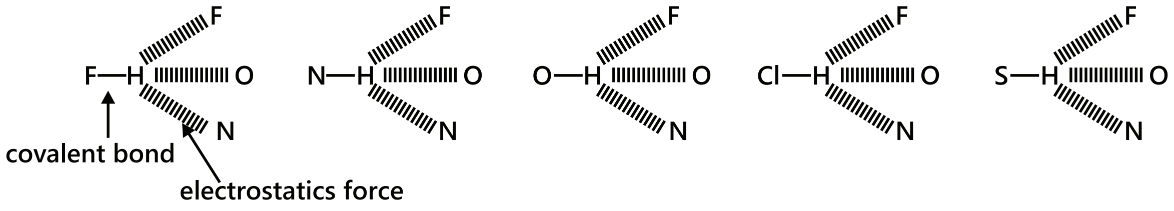
(a) This exists mainly in polar molecules. Here there is attraction of the positive end of one polar molecule for the negative end of another polar molecule.

In acetaldehyde the relatively –ve



As a result of dipole-dipole interactions the molecules are generally near to each other more strongly than all the non-polar molecules of comparable molecular mass.

(b) H–bonding [king of dipole-dipole interaction]. Here the H-atom seems to act as a bridge between two electronegative atoms, holding one by a covalent bond and the other by purely an electrostatic force.



Also the strength of hydrogen bonding order is

F||||||||||H > O ||||||||||H >>>> N||||||||||H.

5.1.5 Non-Polar Forces

It has been found that even non- polar molecules solidify and hence there must be some forces which exist in order for this to happen. Such attractive forces are called Van der Waal forces. Quantum mechanics accounts for the existence of these forces, as it states that the average distribution of charge about e.g., CCl_4 molecule is symmetrical, so there is no net dipole moment. However, electrons move about, so at any instant the distributions become distorted leading to a small dipole. This momentary dipole induces another small dipole moment in another molecule and so on and so forth to the neighbouring molecules.

Though the momentary dipole and induced dipoles are constantly changing, the net result is the attraction between the two molecules.

These Van der Waals forces have a very short range, they act only between the portions of different molecules that are in close contact in between the surfaces of molecules.

(a) Van der Waals forces are directly proportional to molecular mass.

(b) Van der Waals forces are directly proportional to surface area.

The molecular forces of attraction are very useful in comparing the rates of evaporation, vapour pressures, boiling points, melting points, viscosity, etc.

MASTERJEE CONCEPTS

(a) Hybridization: Some special case of hybridization are –

- **(i)** Carbanion is sp^3 hybridized.
- **(ii)** Carbocation is sp^2 hybridized.
- **(iii)** CH_3 Radical is sp^2 hybridized while CF_3 is sp^3 hybridized. Electronegativity of fluorine is responsible for the latter case.
- **(iv)** Triplet carbine is sp hybridized while singlet carbene is sp^2 hybridized.

(a) Polarity:

- **(i)** Dipole moment = q x d
- **(ii)** Polarity determines many physical factors like intermolecular interaction, boiling and melting points, solubility.
- **(iii)** Greater the polarity, greater is the intermolecular interaction.
- **(iv)** Greater the polarity, higher are the boiling and melting points.
- **(v)** Polar molecules are soluble in polar solvent while non-polar molecules are soluble in non-polar solvent.

(a) Molecular interactions:

- **(i)** Dipole-dipole interactions – attraction between two polar molecules.
- **(ii)** Van der Waals forces – increases with increase in molecular weights.
- **(iii)** Hydrogen bonding – occurs with hydrogen attached with fluorine, nitrogen and oxygen only.
- **(iv)** Magnitude of molecular interaction – H bonding > Dipole – dipole interactions > Van der waals forces.

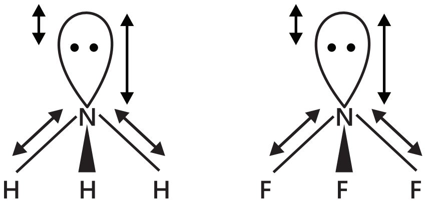
Saurabh Gupta (JEE 2010, AIR 443)

Illustration 5: Explain why μ of NH_3 > NF_3? **(JEE MAIN)**

Sol: Explain this question by taking into account the direction of contribution of N-H and N-F bond and the lone pair electrons.

In NH_3, the net moment of (N – H) bonds and the contribution from the LP eletrons (lone pair electrons) are in the same direction and are additive. The net moment of the (N – F) bonds opposes the dipole effect of the LP electrons in the NH_3 and the resultant is less μ. So μ of NH_3 > NF_3.

i.



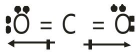
(sp^3 H.O.) (a) (sp^3 H.O.) (b)

Illustration 6: Explain why μ of CH_3Cl > CH_3F > CH_3Br > CH_3I **(JEE MAIN)**

Sol: The electro-negativities of halogens decrease from F to I so μ of HF > HCl > HBr > HI, but μ of CH_3F is smaller than CH_3Cl due to shorter (C – F) bond distance, although EN of F is greater than that of Cl.

Illustration 7: Explain why CO_2 has dipole moment zero whereas for SO_2 its non-zero? **(JEE ADVANCED)**

Sol: In CO_2, C is sp hybridized and linear. The dipole moments of (C – O) are equal and in opposite directions and cancel each other. Hence, μ is zero.



In SO_2 , S is sp^2 hybridized having one LP on S atom. The (O – S – O) bond angle is nearly 120º; (S – O) bond moment does not cancel and shows a net resultant μ.

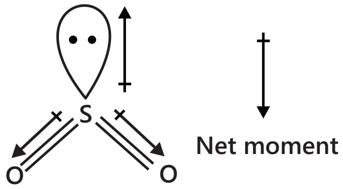


Illustration 8: Explain why the lone pairs of electrons has no effect on the μ of PH_3.The bond angle in PH_3 is 92º **(JEE ADVANCED)**

Sol: The 92º bond angle suggests that P uses three p atomic orbitals in forming bonds with H, with one LP $\bar{e}$ in 3s atomic orbital, i.e., P in PH_3 is sp^2 hybridized (unlike NH_3, in which N is sp^3 hybridized)

Therefore, due to the presence of LP $\vec{e}$ s in 3s atomic orbital of P, which is spherical symmetrical, the polarity of the molecule is not affected enough to affect the polarity of the molecule, the $\vec{e}$'s must be in a directional orbital. Moreover, EN of P and H are nearly same, so PH_3 molecule is almost nonpolar,

Illustration 9: (a) Describe heterolytic (polar) bond cleavage of:

i. AgI, ii. $\overset{\oplus}{N}\overset{\ominus}{B}F_3$ iii. $[Cu(OH_2)_4]^{\ominus}$

(b) Name the reverse of heterolytic cleavage.

(c) Describe hemolytic bond cleavage of $CH_3 – CO – CO – CH_3$.

(d) Compare the relative energies of singlet and triplet carbenes.

(e) Of X_2C : (singlet) and X_2Cl :(triplet), which is stable ?

(f) Of F_3C :, Cl_2C:, Br_2C :, I_2C : (singlet), which is more stable ?

(g) Compare and explain the difference in the IE and EA of $^+CH_3$. **(JEE ADVANCED)**

Sol: (a) (i) $Ag - I \rightarrow Ag^+ + I^-$ (More EN atoms acquire negative charge.)

(ii) $H_3\overset{\oplus}{N}\overset{\ominus}{B}F_3 \longrightarrow H_3N : BF_3$ (Bonded atoms with formal charges give uncharged products.)

(iii) $[Cu(OH_2)_4]^{2+} \longrightarrow Cu^{2+} + 4H_2O$

(b) Coordinates covalent bonding.

(c) $H_3C - CO - CO - CH_3 \rightarrow \underset{(\text{A radical})}{2CH_3CO^{\bullet}}$

(d) Triplet carbene has lower energy because with two e^-'s in different orbitals there is less electrostatic repulsion than when both are in the same orbital.

(e) X_2C: Singlet is more stable, because of the lone pair of electrons on X which can overlap laterally with the empty orbital.

(f) F_3C is the most stable singlet, since F and C are in the same period of the periodic table and are about the same size permitting a more efficient overlap (2p(F) –2p(C) ore $p\pi - p\pi$ bond). Moreover, (F – C) bond length is the shortest bond length and provides a more extensive lateral overlap.

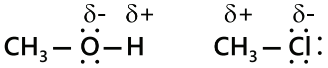
(g) The EA is less than IE. When – CH_3 gains an e^- to become carbanion, C acquires a stable octet of e^-s. When it loses an e^-, it becomes unstable with only 6 e^- s.

6. ELECTRONIC EFFECTS

6.1 Inductive Effect

The Inductive effect is an electronic effect due to the polarization of **σ bonds** within a molecule or ion.

- This is typically due to an electronegativity difference between the atoms at either end of the bond.
- The more electronegative atom pulls the electrons in the bond towards itself creating some bond polarity for example the O-H and C-Cl bonds in the following examples:



$CH_3 - \overset{\delta-}{\ddot{O}} - \overset{\delta+}{H}$ $\overset{\delta+}{CH_3} - \overset{\delta-}{\ddot{Cl}}:$

The inductive effect is divided into two types depending on their strength of electron withdrawing or electron releasing nature with respect to hydrogen.

(a) Negative inductive effect (-I): The electron withdrawing nature of groups or atoms is called the negative inductive effect. It is indicated by -I. Following are the examples of groups in the decreasing order of their -I effect:

$NH_3+ > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H$

(b) Positive inductive effect (+I): It refers to the electron releasing nature of the groups or atoms and is denoted by +I. Following are the examples of groups in the decreasing order of their +I effect.

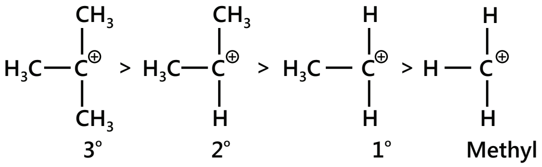
$C(CH_3)_3 > CH(CH_3)_2 > CH_2CH_3 > CH_3 > H$

Why do alkyl groups show a positive inductive effect?

Though the C-H bond is practically considered as non-polar, there is partial positive charge on hydrogen atom and partial negative charge on carbon atom. Therefore each hydrogen atom acts as electron donating group. This cumulative donation turns the alkyl moiety into an electron donating group.

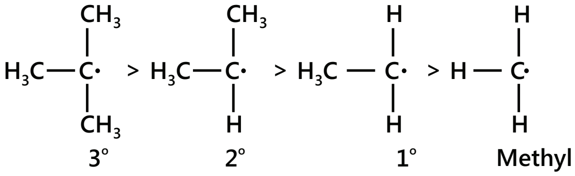
6.1.1 Applications of Inductive Effect

(a) **Stability of Carbonium Ions:** The stability of carbonium ions increases with the increase in the number of alkyl groups due to their +I effect. The alkyl groups release electrons to carbon, bearing a positive charge and thus stabilizes the ion. The order of stability of carbonium ions is:



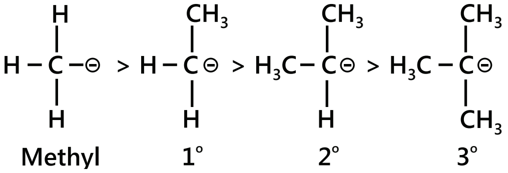
$$H_3C-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} > H_3C-\underset{H}{\overset{CH_3}{C^{\oplus}}} > H_3C-\underset{H}{\overset{H}{C^{\oplus}}} > H-\underset{H}{\overset{H}{C^{\oplus}}}$$

(b) **Stability of Free Radicals:** In the same way the stability of free radicals increases with increase in the number of alkyl groups. Thus the stability of different free radicals is:



$$H_3C-\underset{CH_3}{\overset{CH_3}{C\cdot}} > H_3C-\underset{H}{\overset{CH_3}{C\cdot}} > H_3C-\underset{H}{\overset{H}{C\cdot}} > H-\underset{H}{\overset{H}{C\cdot}}$$

(c) **Stability of Carbanions:** However the stability of carbanions decreases with increase in the number of alkyl groups since the electron donating alkyl groups destabilize the carbanions by increasing the electron density. Thus the order of stability of carbanions is:



$$H-\underset{H}{\overset{H}{C}}-\ominus > H-\underset{H}{\overset{CH_3}{C}}\ominus > H_3C-\underset{H}{\overset{CH_3}{C}}\ominus > H_3C-\underset{CH_3}{\overset{CH_3}{C}}\ominus$$

(d) **Acidic Strength of Carboxylic Acids and Phenols:** The electron withdrawing groups (-I) decrease the negative charge on the carboxylate ion by stabilizing it. Hence the acidic strength increases when -I groups are present.

