#### Downloaded from www.studiestoday.com <u>Subject: Chemistry</u> <u>Class: XI</u> <u>Chapter: Organic Chemistry</u> <u>Top concepts</u>

1. Study of chemistry of hydrocarbons and their derivatives is called organic chemistry

2. Reactivity of  $\pi$  – bonded compounds: The electron charge cloud of the  $\pi$  – bond is located above and below the plane of bonding atoms. These electrons are more exposed and therefore easily available to the electron seeking attacking reagents. Therefore  $\pi$  – bonds provide the most reactive centres in the molecules containing multiple bonds

	Example:
Lewis structure : In this representation bond between atoms are represented by pairs of dots or lines and lone pairs on atoms are represented by a pairs of dots	нннё: н:с:с:с:с:о:н ннн
	Or H H H Ö: I I I II H C C - C - C - O - H I I I H H H
Complete structural Formula: In this representation, a single bond is represented by single dash (-), double bond by double dash (=) and triple bond by triple dash (=).Lone pair may or may not be shown on heteroatoms (for e.g. N, S, O etc.)	H H H O          H-C-C-C-C-O-H       H H H
Condensed structural formula: In this representation atoms are shown but bonds (dashes) between some or all atoms may be omitted and number of identical groups attached to an atom are indicated by a subscript	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH or CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH
Bond-line structural formula:	

3. Structural representation of Organic compounds:



4. Three –dimensional representation of organic molecules: Solid-wedge is used to indicate a bond projecting out of the plane of paper, towards the observer. Dashed-wedge is used to depict the bond projecting out of the plane of the paper and away from the observer. Wedges are shown in such a way that the broad end of the wedge is towards the observer. The bonds lying in plane of the paper are depicted by using a normal line



1. Acyclic or open chain compounds: Compounds contain open chain of carbon atoms in their molecule .Chains may be either branched chain or straight chain. Examples:



2. Closed chain or cyclic or ring compounds:

(a)Alicyclic or closed chain or ring compounds: These compounds contain ring of three or more carbon atoms in them. These compounds resemble aliphatic compounds in many of their properties. Examples:



(b)Aromatic Compounds: These compounds have a cyclic system containing at least one benzene ring. Aromatic compounds have delocalised  $\pi$  - electron system

Benzenoid a	romatic com	ipounds	Non-benzenoid compound
These comp	ounds conta	in benzene or	These compounds show aromaticity but
other relate	d ring compo	ounds and	do not contain any benzene ring
exhibits aro	maticity		
			Example:
Examples:			
	$NH_2$		
			Ĭ
			0
$\searrow$		$\sim$	Tropolone
Benzene	Aniline	Naphthalene	<u>F</u>
		1	

Classification of Aromatic compounds:

3. Heterocyclic compounds: In these compounds ring contains one or more atoms of N, O or S in addition to carbon atoms. Atom other than C (i.e. N, O or S) is called heteroatom

Examples:



#### Furan

Thiophene

6. Functional group: An atom or group of atoms that determine the characteristic chemical properties of an organic compound

7. Homologous Series: A series of similarly constituted compounds in which members possess the same functional group and have similar chemical characteristics. Two consecutive members differ in their molecular formula by  $-CH_2$  group .Different members of the series are known are known as homologous

8. Isomerism: The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers



Different types of isomerism:

(a) Structural isomerism: Compounds having same molecular formula, but different structures i.e. arrangement of atoms or groups of atoms within molecules are called structural isomers and phenomenon is called structural isomerism

Classification of structural isomerism

1. Chain isomerism: Compounds having same molecular formula but different arrangement of carbon chains (skeletons), within the molecule are called chain isomers and the phenomenon is termed as chain isomerism

Example: Chain isomers of  $C_5H_{12}$ :



(b) Stereoisomerism. The isomers which have the same structural formula but have different relative arrangement of atoms or groups of atoms in space are called stereo isomers and the phenomenon is called stereo isomerism.