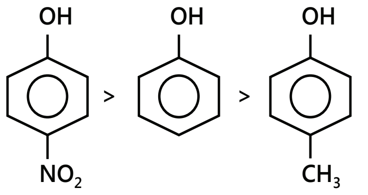
However the +I groups decrease the acidic strength.

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

$CH_3COOH < CH_2FCOOH < CHF_2COOH < CF_3COOH$

(ii) Formic acid is a stronger acid than acetic acid since the $-CH_3$ group destabilizes the carboxylate ion. On the same lines, the acidic strength of phenols increases when -I groups are present on the ring.

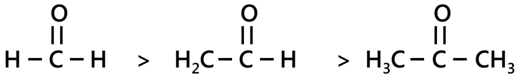
E.g. p-nitrophenol is a stronger acid than phenol since the $-NO_2$ group is a -I group and withdraws electron density. Whereas the para-cresol is a weaker acid than phenol since the $-CH_3$ group shows a positive (+I) inductive effect. Therefore the decreasing order of acidic strength is:



p-nitrophenol phenol p-cresol

(e) **Basic strength of amines:** The electron donating groups like alkyl groups increase the basic strength of amines whereas the electron with drawing groups like aryl groups decrease the basic nature. Therefore alkyl amines are stronger Lewis bases than ammonia, whereas aryl amines are weaker than ammonia. Thus the order of basic strength of alkyl and aryl amines with respect to ammonia is: $CH_3NH_2 > NH_3 > C_6H_5NH_2$

(f) **Reactivity of Carbonyl Compounds:** The +I groups increase the electron density at the carbonyl carbon. Hence their reactivity towards nucleophiles decreases. Thus, formaldehyde is more reactive than acetaldehyde and acetone towards nucleophilic addition reactions. Thus the order of reactivity follows:

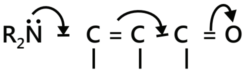


$$H-\overset{\overset{O}{||}}{C}-H \;>\; H_2C-\overset{\overset{O}{||}}{C}-H \;>\; H_3C-\overset{\overset{O}{||}}{C}-CH_3$$

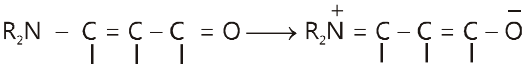
Formaldehyde Acetaldehyde Acetone

6.2 Electromeric Effect

A molecular polarizing effect occurring by an intermolecular electron displacement (sometimes called the 'conjugative mechanism' and, previously, the 'tautomeric mechanism') characterized by the substitution of one electron pair for another within the same atomic octet of electrons. It can be indicated by curved arrows symbolizing the displacement of electron pairs, as in:



$$R_2\ddot{N} - \underset{|}{C} = \underset{|}{C} - \underset{|}{C} = O$$



$$R_2N - \underset{|}{C} = \underset{|}{C} - \underset{|}{C} = O \longrightarrow R_2\overset{+}{N} = \underset{|}{C} - \underset{|}{C} = \underset{|}{C} - \overset{-}{O}$$

which represents the hypothetical electron shift -

6.3 Mesomeric Effect

The Mesomeric effect (on reaction rates, ionization equilibria, etc.) is attributed to a substituent due to the overlap of its p- or π-orbitals with the p- or π-orbitals of the rest of the molecular entity. Delocalization is thereby introduced or extended, and electronic charge may flow to or from the substituent. The effect is symbolized by M. Strictly understood, the mesomeric effect operates in the ground electronic state of the molecule. When the molecule undergoes electronic excitation or its energy is increased on the way to the transition state of a chemical reaction, the mesomeric effect may be enhanced by the electromeric effect, but this term is not much used, and the mesmeric and electromeric effects tend to be assumed to be taken in the term resonance effect of a substituent. Mesomeric effect is divided into 2 parts on basis of withdrawal or donation of electrons.

Negative resonance or mesomeric effect (-M or -R): It is shown by substituents or groups that withdraw electrons by the delocalization mechanism from rest of the molecule and are denoted by -M or -R. The electron density on rest of the molecular entity is decreased due to this effect.

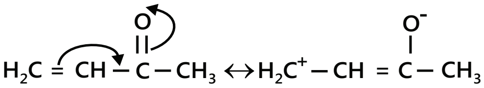
E.g. $-NO_2$, Carbonyl group (C=O), $-C\equiv N$, -COOH, $-SO_3H$ etc.

Positive resonance or mesomeric effect (+M or +R): The groups show a positive mesomeric effect when they release electrons to the rest of the molecule by delocalization. These groups are denoted by +M or +R. Due to this effect, the electron density on rest of the molecular entity is increased.

E.g. -OH, -OR, -SH, -SR, $-NH_2$, $-NR_2$ etc.

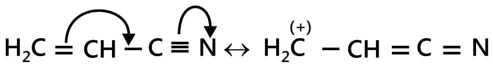
Applications of Resonance Effect (Or) Mesomeric Effect

(a) The negative resonance effect (-R or -M) of the carbonyl group is shown below. It withdraws electrons by delocalization of π electrons and reduces the electron density particularly on 3rd carbon.



$$H_2C = CH - \overset{\overset{O}{||}}{C} - CH_3 \leftrightarrow H_2C^+ - CH = \overset{\overset{O^-}{|}}{C} - CH_3$$

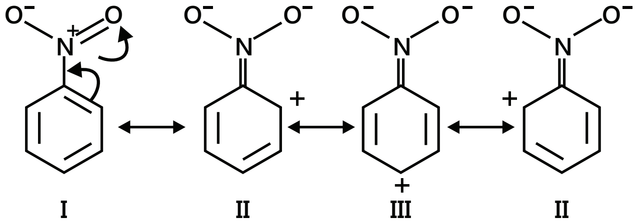
(b) The negative mesomeric effect (-R or -M) shown by the cyanide group in acrylonitrile is illustrated below. The electron density on the third carbon decreases due to delocalization of π electrons towards cyanide group.



$$H_2C = CH - C \equiv N \leftrightarrow H_2\overset{(+)}{C} - CH = C = N$$

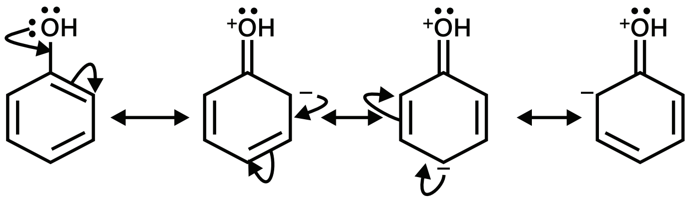
Because of negative resonance effect, the above compounds act as good acceptors.

(c) The nitro group, -NO$_2$, in nitrobenzene shows -M effect due to the delocalization of conjugated π electrons as shown below. Note that the electron density on the benzene ring is decreased particularly on ortho and para positions.



This is the reason for why nitro group deactivates the benzene ring towards the electrophilic substitution reaction.

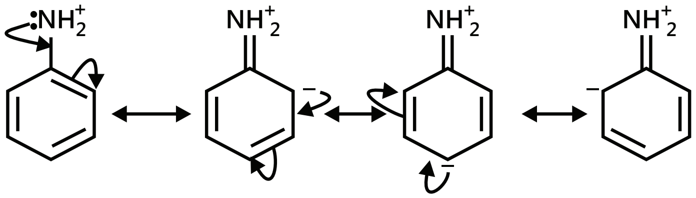
(d) In phenol, the -OH group shows +M effect due to the delocalization of a lone pair on the oxygen atom towards the ring.



Thus the electron density on the benzene ring is increased particularly on ortho and para positions.

Hence phenol is more reactive towards electrophilic substitution reactions. The substitution is favoured more at ortho and para positions.

(e) The -NH$_2$ group in aniline also exhibits +R effect. It releases electrons towards the benzene ring through delocalization. As a result, the electron density on the benzene ring increases particularly at the ortho and para positions. Thus, aniline activates the ring towards electrophilic substitution.

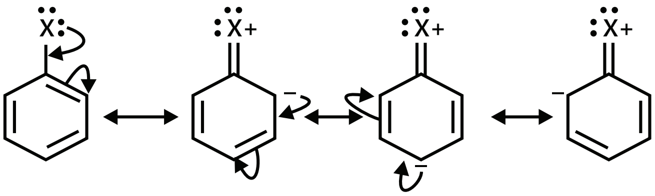


It is also worth mentioning that the electron density on nitrogen in aniline decreases due to the delocalization which is the reason for its less basic strength when compared to ammonia and alkyl amines.

Inductive Effect Vs Resonance Effect

In most cases, the resonance effect is stronger and outweighs inductive effect.

For example, the -OH and -NH$_2$ groups withdraw electrons by the inductive effect (-I). However they also release electrons by delocalization of lone pairs (+R effect). Since the resonance effect is stronger than the inductive effect the net result is of the electron releasing to rest of the molecule. This is clearly observed in phenol and aniline, which are more reactive than benzene towards electrophilic substitution reactions.

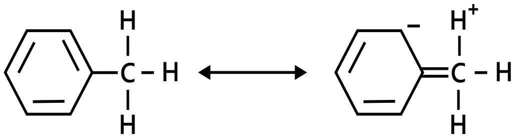


Whereas the inductive effect is stronger than the resonance effect in case of halogen atoms. These are electronegative and hence exhibit -I effect. However, at the same time they also release electrons by the delocalization (+R effect) of the lone pair. This is evident in the case of the reactivity of halobenzenes, which are less reactive than benzene towards electrophilic substitution due to -I effect of halogens.

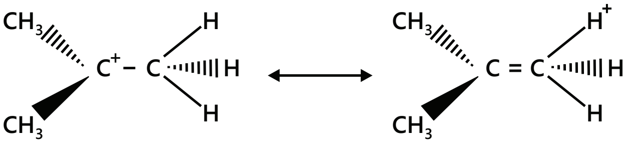
However, it is interesting to note that the substitution is directed at ortho and para positions rather than meta position. It can be ascribed to the fact that the electron density is increased at ortho and para positions due to +R effect of halogens as shown below.

6.4 Hyper Conjugation

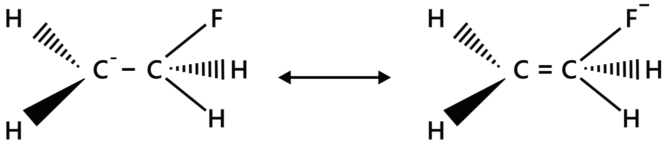
The displacement of σ-electrons towards the multiple bond occurs when there are hydrogens on the α-carbon (which is adjacent to the multiple bond). This results in the polarization of the multiple bond. In the formalism that separates bonds into σ and π types, hyper conjugation is the interaction of σ-bonds (e.g. C–H, C–C, etc.) with a π network. This conjugation between electrons of single (H-C) bond with multiple bonds is called hyperconjugation. This occurs when the sigma (s) electrons of the H-C bond that is attached to an unsaturated system, such as double bond or a benzene ring, enter into conjugation with the unsaturated system. This interaction is customarily illustrated by contributing structures, e.g. for toluene (below), sometimes said to be an example of 'heterovalent' or 'sacrificial hyper conjugation', so named because the contributing structure contains one two-electron bond less than the normal Lewis formula for toluene:



At present, there is no evidence for sacrificial hyper conjugation in neutral hydrocarbons. The concept of hyper conjugation is also applied to carbonium ions and radicals, where the interaction is now between σ-bonds and an unfilled or partially filled π- or p-orbital. A contributing structure illustrating this for the *tert*-butylcation is:



This latter example is sometimes called an example of 'isovalent hyper-conjugation' (the contributing structure containing the same number of two-electron bonds as the normal Lewis formula). Both structures shown on the right hand side are also examples of 'double bond-no-bond resonance'. The interaction between filled π- or p-orbitals and adjacent antibonding σ* orbitals is referred to as 'negative hyperconjugation', as for example in the fluoroethyl anion:

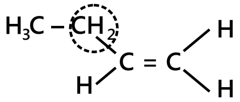


Consequences and Applications of Hyperconjugation

(a) Stability of alkenes: A general rule is that, the stability of alkenes increases with increase in the number of alkyl groups (containing hydrogens) on the double bond. It is due to the increase in the number of contributing no bond resonance structures.

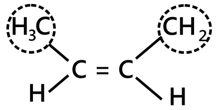
For example, 2-butene is more stable than 1-butene. This is because in 2-butene, there are six hydrogens involved in hyperconjugation whereas there are only two hydrogens involved in case of 1-butene. Hence the contributing structures in 2-butene are more and is more stable than 1-butene.

2 hydrogens



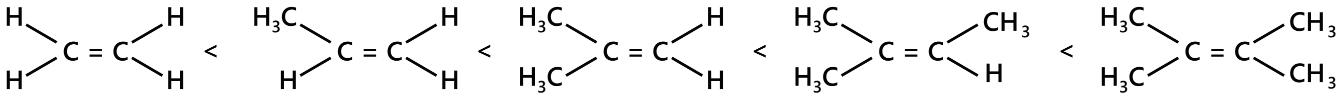
1-butene

6 hydrogens

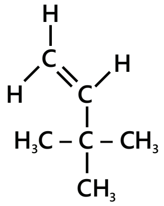


2-butene

The increasing order of stability of alkenes with increases in the number of methyl groups on the double bond is depicted below.



This order is supported by the heat of hydrogenation data of these alkenes. The values of heats of hydrogenation decrease with the increase in the stability of alkenes. Also the heats of formation of more substituted alkenes are higher than expected. However it is important to note that the alkyl groups attached to the double bond must contain at least one hydrogen atom for hyperconjugation. For example, in case of the following alkene containing a tert-butyl group on doubly bonded carbon, the hyperconjugation is not possible.

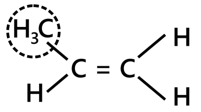


No H atoms on a carbon
Hence no hyperconjugation.

It is also important to note that the effect of hyperconjugation is stronger than the inductive effect.

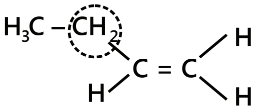
For example, the positive inductive effect of ethyl group is stronger than that of methyl group. Hence, based on inductive effect, 1-butene is expected to be more stable than propene. However propene is more stable than 1-butene. This is because there are three hydrogens on α-methyl group involved in hyperconjugation. Whereas, in 1-butene there are only two hydrogen atoms on -CH_2 group that can take part in hyperconjugation.

3 hydrogens



propene

2 hydrogens

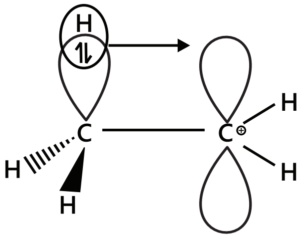


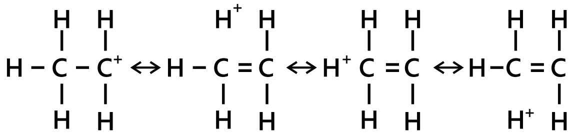
1-butene

(b) Stability of carbocations (carbonium ions): The ethyl carbocation, CH_3-CH_2+ is more stable than the methyl carbocation, CH_3+.

This is because, the σ-electrons of the α-C-H bond in ethyl group are delocalized into the empty p-orbital of the positive carbon center and thus by giving rise to the 'no bond resonance structures' as shown below.

Whereas hyperconjugation is not possible in methyl carbocation and hence is less stable.

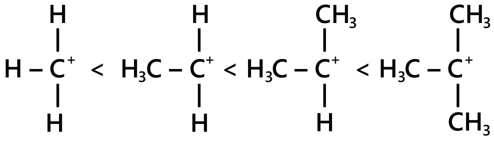




hyperconjugation in ethyl carboninum ion

In general, the stability of carbonium ions increases with the increase in the number of alkyl groups (containing hydrogen) attached to the positively charged carbon due to increase in the number of contributing structures to hyperconjugation.

Note: This type of hyperconjugation can also referred to as isovalent hyperconjugation since there is no decrease in the number bonds in the no bond resonance forms. Thus the increasing order of stability of carbocations can be given as: methyl < primary < secondary < tertiary as depicted below:

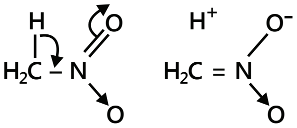


$$\underset{\text{methyl}}{H-\overset{H}{\underset{H}{C^+}}} < \underset{1^\circ}{H_3C-\overset{H}{\underset{H}{C^+}}} < \underset{2^\circ}{H_3C-\overset{CH_3}{\underset{H}{C^+}}} < \underset{3^\circ}{H_3C-\overset{CH_3}{\underset{CH_3}{C^+}}}$$

(c) **Stability of free radicals:** The stability of free radicals is influenced by hyperconjugation as in case of carbonium ions. The σ-electrons of the α-C-H bond can be delocalized into the p-orbital of carbon containing an odd electron. Due to hyperconjugation, the stability of free radicals also follow the same order as that of carbonium ions i.e., methyl < primary < secondary < tertiary.

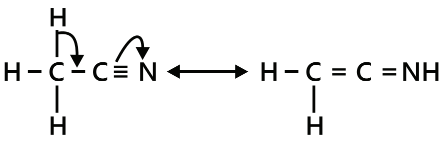
(d) **Dipole moment and bond length:** The dipole moment of the molecules is greatly affected due to hyperconjugation since the contributing structures show considerable polarity. The bond lengths are also altered due to change in the bond order during hyperconjugation. The single bond may get a partial double bond character and vice versa.

E.g. The observed dipole moment of nitro methane is greater than the calculated value due to hyperconjugation. The observed C –N bond length is also less than the expected value due to same reason.

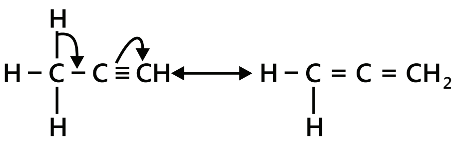


Hyperconjugation in nitroethane

The same arguments can be applied to shortening of C-C bond adjacent to -C≡N in acetonitrile and also the C-C bond adjacent to the -C≡C in propyne. Also note that the observed dipole moments are again different from their expected values.



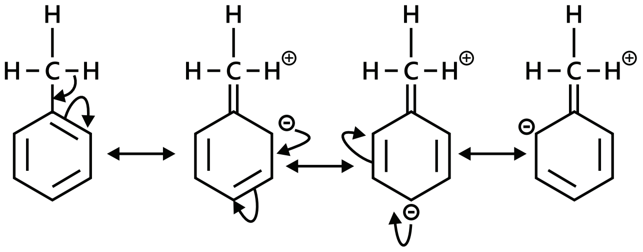
Acetonitrile



Propyne

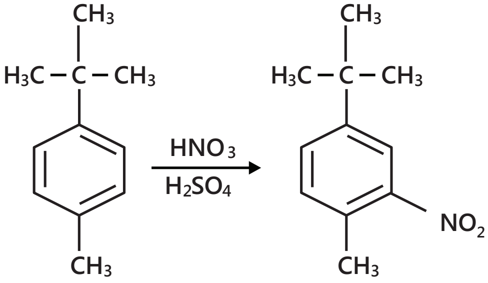
(e) **Reactivity & orientation of electrophilic substitution on benzene ring:** In Toluene, the methyl group releases electrons towards the benzene ring partly due to the inductive effect and mainly due to hyperconjugation. Thus the reactivity of the ring towards electrophilic substitution increases and the substitution is directed at ortho and para positions to the methyl group.

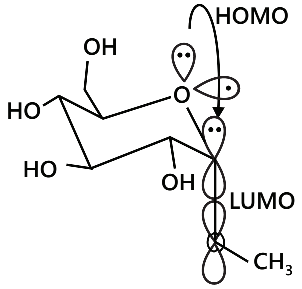
The no bond resonance forms of toluene due to hyperconjugation are shown below.



Hyperconjugation in toluene

From the above diagram, it can be seen clearly that the electron density on the benzene ring is increased especially at ortho and para positions. Since the hyperconjugation overpowers the inductive effect, the substitution (e.g. nitration) on the following disubstituted benzene occurs ortho to the methyl group. In the tert-butyl group, there are no hydrogens on the carbon directly attached to the benzene ring. Hence it cannot be involved in hyperconjugation.

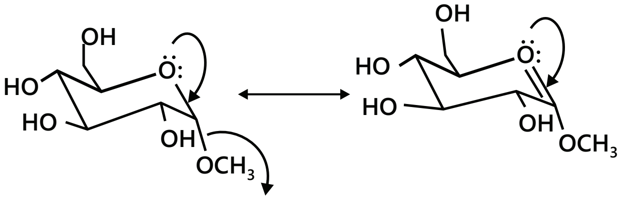




Anit periplanar arrangement is only possible in α from

Also note that the tert-butyl group is bulky and hinders the approach of electrophile.

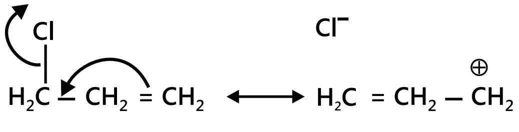
(f) **Anomeric effect:** The general tendency of anomeric substituents to prefer an axial position is called the Anomeric effect. For example, the α-methyl glucoside is more stable than the β-methyl glucoside due to hyperconjugation. In α-methyl glucoside, the non-bonding HOMO with a pair of electrons on the ring oxygen is antiperiplanar to the antibonding LUMO of C-O bond in the methoxy group. This allows hyperconjugation between them and thus stabilizes the α-form.



Hyperconjugation in α-D-methylglucosicle

Whereas, in β-methyl glucoside the methoxy group is at an equatorial position and cannot involve in hyperconjugation since it is not antiperiplanar to the lone pair on the ring oxygen. Therefore β-methyl glucoside is less stable than the α- methyl glucoside.

(g) **Reverse hyperconjugation:** In case of α-halo alkenes, the delocalization of electrons occurs towards the halogen group through the hyperconjugative mechanism. It is referred to as reverse hyperconjugation. The dipole moments of α-halo alkenes are augmented due to this phenomenon.



$$\overset{Cl}{H_2C} - CH_2 = CH_2 \longleftrightarrow \overset{Cl^-}{H_2C} = CH_2 - \overset{\oplus}{CH_2}$$

reverse hyperconjugation

MASTERJEE CONCEPTS

(a) Inductive effect : It operatives through sigma bonds and is permanent effect

(b) Mesomeric effect : It operates through pi bonds and is permanent effect.

(c) Resonance effects :

(i) Conditions –

- Same positions of atoms.
- Same number of paired and unpaired elections
- The should differ only in the arrangement of electrons

(ii) Misconception –

- The canonical forms have no real existence.
- The molecule does not exist for a certain fraction of time in one canonical from and other fractions of time in other canonical forms.
- The molecule as such has a single structure which is the resonance hybrid of the canonical forms and which cannot be represented by a single Lewis structure,

(d) Hyperconjugation : it involves the delocalization of the σ electrons of the C-H bond with the unshared p- orbital.

(e) Electromeric effect: It involves temporary polarization in the presence of a polar reagent.

(f) Generally the mesomeric effect is the strongest followed hyperconjugation and then the inductive effect.

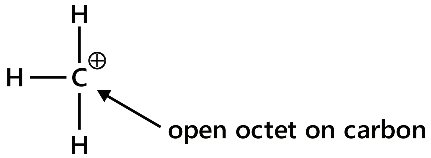
Neeraj Toshniwal (JEE 2010, AIR 443)

7. REACTION INTERMEDIATES

7.1 Carbocations

7.1.1 Introduction

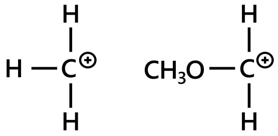
A molecule in which a carbon atoms bears three bonds and a positive charge is called a carbocation. Carbocations are generally unstable because they do not have eight electrons to satisfy the octet rule.



7.1.2 Classification of Carbocation

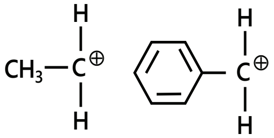
In order to understand carbocations, we need to learn some basic carbocation nomenclature. A primary carbocation is one in which there is one carbon group attached to the carbon bearing the positive charge. A secondary carbocation is one in which there are two carbons attached to the carbon bearing the positive charge. Likewise, a tertiary carbocation is one in which there are three carbons attached to the carbon bearing the positive charge.