Classification of structural isomerism

1. Geometrical isomerism: Isomerism due to the difference in spatial arrangements of groups about the doubly bonded carbon atoms is known as geometrical



9. Tautomerism: It is a special type of functional isomerism in which the isomers differ in the arrangement of atoms but they exist in dynamic equilibrium with each other and this phenomenon is termed ad tautomerism. Example: Acetaldehyde and vinyl alcohol are tautomers which exist in equilibrium as shown.



10. Substrate: In an organic reaction, reactant which supplies carbon to the new bond

11. Attacking reagent: In an organic reaction, chemical substance that attacks the organic molecule (substrate) and leads to the formation of product

12.Reaction mechanism: Sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics)

13. Homolytic cleavage of a covalent bond: Symmetrical cleavage of covalent bond between two atoms takes place resulting in the formation of neutral species (atoms or groups of atoms) having unpaired electrons called free radicals.



14. Heterolytic cleavage of a covalent bond: Unsymmetrical cleavage of covalent bond takes place resulting into two charged particles. The species that has a sextet at the carbon and is positively charged is called a carbocation. The species that has

**Downloaded from www.studiestoday.com** a carbon atom with the shared pair of electrons and carrying a negative charge is called carbanion



Positively charged species is carbocation Negatively charged species is carbanion

	15.	Reaction	Intermediates:	Species	produced	during	cleavage of	of bonds
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Name of the	Oder of stability of the species	Reason for stability order
Free radical: An atom or group of atoms having an unpaired electron.	СН <sub>3</sub> < 1° 2° <3°	Order of stability of alkyl free radical can be explained on the basis of hyperconjugation. Larger the number of alkyl groups attached to the carbon atom carrying the odd electron, greater is the delocalization of the odd electron and hence more stable is the free radical. Thus, the tertiary free radical with three alkyl groups attached to the carbon atom carrying the odd electron is more stable than the secondary free radical containing two alkyl groups and so on.
Carbocation: Group of atoms which contain positively charged carbon having only six electrons (sextet of electrons)	CH <sub>3</sub> <sup>+</sup> < 1° 2° <3°	The alkyl group attached to positively charged carbon atom tends to release electron towards carbon due to +I inductive effect i.e., electron releasing. As a result, it decreases the +ve charge on the carbon atom but itself becomes somewhat positive. As a result, the positive charge on the carbon atom gets dispersed. The dispersal of charge results into stability. Therefore, more the number of alkyl groups, the greater will be the dispersal of charge and therefore, more stable will be the carbocation. Note: Triphenyl carbocation (Ph <sub>3</sub> C <sup>+</sup> ) is most stable because of resonance stabilization among three phenyl groups
Carbanion:		The alkyl group attached to negatively charged carbon atom tends to release electron towards

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Group of atoms which contain negatively charged carbon carrying negative charge	$CH_{3}^{-} > 1^{\circ} > 2^{\circ} > 3^{\circ}$	carbon due to +I inductive effect i.e., electron releasing. This increases electron density on the negatively charged carbon atom and hence makes it unstable. Larger the number of alkyl groups attached to the negatively charged carbon atom, greater will be the electron density on the carbon atom and lower will be its stability.	
charge			

#### 16. Different types of attacking reagent

Attacking Reagent	Examples
Free radical: An atom or group of atoms having an unpaired electron.	$CH_3$ , $C_2H_5$ , Cl etc.
Electrophile: Positively charged or neutral species which are electron deficient and can accept a pair of electrons i.e. an electrophile takes away an electron pair	Positively charged: $H^+$ , $H_3O^+$ , $CH_3^+$ , $NO_2^+$ etc.
	Neutral: $AICl_3$ , $BF_3$ , $SO_3$ etc.
Nucleophile: Species that is electron rich and looks for electron deficient sites, i.e., nucleus loving or nucleus seeking (Nu) i.e. a nucleophile brings an electron pair with it	Negatively charged: $X^-$ , $OH^-$ , $CN^-$ , $RCOO^-$ etc.
	Neutral: <sup>NH</sup> 3, R <sub>3</sub> N, H <sub>2</sub> O: , RÖH , RÖR etc.

17 Inductive Effect: The process of electron displacement along the chain of carbon atoms due to the presence of a polar covalent bond at one end of the chain is called inductive effect (or I-effect). It is a permanent effect.