Methyl carbocations



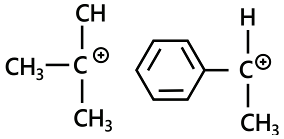
No C – C′ bonds

Primary (1º) carbocations



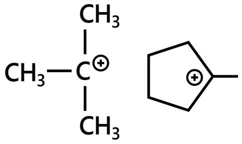
One C–C′ bonds

Secondary (2º) carbocations



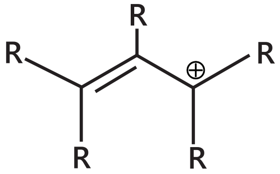
Two C – C⁺ bonds

Tertiary (3º) carbocations

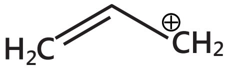


Three C – C⁻ bonds

If the carbon bearing the positive charge is immediately adjacent to a carbon-carbon double bonds, the carboacation is called an allylic carbocation. The simplest case (all R—H) is called the allyl carbocation.

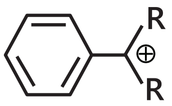


Generic allylic carbocation

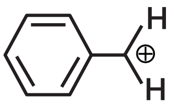


The allyl carbocation

If the carbon bearing the positive charge is immediately adjacent to benzene ring, the carbocation is termed a benzylic carbocation. The simplest case is called the benzyl carbocation.

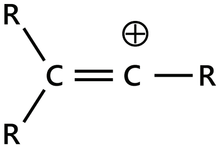


Gneric benzylic carbocation

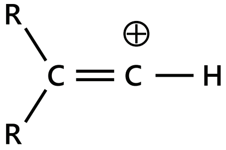


The benzyl carbocation

If the carbon bearing the positive charge is part of an alkene, the carbocation is termed a vinylic carbocation. The simplest case is called the vinyl carbocation. Note that the carbon bearing the positive charge has two attachments and thus adopts sp hybridations and linear geometry.

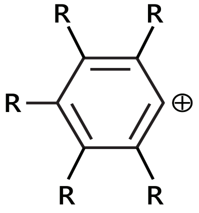


Gneric benzylic carbocation

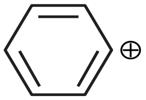


The vinyl carbocation

If the carbon bearing the positive charge is part of a benzene ring, the carbocation is termed as an aryl carbocation. The simplest case is called the phenyl carbocation.



Generic aryl carbocation

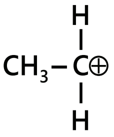


The phenyl carbocation

7.1.3 Carbocation Stability

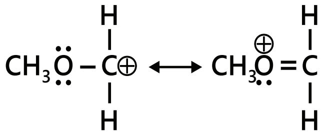
The stability of carbocations is dependent upon a few factors. One factor that decides the stability of a carbocation is resonance. Resonance is a stabilizing feature to a carbocation because it delocalizes the positive charge and creates additional bonding between adjacent atoms. Decreasing the electron deficiency increases the stability.

Consider the following:



$CH_3-\underset{H}{\overset{H}{C}}\oplus$

NO resonance



$CH_3\underset{..}{\ddot{O}}-\underset{H}{\overset{H}{C}}\oplus \longleftrightarrow CH_3\underset{..}{\overset{\oplus}{O}}=\underset{H}{\overset{H}{C}}$

Resonance

The structure on the left does not have any resonance contributors in which electrons are donated to the carbon with the open octet. Compare this with the carbocations that has resonance and a delocalized positive charge. Charge delocalization imparts stability, so the structure with resonance is lower in energy.

In the example shown above, an oxygen atom lone pair is involved in resonance that stabilizes a Allylic and benzylic carbocations enjoy resonance stabilization by delocalization of the positive charge to the adjacent π bond(s). Vinylic and aryl carbocations do not enjoy resonance stabilization because their p electron clouds are perpendicular to the vacant p orbitals of the carbocation. (Recall that resonance requires the interacting orbitals to be parallel so they can overlap. Without overlap there can be no resonance.)

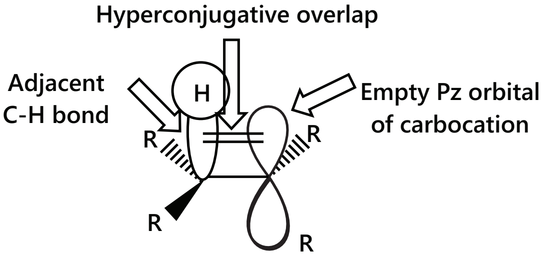
Note the influence of the inductive effect versus the resonance on the energies of these molecules. The oxygen atom that is bonded to the carbocation on the right is more electronegative than the corresponding hydrogen atom in the left-hand structure. We would think that the inductive effect would pull electron density away from the carbocation, making it higher in energy. In this case, the carbocation stabilization by resonance electron donation is a more significant factor than carbocation destabilization by inductive electrons withdrawal.

Methyl and primary carbocations without resonance are very unstable, and should never be invoked in a reaction mechanism unless no other pathway is possible. More stable carbocations (secondary or tertiary with resonance, or any carbocation with resonance) are sufficiently stable to be formed in a mechanism under reasonable reaction conditions.

The second factor that should be considered when thinking about carbocation stability is the number of carbons attached to the carbon carrying the positive charge. We look at the number of

bonding electrons that are attached to the carbocation because those bonding electrons will help in alleviating the positive charge. Bonding electrons from adjacent s bonds may overlap with the unoccupied p orbital of the carbocation.

This phenomenon is termed hyper conjugation. Since the overlap supplies electron density to the electron-deficient carbocation carbon, we predict that increasing the number of hyper conjugative interactions increases carbocation stability. Extending this idea, we predict that increasing the number of bonds adjacent to the carbocation by increasing the number of alkyl groups attached to the carbocation carbon results in an increases in carbocation stability. For example, a tertiary carbocation should be more stable than a secondary carbocation. This predication is accurate.



This suggests that any adjacent bonding electron pair will participate in carbocation hyperconjugation. However, only C—H and C—C bonds provide a significant level of increased stability.

Despite the importance of both the factors of resonance and hyperconjugation, resonance usually wins out. For example. a primary carbocation with resonance is more stable than a secondary carbocation without resonance and is usually more stable than a tertiary carbocation without resonance.

The general rules for carbocation stability can be summarized as follows.

(a) Increasing substitution increases stability.

CH_3^+ (methyl; least stable) < RCH_2^+ (1°) <R_2CH^+ (2°) < R_3C^+ (3° ; most stable)

(b) Resonance is more important than substitution. For example, a secondary carbocation without resonance is generally less stable than a primary carbocation with resonance.

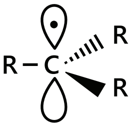
In vinylic carbocation, the positive charge is assigned to a carbon with sp hybridization. How does this influence the carbocation's stability? A sp orbital has more character than an sp^2 orbital. Electrons in an s orbital are closer to the nucleus and therefore more tightly held than electrons in a p orbital. This can be taken to mean that the electronegativity of carbon increases with the increasing s character. Thus sp carbon (most s character, most electronegative) > sp^2 > sp^3 (least s character; least electronegative). Electronegativity is a measure of electron attraction. So the stability of a cation is affected by the electronegativity of the atom bearing the positive charge. The more electronegative the atom, the less stable the cation. A vinylic carbocation carries the positive charge on a sp carbon which is more electronegative than an sp^2 carbon of an alkyl carbocation. Therefore a primary vinylic carbocation is less stable then a primary alkyl carbocation. Similar reasoning explains why an aryl carbocation is less stable than a typical secondary alkyl carbocation such as cyclohexyl carbocation.

Because of their reduced stability, vinyl and aryl carbocations are not often encountered.

7.2 Free Radical

A molecular entity such as $\cdot CH_3$ or $\cdot SnH_3$ or $\cdot Cl$ possessing an unpaired electron. (In these formulae, the dot symbolizing the unpaired electron should be placed so as to indicate the atom of highest spin density, if this is possible.) Paramagnetic metal ions are not normally regarded as radicals. However, similarities have been found between certain paramagnetic metal ions and radicals. Depending upon the core atom that possesses the unpaired electron, the radicals can be described as carbon-, oxygen-, nitrogen-, metal-centred radicals. If the unpaired electron occupies an orbital having considerable s or more or less pure p character, the respective radicals are termed σ- or π-radicals. In the past, the term 'radical' was used to designate a substituent group bound to a molecular entity, as opposed to 'free radical', which nowadays is simply called radical. The bound entities may be called groups or substituents, but should no longer be called radicals.

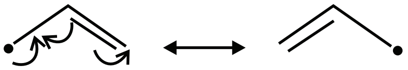
Radical Structure: We can present the general radical as R_3C.



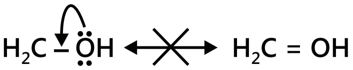
Note that the radical is NOT charged (its reactivity and electrophilic nature does not come from a charge but from its unpaired electron). Also, note how the radical looks sp^2 with a planar configuration. The unpaired electron occupies the unhybridized 2p orbital.

Radical Stability: Like carbocations, radicals are electron deficient. Therefore, we can think of the same factors in carbocation stability and see if they apply in radical stability:

Resonance: Like carbocations, radicals can gain stability through resonance. That is, a radial with resonance that can delocalize the electron deficiency is more stable. Recall that reactions tend to produce the more stable product. Therefore, reactions will tend towards the more stable radical. This will become important when we are considering a radical reaction and determining the favoured product:



However, unlike carbocations, radicals do not gain resonance from lone pairs. Why?



$$H_2\dot{C}-\ddot{\underset{\cdot\cdot}{O}}H \not\longleftrightarrow H_2C=OH$$

Look at this resonance stabilization step carefully; note that the carbon has 9 electrons attributed to it. This is not possible .

Number of substituents: We know that radicals are electron deficient species. Therefore, stability is increased with increasing numbers of electron-donating substituents, such as alkyl group:

$$\dot{C}H_3 < R\dot{C}H_2 < R_2\dot{C}H < R_3\dot{C}$$

Recall that we have almost never worked with methyl carbocations. However, methyl radicals are sometimes considered because unlike carbocations, methyl radicals are only missing one electron (not a pair of electrons) and thus are slightly more stable than the methyl carbocation.

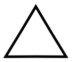
7.3 Carbanion

A **carbanion** is an anion in which carbon has an unshared pair of electrons and bears a negative charge usually with three substituents for a total of eight valence electrons.[1] The carbanion exists in a trigonal pyramidal geometry. Formally, a carbanion is the conjugate base of a **carbon acid**.

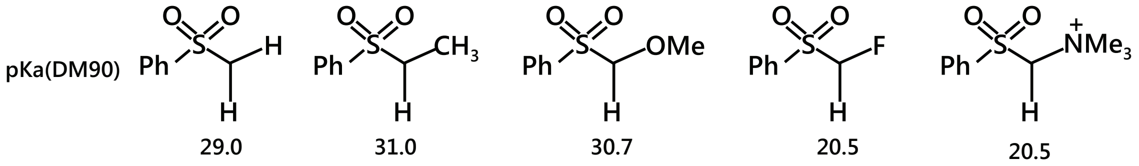
$R_3CH + B \rightarrow R_3C^- + H—B$ where B stands for the base. A carbanion is one of several reactive intermediates in organic chemistry.

7.3.1 Effect of Substituents on Carbanion Stability

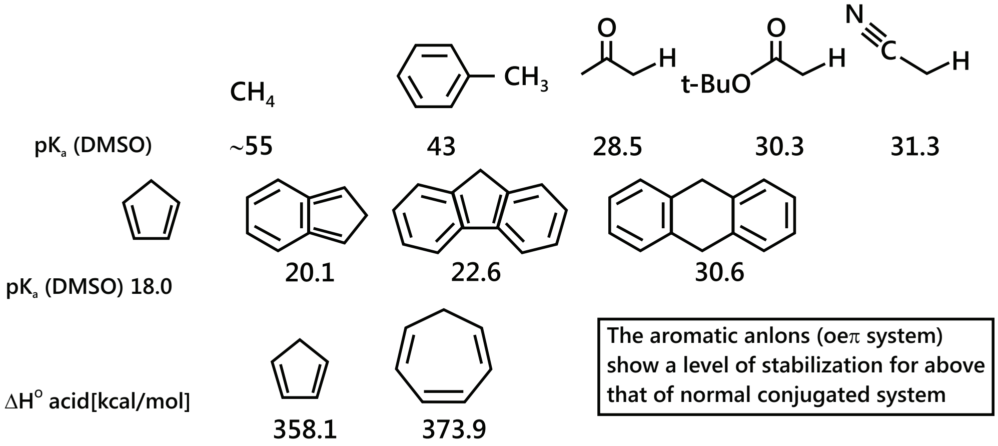
(a) **Hybridization:** In almost all areas of organometallic chemistry the primary subdivision of reactivity types is by the hybridization of the C-M carbon atom (methyl/alkyl, vinyl/aryl, alkynyl). A key second subdivision is the presence of conjugating substituents (allyl/allenyl/propargyl/benzyl). The fractional s-character of the C-H bonds has a major effect on the kinetic and thermodynamic acidity of the carbon acid. Only s-orbitals have electron density at the nucleus, and a lone pair with highly fractional s character has its electron density closer to the nucleus, and is hence stabilized. This can be easily seen in the gas-phase acidity of the prototypical C-H types, ethane, ethylene and acetylene, as well as for cyclopropane, where the hybridization of the C—H types, ethane, ethylene and acetlylene, as well as for cyclopropane, where the hybridization of the C—H bond is similar to that in ethylene.

	CH_3-CH_3		$CH_2=CH_2$	$CH\equiv CH$
ΔH^o acid (kcal/mol)	420	411	406	375

(b) **Inductive effects:** Electron-withdrawing substituents will inductively stabilize negative charges on nearby carbons. These effects are complex, since electronegative substituents interact with carbanions in other ways as well (e.g. O and F substituents have lone pairs, which tends to destabilize adjacent carbanion centers.)



(c) Conjugation and Delocalization: Delocalization of negative charge, especially onto electronegative atoms, provides potent stabilizations of carbanionic centers. Since almost all conjugating substituents are also more electronegative than H or CH_3, there is usually a significant inductive contribution to the stabilization.



The aromatic anlons (oeπ system) show a level of stabilization for above that of normal conjugated system

(d) Lone Pair Effects: For the first low elements N, O, F and sometimes also for higher elements, the presence of lone pairs has a strong destabilizing effect on a directly bonded carbanion centre. This has several effects on carbanion structure : there are substantial rotational barriers around the C—C bond and the carbanion center is usually more pyramidal in nature.

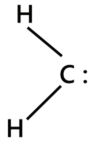
Measurement of CH acidities in solution

pK =	0-16	direct measurements in water.
pK =	0-33	Direct measurements in dimethyl sulfoxide (DMSO).
pk =	33-45	Direct measurements in THF and ether on ion pairs
pK =	45+	Only indirect measurements in nonpolar solvents.

- Kinetic acidities
- Bronsted equation Ka = ak
- Usually only on contact ion pairs
- Aggregates are frequently present
- Gas phase acidities ($\Delta H°_{acid}$)

7.4 Carbene

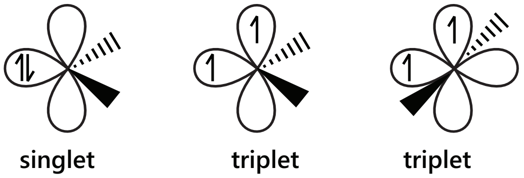
In chemistry, a **carbene** is a molecule containing a neutral carbon atom with a valence of two and two unshared valence electrons. The general formula is R-(C**:**)-R′ or R=C**:**. The term "carbene" may also refer to the specific compound H_2C**:** , also called methylene, the parent hydride from which all other carbene compounds are formally derived. Carbenes are classified as either singlets or triplets depending upon their electronic structure. Most carbenes are very short lived, although persistent carbenes are known. One well studied carbene is Cl_2C**:** or dichlorocarbene, which can be generated *in situ* from chloroform and a strong base.



methylene (carbene)

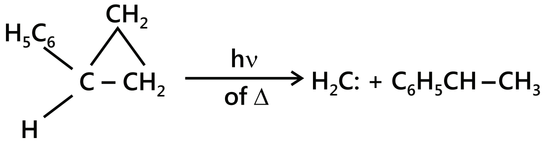
7.4.1 Structure and Bonding

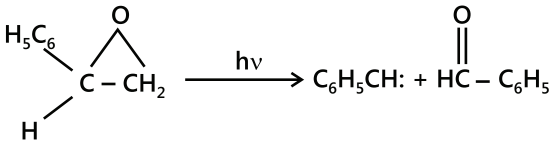
Singlet and Triplet Carbenes



The two classes of carbenes are singlet and triplet carbenes. Singlet carbenes are spin-paired. In the language of valence bond theory, the molecule adopts a sp^2 hybrid structure. Triplet carbenes have two unpaired electrons. They may be either linear or bent, i.e. sp or sp^2 hybridized, respectively. Most carbenes have a nonlinear triplet ground state, except for those with nitrogen, oxygen, or sulfur atoms, and halides directly bonded to the divalent carbon. Carbenes are called singlet or triplet depending on the electronic spins they possess. Triplet carbenes are paramagnetic and may be observed by electron spin resonance spectroscopy if they persist long enough. The total spin of singlet carbenes is zero while that of triplet carbenes is one .Bond angles are 125-140° for triplet methylene and 102° for singlet methylene (as determined by EPR). Triplet carbenes are generally stable in the gaseous state, while singlet carbenes occur more often in aqueous media. For simple hydrocarbons, triplet carbenes usually have energies 8 kcal/mol (33 kJ/mol) lower than singlet carbenes. thus, in general, triplet is the more stable state (the ground state) and singlet is the excited state species. Substituents that can donate electron pairs may stabilize the singlet state by delocalizing the pair into an empty p-orbital.

Formation: From photochemical or thermal cleavage of cyclopropanes and oxiranes



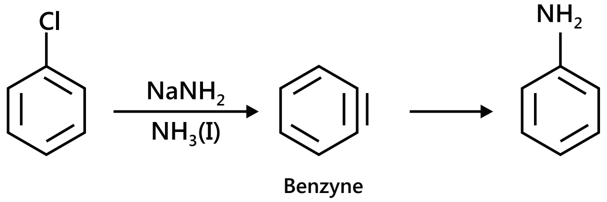


7.5 Nitrene

In chemistry, a **nitrene** (R-N:) is the nitrogen analogue of a carbene. The nitrogen atom has only 6 valence electrons and is therefore considered an electrophile. A nitrene is a reactive intermediate and is involved in many chemical reactions. In the most simple nitrene, the linear Imidogen (:N-H), two of the 6 available electrons form a covalent bond with hydrogen, two others create a free electron pair and the two remaining electrons occupy electrons in each of the p orbitals and the high energy form is the singlet state with an electron pair filling one p orbital and leaving the other one vacant. $R-\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}:$ nitrene

7.6 Benzyne

Arynes or **benzynes** are highly reactive species derived from an aromatic ring by removal of two ortho substituents. Arynes usually are best described as having a strained triple bond; however, they possess some biradical character as well.



MASTERJEE CONCEPTS

(a) Carbocation

- **(i)** They cannot be optically active because of their planar structure.
- **(ii)** Stability: Electron donating groups and hyperconjugation stabilizes the carbocation whereas the electron withdrawing group destabilizes the carbocation.
- **(iii)** Generally aromatic cations are the most stable
- **(iv)** Methyl cyclopropyl cation is exceptionally stable.
- **(v)** Tert-butyl cation is also very stable due to a larger number of hyperconjugating structures and the inductive effect of 3 alkyl groups.

(b) Carbanion

- **(i)** They can be optically active.
- **(ii)** Stability: Electron donating groups destabilize the carbanion whereas the electron withdrawing group stabilizes the carbanion.
- **(iii)** Aromatic carbanions are generally most stable.

(c) Carbenes: Are an electron deficient species with 6 electrons.

- **(i)** Triplet: They have 2 unpaired electrons in 2 different orbitals.
- **(ii)** Singlet: They have two paired electrons in a single orbital.

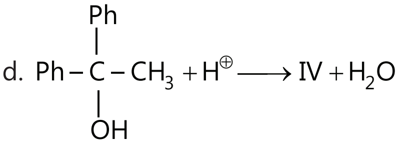
Aman Gour (JEE 2010, AIR 443)

Illustration 10: Name the intermediate species formed in the following reactions:

a. $CH_3CH_2-\underset{\oplus}{N}\equiv\underset{\bullet\bullet}{N}\longrightarrow I+:N\equiv N:$

b. $CH_3CH_2-C\equiv C-H+\overset{\oplus}{K}\overset{\ominus}{N}H_2\longrightarrow II+H_3$

c. $Ph-CH=CH-Me+HBr\longrightarrow III+Br^-$

d. 

$Ph-\overset{\displaystyle Ph}{\underset{\displaystyle OH}{C}}-CH_3+H^{\oplus}\longrightarrow IV+H_2O$

e. $CH_3CH_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}H\xrightarrow{-\bar{e}}V\longrightarrow VI+CH_3$

f. $CH_3-\overset{\bullet\bullet}{N}=\overset{\bullet\bullet}{N}-CH_3\xrightarrow{\Delta}VII+N_2$

g. $CH_3-CHI_2+Zn/Cu\xrightarrow{\Delta}VIII+ZnI_2$

h. $PhCH_2Cl+AlCl_3\longrightarrow IX+[AlCl_4]^{\ominus}$

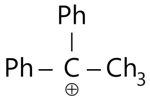
i. $CH_3-C\equiv C-CH_3+Li\xrightarrow[C_2H_5OH]{liq.NH_3}X+Li^{\oplus}$ **(JEE ADVANCED)**

Sol:

a. $CH_3\overset{\oplus}{C}H_2$ (Carbocation)

b. $CH_3CH_2-C\equiv C^{\ominus}\,K^{\oplus}$ (carbanion)

c. $Ph\overset{\oplus}{C}H-CH_2Me$ (2^o Benzylic carbocation)

d. 
$$Ph-\underset{\oplus}{\overset{\overset{\displaystyle Ph}{|}}{C}}-Ch_3$$

e. **$[CH_3CH_2-\dot{O}\!:\!-H]^{\oplus}$ (Radical cation, loss of e^- s from O atom can occur since it has higher energy than bonded e^- S)**

$[\dot{C}H_3+CH_2=\overset{\oplus}{\underset{\cdot\cdot}{O}}-H\leftrightarrow\overset{\oplus}{C}H_2-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H]$
(Resonance stabilised cation)

f. $2CH_3$- (free radical)

g. Simmons – Smith reaction

(CH_3CH:) (singlet carbene)

h. $Ph\overset{\oplus}{C}H_2$ (Benzyl carbocation)

i. $(X)\underset{1}{C}H_3-\underset{2}{C}-\underset{3}{\overset{\overset{\bullet\bullet}{\oplus}}{C}}-\underset{4}{CH_3}$ (Radical anion C^2 is vinyl radical and C^3 is vinyl carbanion.

8. ACIDITY AND BASICITY IN ORGANIC COMPOUNDS

8.1 Acidity

Five key factors that influence acidity:

Factor #1 – Charge: Removal of a proton, H^+, decreases the formal charge on an atom or molecule by one unit. This is, of course, is the 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:

Acidity increases with the increasing positive charge on an atom.

$$\begin{array}{lccccc} & HO^{\ominus} & < & H_2O & < & H_3O^{\oplus} \\ \text{pKa} & & & 15.7 & & -1.7 \end{array}$$

$$\xrightarrow{\text{increasing acidity}}$$

$$\begin{array}{lccccc} & NH_2^{\ominus} & < & NH_3 & < & NH_4^{\oplus} \\ \text{pKa} & & & 38 & & 9.2 \end{array}$$

Note that once a conjugate base (B^-) is negative, a second deprotonation will make the dianion (B^{2-}). While far from impossible, forming the dianion can be difficult due to the build-up of negative charge and the corresponding electronic repulsions that result.

Factor #2 – The Role of the Atom: This point causes a lot of confusion due to the presence of two seemingly conflicting trends. Here's the first point: acidity increases as we go across a row in the periodic table. This makes sense, right? It makes sense that HF is more electronegative than H_2O, NH_3, and CH_4 due to the greater electronegativity of fluorine versus oxygen, nitrogen, and carbon. A fluorine bearing a negative charge is a happy fluorine.

But here's the seemingly strange thing. HF itself is not a "strong" acid, at least not in the sense that it ionizes completely in water. HF is a weaker acid than HCl, HBr, and HI. What's going on here?

Across the periodic table, acidity increases with electronegativity

	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
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 sulphur .....

	H_2O	<	H_2S
pKa	15.7		7.0
	H_3COH	<	H_3CSH
pKa	15.5		10

You could make two arguments for why this is. 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 unfavourable: for one thing, F^- begs for solvation, which will lead to a lower entropy term in the ΔG. Note that this trend also holds for H_2O and H_2S, with H_2S being about 10 million times more acidic.