NOTE: Inductive effect decreases on moving way from the atoms involved in the initial polar bond and becomes negligible from the fourth atom onwards

For comparing the relative effects, hydrogen is taken as standard and the atoms or groups can be classified into two categories:

(i) Atoms or groups of atoms having electron-attracting more than hydrogen are referred to as having -I (electron withdrawing or attracting) effect. Example:  $-NO_2 > -CN > -COOH > -COOR > -F > -CI > -Br > -I > -OH > -OCH_3 > -C_6H_5 > H$ 

(ii)Atoms or groups of atoms having smaller electron attracting power than hydrogen are referred to as having + I (electron donating or repelling) effect.

 $(CH_3)_3C - > (CH_3)_2CH - > CH_3CH_2 - > CH_3 - Example:$ 

18. Electromeric Effect: It is a temporary effect which takes place between two atoms joined by a multiple bond, i.e., a double or a triple bond. This occurs at the requirements of the attacking reagent and involves instantaneous transfer of a shared pair of electrons of the multiple bonds to one of the linked atoms.

The electromeric effect is classified as +E effect and-E effect:

(i) When the  $\pi$ -electrons of the multiple bond are transferred to that atom to which the reagent gets attached, it is called +E (positive electromeric) effect.

Example:



(ii) When the  $\pi$  - electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached, it is called-E (negative electromeric) effect.

Example:



19. Resonance or Mesomeric Effect: If a molecule can be assigned two or more Lewis structures, none of which is capable of describing all the known properties of the compound, then the actual structure is intermediate or resonance hybrid of these structures. This phenomenon is called resonance. The various structures written are called resonating structures.

Example: Resonating structures of CO<sub>2</sub> are shown below

 $O = C = O \iff \overline{O} - C \equiv O^{+} \iff O^{+} \equiv C - O^{-}$ (i)
(ii)
(iii)
(iii)

Resonance effect is classified as +R effect and -R effect:

(i)If a substituent has tendency to donate electrons to double bond or conjugated system, effect is called positive resonance effect of +R effect. Groups like -OH,-OR,-NH<sub>2</sub>,-NHR,-NR<sub>2</sub>,-Cl,-Br,etc show +R effect

(ii) If a substituent has tendency to withdraw electrons from a double bond or a conjugated system towards itself, effect is called negative resonance effect or -R effect. Groups like >C=O,-CHO,-CN,-NO<sub>2</sub>,-COOR,etc show -R effect

20. Hyperconjugation: It involves delocalisation of ( $\sigma$ ) electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared p orbital. The ( $\sigma$ ) electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p orbital. The interaction between the electrons of  $\pi$  systems (multiple bonds) and the adjacent  $\sigma$  bonds (single H-C bonds) of the substituent groups in organic compounds is called hypercojugation. It is a permanent effect

Example: Hypercojugation in propene

Since there is no bond between the  $\alpha$ -carbon atom and one of the hydrogen atoms, the hyperconjugation is also called no-bond resonance. Although a free proton has been shown in the above structures, it is still bound quite firmly to the  $\pi$ -cloud and hence is not free to move.

Order of hyperconjugation:  $CH_3^- > CH_3^- CH_2^- > (CH_3)_2^- > (CH_3)_3^- CH_3^- > (CH_3)_3^- CH_3^- > (CH_3^-)_3^- CH_3^- CH$ 

20. Filtration: Technique used separate on insoluble solid component of the mixture from the soluble component in a given solvent.

21. Recrystallisation: This method is based on the differences in the solubility of the organic compound and its impurities in a suitable solvent.

22. Simple Distillation: Method is used for the purification of liquids which boil without decomposition and contain non-volatile impurities. The simple distillation involves the heating of the liquid to its boiling point so that it is converted into vapours. On cooling the vapours, pure liquid is obtained and collected separately.

23. Fractional Distillation: Method is used to separate a mixture of two or more miscible liquids which have boiling points close to each other. Distillation is carried out by using fractionating columns. Fractionating column provides many surfaces for heat exchange between the ascending vapours and the descending condensed liquid.