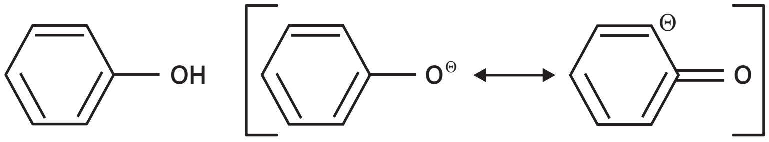
Factor #3 – Resonance: A huge stabilizing factor for a conjugate base is if the negative charge can be delocalized through resonance. The classic examples are with phenol (C_6H_5OH) which is about a million times more acidic than water. Remember, any structural feature that increases the stability of 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 increases the stability of the conjugate base (therefore in increasing acidity) because the negative charge can be delocalized

Example.1 Contrast methanol versus phenol:

CH_3OH

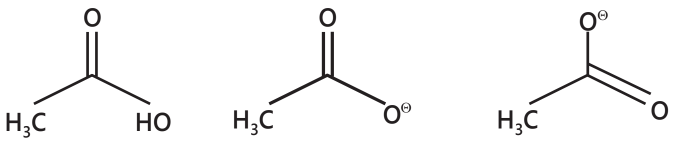


pKa 15 < 10 more acidic

The anion of phenol can be stabilized through resonance

Example.2 Alcohols (e.g. methanol) versus carboxylic acids

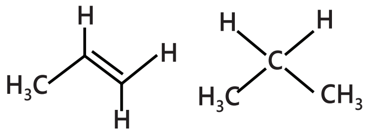
CH_3OH



pKa 15 < 4 more acidic

The anion of phenol can be stabilized through resonance

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



With acetic acid (pKa of ~5).

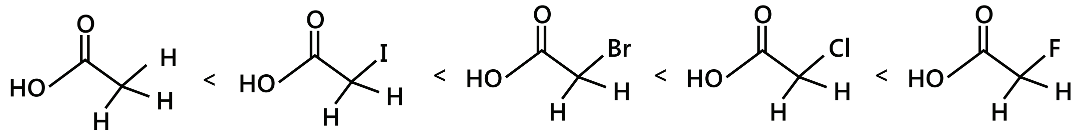
Watch out though – it isn't enough for a π system to simply be adjacent to a proton – the electrons of the conjugate base have to be in an orbital which allows for the effective overlap.

Factor #4 – Inductive effects: Electronegative atoms can draw negative charge toward themselves, which can lead to considerable stabilization of conjugate bases. Check out these examples:

Electronegativity and inductive effects:

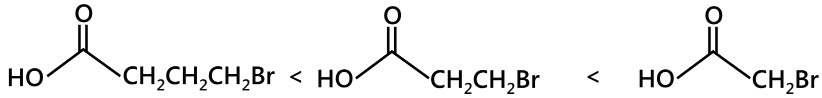
Two principles – electron withdrawing substituents can increase the acidity of 8 nearby atoms, which increases with electronegativity and decreases with increasing distance to the atom.

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



pKa 4.76 3.15 2.86 2.81 2.66

More acidic

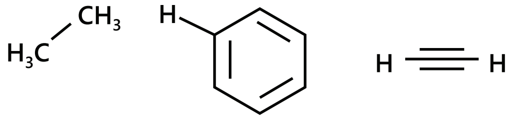


pKa 4.59 4.01 2.86

Predictably, this effect is going to be related to two major factors: The electronegativity of the element (the more electronegative, the more acidic) and the distance between the electronegative element and the negative charge.

Factor #5 – Orbitals: Again, the acidity relates nicely to the stability of the conjugate base, and the stability of the conjugate base depends on how well it can accommodate its newfound pair of electrons. The more s character in the orbital, the closer the electrons will be to the nucleus, and the lower in energy (= stable!) they will be. The higher the s-character of bond to hydrogen, the more acidic it will be.

sp^3	>	sp^2	>	sp
25%		**33%**		**50%**
s-character		**s-character**		**s-character**



pKa 50 42 25

increasing acidity

Illustration 11: Arrange the following: **(JEE MAIN)**

a. In decreasing order of pK_b

I. $C_2H_5NH_2$ II. PhNHMe III. $(C_2H_5)_2NH$ IV. $PhNH_2$

b. In increasing order of basic strength

I. $PhNH_2$ II. $PhNMe_2$ III. $(C_2H_5)_2NH$ IV. $MeNH_2$

c. I. $PhNH_2$ II. P-nitroaniline III. p-Toluidine

d. I. $PhNH_2$ II. PhNHMe III. $PhCH_2NH_2$

e. In decreasing order of basic strength in gas phase.

I. $C_2H_5NH_2$ II. $(C_2H_5)_2NH$ III. $(C_2H_5)_3N$ IV. NH_3

Sol: The electron donating groups like alkyl groups increase the basic strength of amines whereas the electron with drawing groups like aryl groups decrease the basic nature.

a. IV < II < I < III (aromatic amine < EDG, –Me increase basicity <1° amine < 2° amine)

b. I < II < IV < III (aromatic amine < EDG, –2Me increase basicity < 1°amine < 2° amine)

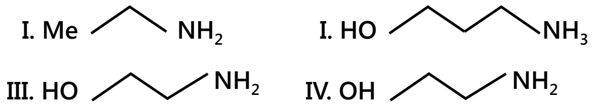
c. II < I < III < (EWG, $-NO_2$, decrease and EDG, $-CH_3$, increase basicity)

d. I < II < III (aromatic amine < EDG, – Me increase basicity < benzylamine, aliphatic amine)

e. IV < I < II < III (–Me increase basicity)

Illustration 12: Arrange the following in decreasing order of basicities **(JEE MAIN)**

a.



b. I. $EtNH_2$ II. $MeCONH_2$ III. $PhCONH_2$

c. I. $PrNH_2$ II. $HC\equiv C{-}CH_2NH_2$ III. $H_2C=CH{-}CH_2NH_2$

Sol: a. I > II > III > IV

The –I effect of OH group decreases the electron density on N atom, and thus decrease its basicity. If –I effect is large distance operating from $(-NH_2)$, then the base is stronger, and vice versa, So, basicity II > III > IV.

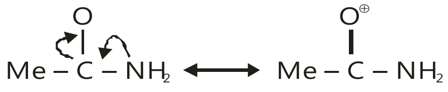
(I) is the strongest base due to +I effect of $(MeCH_2)$ group,

b. I > III > II

i. The +I effect of (Et–) group increases the electron density on N atom and thus increases

basicity and is the strongest base.

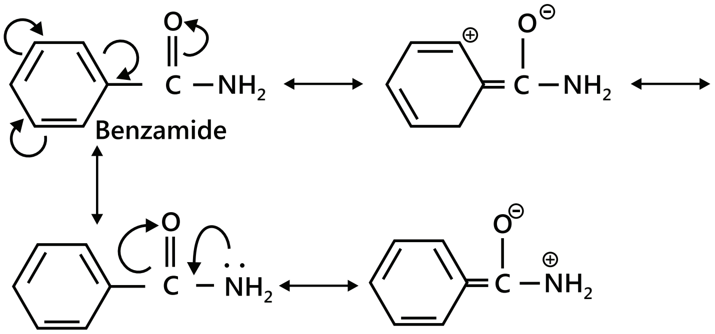
ii. (C =O) is EWG and decreases the basicity by the delocalization of electron density from N to O.



Acetamide

Both the amides are weaker bases then amine. Unlike amines, amides are amphoteric in nature, i.e., they are insoluble in aqueous acids and do not form salts..

iii. In benzamide $(PhCONH_2)$, there is cross conjugation of (C =O) with Ph groups and with NH_2 group, as shown below.

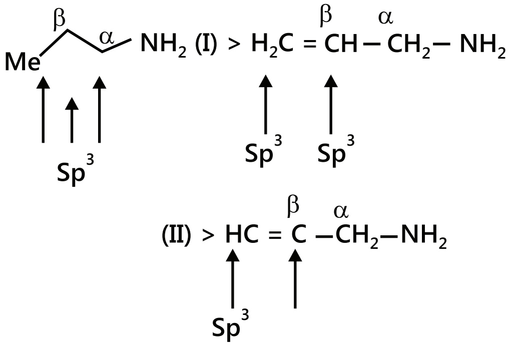


Therefore, electron density on N in benzamide (III) is slightly more than aliphatic amide (II), So, (III) is more basic than (II). Hence, basicity order is $EtNH_2 > PhCONH_2 > MeCONH_2$.

c. Static of hybridization decides the basic character. Basic order is $sp^3 > sp^2 >$ sp hybrid orbitals.

Conversely, the more the s character (as in sp hybrid orbitals) of β-C atom, the more is the electron withdrawing -I effect, and weaker the base. So, the basicity order is:

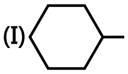
(I)



Alternatively, electron withdrawing -I effect of:

$HC \equiv C - CH_2 - >$ $CH_2 = CH—CH_2—$ $>$ $CH_3—CH_2—CH_2—$

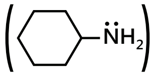
Propargyl Allyl Propyl

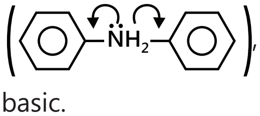
Illustration 13: a.  **NH_3 II. PH_2NH (III) $PhNH_2$** **(JEE MAIN)**

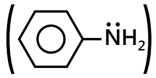
b. Write the conjugate base and conjugate acid of (I) $HOCH_2CH_2NH_2$.

Sol: The electron donating groups like alkyl groups increase the basic strength of amines whereas the electron with drawing groups like aryl groups decrease the basic nature.

a. I > III > II

In (I)  electron density on Na atom is localized and hence most base.

In (II) , electron density on N atom can be delocalized in both the Ph rings and is hence, least basic.

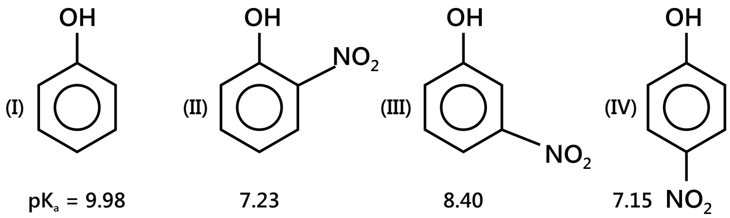

In (III) electron density on N atom is delocalized only in one Ph ring, and hence is less basic than (I) and more basic than (II).

Moreover, (I) is an aliphatic (cyclic) amine, and (II) and (III) are aromatic amines which are less basic than (I), In aromatic amines, L.P. electron on N atoms are delocalized into the ring mainly at o and p positions, thereby weakening the basicity.

b. i. In (I) ($HO—CH_2—CH_2—NH_2$, OH is more acidic then NH_2, So, conjugate base of (I) is $O^{\ominus}—CH_2—CH—NH_2$.

ii. In (I) NH_2 is more basic than OH, so conjugate acid of (I) is $HO—CH_2—CH_2—\overset{\oplus}{N}H_3$

Illustration 14: Compare the acidity of substituted phenolic compounds: **(JEE MAIN)**



Sol: Due to – Inductive effect and – Resonance effect of ($–NO_2$) group, in both II and IV, but (–I) at o^n > p^n, II should be a stronger acid than IV. But is stronger than II. This is due to intermolecular Hydrogen Bonding formed between hydrogen of OH and Nitro group in II, which results in the release of $H^{\oplus}$ slightly difficult than in IV.

Acidic character: should be II > IV > III > I. But, the observed order is IV > II> III> I (p^n > o^n > m^n > phenol)

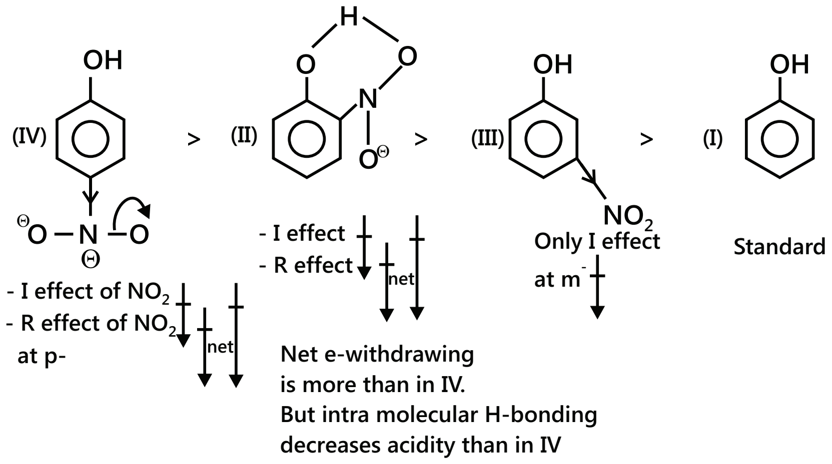
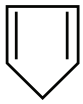
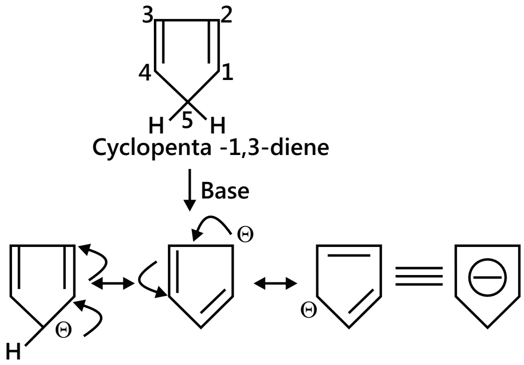


Illustration 15: Give the resonance structures of the conjugate base of the following: **(JEE MAIN)**

I.  II. $Ph-CH_2-Ph$

Sol:



(Aromatic) six e^- system in delocalization

$$Ph-CH_2-Ph \xrightarrow{Base} Ph-CH-Ph$$

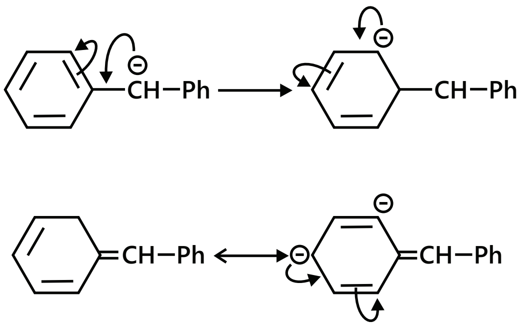
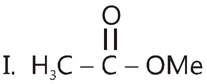
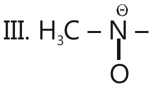


Illustration 16: Give the decreasing order of acidities of: **(JEE ADVANCED)**



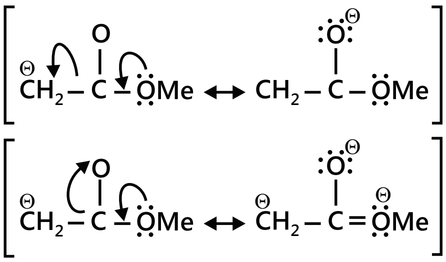
I. $H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OMe$ II. $H_3C-CH=O$



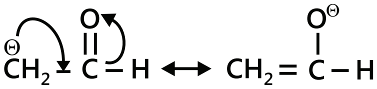
III. $H_3C-\underset{\underset{\displaystyle O}{|}}{\overset{\ominus}{N}}-O$ and explain.

Sol: Extent of Acidity of any compound depends on the stability of carbanion formed. More stable the anion, more acidic is the parent compound.

In the anion of (I), due to the cross conjugation with the delocalization of the negative charge on (CH_2) group and the O atoms of (OMe) group, complement each other, thereby making the anion a stronger base, hence its parent compound is a weak acid.



The negative charge on the anion of (II) is delocalized to the more electronegative O atom.



However, the negative charge on the anion of (III) is most extensively delocalized to two more electronegative O atoms. Moreover, – I effect of $N^{\oplus}$ provides additional stabilization.

Hence, the anion of (III) is more stabilized than the anion of (II), which in turn is more stabilized than the anion of (I).

Stability order of anion is: III > II > I.

Acidic order is: III > II > I.

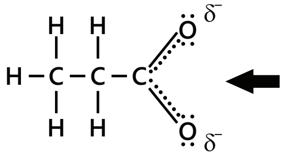
8.2 Basicity

So what are the various factors that can influence basicity?

- Resonance
- Electro-negativity
- Size of atomic radius
- Inductive effect
- Formal charges

1. Resonance: Let us recall that resonance delocalizes electrons. If an atom is involved in resonance, it has a negative formal charge, it delocalizes that formal charge.

Example:



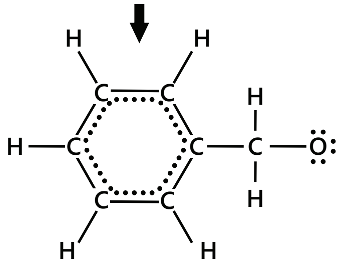
Electron Delocalization casued by resonance

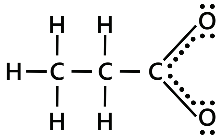
In the $CH_3CH_2CO_2$ – molecule, the oxygen atoms are the ones donating electrons to the hydrogen, these oxygen atoms have dilute negative charges, due to resonance, electrons as well as the negative charges are delocalized. This decreases electron density and thus elasticity.

Key point: Resonance usually DELOCALIZES electrons from the atom, thus REDUCING electron density. This causes the molecule to have a lower basicity!

Because resonance does not ALWAYS reduce basicity. Sometimes it has no effect on it.

E.g. **Resonance has no effect on the oxygen atom**



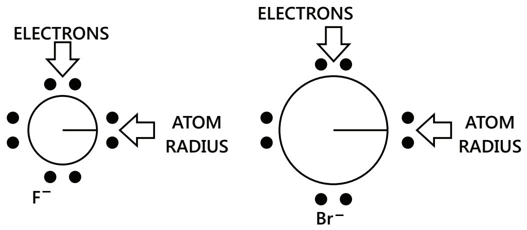


If a basic atom is not involved in resonance, then resonance has no impact on the molecule's basicity! This is because the atom's electron density is not delocalized!

2. Atomic radius: Atoms with smaller atomic radii will have greater electron density, increasing basicity. Atoms with larger atomic radii will have less electron density, reducing basicity.

Key point: LARGER atomic radius means LOWER Basicity, SMALLER atomic radius means HIGHER basicity.

Example: What the difference between F – and Br -?



Br has a larger atomic radius than F.

Notice how the electrons on the F^- are covering more of the atom than compared to that of Br^-.

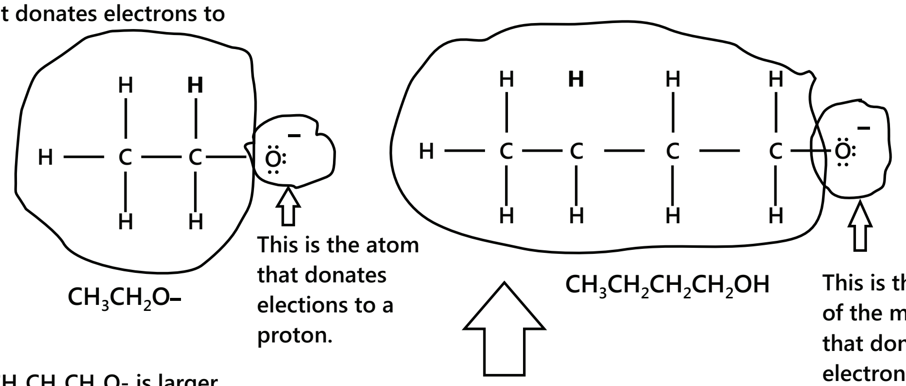
F^- has a greater electron density that Br^-

Therefore, Br^- is less basic than F^-,

We only consider atomic radius of the atom that donates electrons to the hydrogen proton.

The atomic radius concept will not work between CH_3CH_2O – and $CH_3CHCH_2CH_2O$-

This is because the carbon hydrogen chain is not the one donating electrons to a proton, the oxygen is, of course we can say the $CH_3CH_2CH_2CH_2O$- has greater London Dispersion Forces, but that's a different story.



The CH_3CH_2 part of the Molecule has no impact on the oxygen atom, the one that donates electrons to the proton.

CH_3CH_2O–

This is the atom that donates elections to a proton.

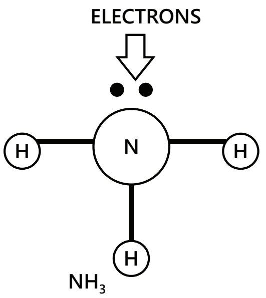
$CH_3CH_2CH_2CH_2OH$

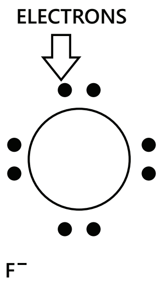
This is the part of the molecule that donates electrons to a proton

Although $CH_3CH_2CH_2O$- is larger than CH_3CH_2O-, their level of basicity is not influenced by the size if the molecule, only the oxygen atom is the one donating Electrons to H^+. When we compare basicity by using atomic radius, We only consider the electron Donating atom.

The $CH_3CH_2CH_2$ part of the molecule has no impact on the oxygen atom, the one that donates electrons to the proton.

3. Electronegativity: When atom has greater electronegativity, this means that the atom is greedier for electrons. It is less willing to share its electron pairs with a proton, reducing the atoms' likelihood to bond with the proton. This reduces basicity.





Key point: If the atom donating electrons to the proton has high electronegativity, then the molecule containing that atom has lower basicity.

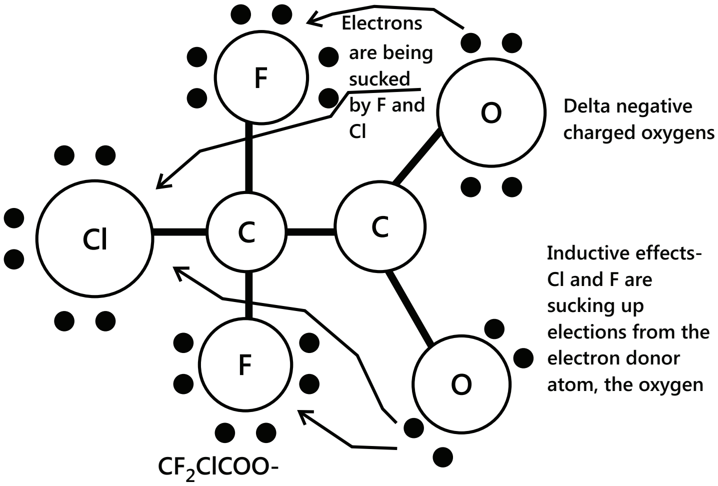
Example: NH_3 vs F -

The electron donating atoms are N and F^-.

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 a bond with H, meaning that F is the less basic out of the two.

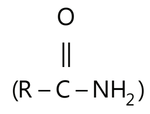
4. Inductive effect: The inductive effect is when other atoms within the molecule can take or are given electrons from the atom donating electrons to a proton. Atoms that do not donate electrons to protons can influence basicity as well. Example of inductive effect taking electrons away.

$CF_2ClCOO–$



CF_2ClCOO-

The atoms involved in the inductive effect are the F, Cl, Br. Since, these atoms are electronegative, the atoms take electrons away from the O^- which acts as the electron donating atom. The closer the atoms are to the electron donating atom, the larger the inductive effect. $CF_2ClCO_2^-$ has a larger inductive effect than $CF_2ClCH_2CO_2^-$

Illustration 17: Why Amides  $(R-\overset{\overset{O}{\|}}{C}-NH_2)$ are less basic than Amines (RNH_2) **(JEE MAIN)**

Sol: Amides are resonance, stabilized by the Lone Pair electrons on N atom, thus resulting in the lack of availability of electrons on N atom.

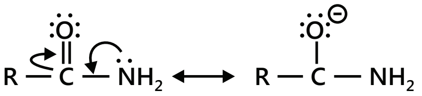
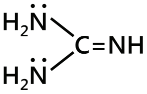


Illustration 18: a. Which N of guanidine (I) is more basic and is more likely to be protonated?

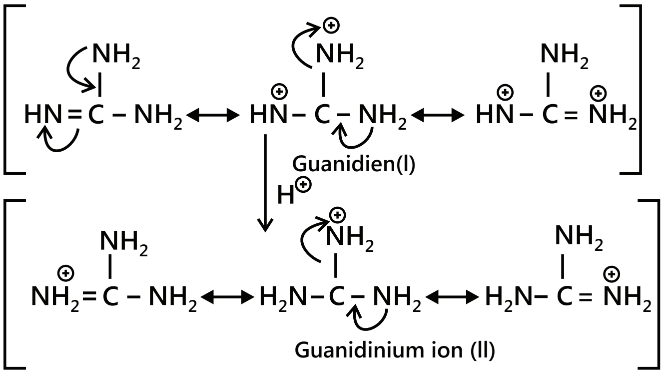
b. Why guanidine is the strongest organic N-base ($K'_b \equiv 1$)? **(JEE ADVANCED)**

Sol: a. The lesser the s character (as in sp^3 HO's), the stronger is the base. The N atom of NH_2 group is sp^3 hybridized with less s character than N of the imino (–NH) group, So, NH_2 group is more basic and is more likely to accept a proton from a water solvent.



Guanidine(I)

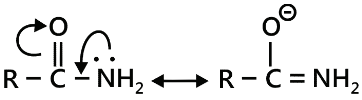
b. Both guanidine and its conjugate acid, the guanidinium ion, are stabilized by delocalization as shown below:



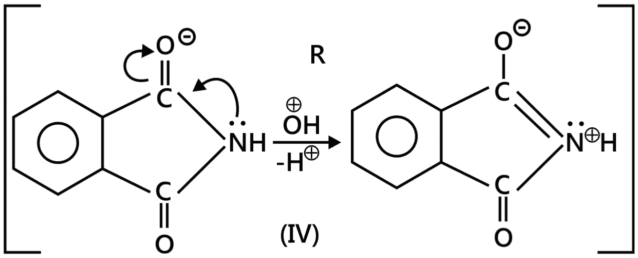
Guanidinium cation (II) is stabilized by the contribution of three exactly equivalent structures, whereas guanidine (I) has the resonating structures involving charge separation. Thus, the conjugate acid is a more stable chain the base and guanidine is therefore, a strong base.

Illustration 19: Why amides (III) are weakly basic (amphoteric), whereas phthalimide (IV) is an acid? **(JEE ADVANCED)**

Sol: Due to more resonance hybrid and extensive delocalisation in phthalimide anion, its parent compound shows acidic character.



(III)



9. THE ATTACKING REAGENT

The attacking reagents are classified into two main groups.

(a) **Electrophiles:** The species which carry +ve charge or are electron deficient are called electrophiles. These species attack regions of high electron density in a molecule.

- **(i)** Positively charged electrophiles. H^+, CH_3^+, NO_2^+, NO^+, Bi^+, $R–C^+=O$
- **(ii)** Neutral electrophiles SO_3, $RCOCl$, $(RCO)_2O$, $AlCl_3$, $ZlCl_3$, BF_3

(b) **Nucleophile:** Those species which carry a negative cleavage/electron rich species or which have some pair of electrons are called nucleophiles. They attack regions of low electron density.

- **(i)** Negatively charge: Br^-, CH^-, CH_2^-, CH_3^-
- **(ii)** Neutral Nucleophiles: NH_3, ROH, ROR, H_2O, RNH_2

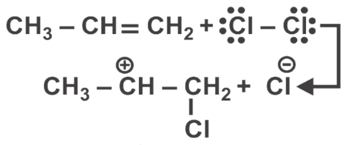
Illustration 20: Designate the species (A) and (B) as electrophile (E) or nucleophile (Nu) in the following reactions:

a. $BEt_3 + Me_2\overset{\bullet\bullet}{O}: \longrightarrow Me_2\underset{\bullet\bullet}{\overset{\ominus}{O}}-\overset{\oplus}{B}Et_3$

b. $CH_2 = O + :\underset{\text{Bisulphite ion}}{\overset{\oplus}{SO_3H}} \longrightarrow CH_2-O-SO_3H$

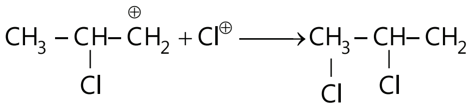
c. $C_2H_5Cl + :CN:^{\ominus} \rightarrow C_2H_5-CN + Cl^{\oplus}$

d.



$CH_3-CH=CH_2 + :\ddot{\underset{\cdot\cdot}{Cl}}-\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow CH_3-\overset{\oplus}{CH}-\underset{Cl}{CH_2} + \overset{\ominus}{Cl}$

e.



$CH_3-\underset{Cl}{CH}-\overset{\oplus}{CH_2} + Cl^{\oplus} \longrightarrow CH_3-\underset{Cl}{CH}-\underset{Cl}{CH_2}$ **(JEE MAIN)**

Sol:

Reaction	(a)	(b)	(c)	(d)
Species A	E	E	E	Nu
Species B	Nu	Nu	Nu	E

10. TYPES OF ORGANIC REACTIONS

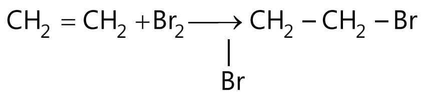
The organic reactions are of following types:

1. Addition Reactions 2. Substitution Reactions 3. Elimination Reactions

(a) **Addition Reactions:** The reactions in which the attacking reagent adds up to the substrate molecule is called a addition reaction. e.g. $CH_2 = CH_2 + HBr$ ¾→ CH_3-CH_2-Br

- **(i)** Electrophilic addition Reactions

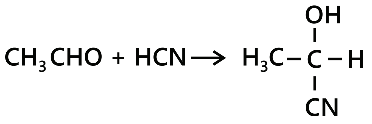
E.g.



$CH_2 = CH_2 + Br_2 \longrightarrow \underset{Br}{CH_2}-CH_2-Br$

(ii) Nucleophilic addition Reactions

E.g.

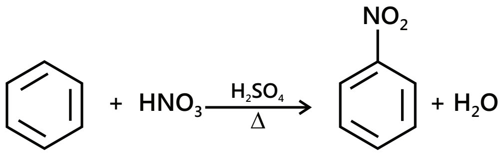


$$CH_3CHO + HCN \longrightarrow H_3C-\underset{\displaystyle CN}{\overset{\displaystyle OH}{C}}-H$$

(iii) (c) Free radical addition Reactions

E.g. $CH_3-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2-CH_2Br$

(b) **Substitution Reaction:** The replacement of an atom ore a group from a molecule by different atom or group is known as substitution reaction. e.g. $CH_3OH + HBr \rightarrow CH_3Br + H_2O$



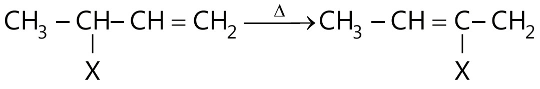
Substitution reactions are of three types: (a) Nucleophilic substitutions reactions
(b) Electrophilic substitution reactions (c) Free radical substitution reactions.

(c) **Elimination Reactions:** These reactions are the reverse of the addition reaction and involve the loss of atoms or group of atoms from a molecule to form a multiple linkage. Most commonly, loss of atoms or groups occurs from adjacent carbon atoms to yield an olefin.

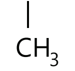
E.g. $CH_3CH_2 \xrightarrow{\text{alc.KOH}} CH_2=CH_2 + HCl$

(d) **Rearrangement:** Rearrangement reactions involve either the migration of functional group to another position in the molecule containing a double bond or change the sequences of atoms forming the base carbon skeleton of the molecule to form a product with a new structure.

E.g.



$$CH_3-\underset{\displaystyle X}{CH}-CH=CH_2 \xrightarrow{\Delta} CH_3-CH=\underset{\displaystyle X}{C}-CH_2$$



$$CH_3CH_2CH_2CH_3 \xrightarrow{AlCl_3} \underset{\displaystyle CH_3}{CH_3}-CH_2-CH_3$$

MASTERJEE CONCEPTS

Acids : Some important points:

(a) More stable the conjugate base more acidic is the molecule.

(b) In case of phenols –M groups at ortho and para positions enhances the acidic strength while +M groups decreases the acidic strength to a drastic extent.

(c) In case of benzoic acids -M groups at ortho and para positions enhances the acidic strength while +M groups decreases the acidic strength. But, ortho substituted carboxylic acids are more acidic compared to para and meta due to the ortho effect

(d) Even –I effect increases the acidic strength to some extent by withdrawing the electrons through σ bonds and +I effect decreases the acidic strength.

MASTERJEE CONCEPTS

(e) Generally thiols are acidic compared to alcohols because its conjugate base is more stable than alkoxide due to its lower charge density.

(f) Acidity of Trinitrophenols are comparable to carboxylic acid and this gives effervescence with $NaHCO_3$.

Bases : Some important points:

(a) More easily the lone pair can be donated, more basic are the Nitrogen containing compounds.

(b) Aniline is less basic compared to amines because the lone pair is delocalized.

(c) In water the order of basicity is secondary > primary > tertiary

Attacking reagent :

(a) Rate of electrophilic reaction increases with the increase in negative charge density and decreases with increase in steric hindrance.

(b) Rate of nucleophilic reaction increases with the increase in positive charge density and decreases with the increases in steric hindrance.

(c) Generally nucleophilic strength decreases along the period and increases on moving down the group.

B Rajiv Reddy (JEE 2010, AIR 443)

POINTS TO REMEMBER

(a) **Inductive Effect:** The Inductive effect is an electronic effect due to the polarization of σ bonds within a molecule or ion.

(i) Negative inductive effect (-I): The electron withdrawing nature of groups or atoms is called the negative inductive effect. It is indicated by -I. Following are the examples of groups in the decreasing order of their -I effect:

$NH_3+ > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H$

(ii) Positive inductive effect (+I): It refers to the electron releasing nature of the groups or atoms and is denoted by +I. Following are the examples of groups in the decreasing order of their +I effect.

$C(CH_3)_3 > CH(CH_3)_2 > CH_2CH_3 > CH_3 > H$

Application of Inductive Effect:

Stability of carbonium ions: The stability of carbonium ions increases with the increase in the number of alkyl groups due to their +I effect.

Stability of free radicals: In the same way the stability of free radicals increases with increase in the number of alkyl groups. Thus the stability of different free radicals is:

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

Acidic strength of carboxylic acids and phenols: The electron withdrawing groups (-I) decrease the negative charge on the carboxylate ion by stabilizing it. Hence the acidic strength increases when -I groups are present.

However the +I groups decrease the acidic strength.

Basic strength of amines: The electron donating groups like alkyl groups increase the basic strength of amines whereas the electron with drawing groups like aryl groups decrease the basic nature.

Reactivity of carbonyl compounds: The +I groups increase the electron density at the carbonyl carbon. Hence their reactivity towards nucleophiles decreases.

(b) Mesomeric Effect: The Mesomeric effect (on reaction rates, ionization equilibria, etc.) is attributed to a substituent due to the overlap of its p- or π-orbitals with the p- or π-orbitals of the rest of the molecular entity. Delocalization is thereby introduced or extended, and electronic charge may flow to or from the substituent.

- **(i) Negative resonance or mesomeric effect (-M or -R):** It is shown by substituents or groups that withdraw electrons by the delocalization mechanism from rest of the molecule and are denoted by -M or -R. The electron density on rest of the molecular entity is decreased due to this effect.

  E.g. $-NO_2$, Carbonyl group (C=O), $-C\equiv N$, -COOH, $-SO_3H$ etc.

- **(ii) Positive resonance or mesomeric effect (+M or +R):** The groups show a positive mesomeric effect when they release electrons to the rest of the molecule by delocalization. These groups are denoted by +M or +R. Due to this effect, the electron density on rest of the molecular entity is increased.

  E.g. -OH, -OR, -SH, -SR, $-NH_2$, $-NR_2$ etc.

(c) Hyperconjugation: In the formalism that separates bonds into σ and π types, hyperconjugation is the interaction of σ-bonds (e.g. C–H, C–C, etc.) with a π network.

Applications of hyperconjugation:

(i) Stability of alkenes:

(ii) Stability of carbocations (carbonium ions):

(iii) Stability of free radicals:

(iv) Dipole moment & bond length:

(v) Reactivity & orientation of electrophilic substitution on benzene ring:

(vi) Anomeric effect:

(vii) Reverse hyperconjugation:

(d) Factors that influence acidity:

- **(i) Charge-** Acidity increases with the increasing positive charge on an atom.
- **(ii) The Role of the Atom-** Across the periodic table, acidity increases with electronegativity but down the periodic table, acidity increases with size.
- **(iii) Resonance-** Any structural feature that increases the stability of the conjugate base will increase acidity.
- **(iv) Inductive effects-** Electron with drawing substituents can increase the acidity of 8 nearby atoms, which increases with electronegativity and decreases with increasing distance to the atom.
- **(v) Orbitals-** The higher the s-character of bond to hydrogen, the more acidic it will be.

(e) Factors that influence Basicity:

- **(i) Resonance-** Resonance usually DELOCALIZES electrons from the atom, thus REDUCING electron density. This causes the molecule to have a lower basicity!
- **(ii) Electro-negativity-** When atom has greater electronegativity, this means that the atom is greedier for electrons. It is less willing to share its electron pairs with a proton, reducing the atoms' likelihood to bond with the proton. This reduces basicity.
- **(iii) Size of atomic radius-** LARGER atomic radius means LOWER Basicity, SMALLER atomic radius means HIGHER basicity.
- **(iv) Inductive effect-** The inductive effect is when other atoms within the molecule can take or are given electrons from the atom donating electrons to a proton.