24. Distillation under reduced pressure or Vacuum Distillation: Certain liquids have a tendency to decompose at a temperature below their boiling points. Such liquids cannot be purified by ordinary distillation. Under reduced pressure, the liquid will boil at a low temperature and the temperature of decomposition will not be reached.

25. Steam Distillation: Method is used for the separation and purification of liquid which is appreciably volatile in steam from non-volatile components of a mixture.

26. Differential Extraction: Method is used to separate a given organic compound present in aqueous solution by shaking with a suitable organic solvent in which the compound is more soluble than water. The basic requirement of the organic solvent is that it should be immiscible with water so that organic and water layers can be easily separated.

27. Chromatography: Technique of chromatography is based on the difference in the rates at which the components of a mixture move through a porous medium (called stationary phase) under the influence of some solvent or gas (called moving or mobile phase).

Based on the principle involved, chromatography is classified as:

(a) Adsorption Chromatography: It is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase because of the different adsorption tendencies.

(i)Column Chromatography: In this method, a suitable adsorbent like alumina $(Al_2O_3)$ , silica $(SiO_2)$ or Fuller's earth is packed as a column in a burette like long tube and this act as a stationary phase. The mixture to be separated is dissolved in a suitable solvent and the solution is poured on the top of the column of the adsorbent. The component which is adsorbed strongly gets adsorbed at the top. The other components with decreasing orders of their absorbability are held up at different zones down the column in the form of bands.	(ii) Thin Layer Chromatography: Method involves separation of mixture of substances over a thin layer of an adsorbent coated on glass plate. The solution of the mixture to be separated is applied as a small spot. After drying the glass plate is placed in a closed jar containing eluant. As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place.
(b) Dartition Chromatography, Mothod is h	asod on differences in tendencies of

(b) Partition Chromatography: Method is based on differences in tendencies of substances to distribute or partition between stationary phase and mobile phase. Paper chromatography is a type of partition chromatography in which mixture to be separated is applied in form of a drop on the paper. This paper is then suspended in a suitable solvent or mixture of solvents. Solvent rises up by capillary action. Paper selectively retains different components according to their differing partition in two phases.

28. Qualitative Analysis of Organic Compounds: Analysis involving detection of all elements present in an organic compound

1. Detection of Carbon and Hydrogen: Carbon and hydrogen are detected by heating the compound with copper (II) oxide. Carbon present in the compound is oxidised to carbon dioxide and hydrogen to water. Carbon dioxide is tested with lime-water. Carbon dioxide makes lime water makes milky and develops turbidity. Water is tested with anhydrous copper sulphate, which becomes blue on absorbing moisture.

Downloaded from www.studiestoday.com  $C + 2CuO \xrightarrow{\Delta} 2Cu + CO_{2}$  $2H + CuO \xrightarrow{\Delta} Cu + H_2O$  $CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$  $5H_2O + CuSO_4 \longrightarrow CuSO_4.5H_2O$ White Blue 2. Detection of Nitrogen: The sodium fusion extract (prepared by boiling fused mass of compound and sodium metal in distill water) is boiled with FeSO<sub>4</sub> (iron (II) sulphate) and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen.  $6CN^{-} + Fe^{2+} \rightarrow [Fe(CN)_e]^{4-}$  $3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} Fe_4[Fe(CN)_6]_3.xH_2O$ Prussian blue 3. Detection of Sulphur: Two tests can be performed for detection of sulphur. (a)On adding lead acetate to acidified sodium fusion extract, formation of black precipitate confirms presence of sulphur  $S^{2-} + Pb^{2+} \longrightarrow PbS$ Black (b)On adding sodium nitroprusside to acidified sodium fusion extract, appearance of violet colour indicates presence of sulphur  $S^{2-}$  + [Fe(CN)<sub>5</sub>NO]<sup>2-</sup>  $\longrightarrow$  [Fe(CN)<sub>5</sub>NOS]<sup>4-</sup> Violet 4. Detection of Halogens: On adding silver nitrate solution to sodium fusion extract acidified with nitric acid white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.  $X^- + Ag^+ \longrightarrow AgX$ X represents a halogen – Cl, Br or I 5. Detection of phosphorous: Compound containing phosphorous is heated with an oxidizing agent (sodium peroxide) which oxidises phosphorus to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.  $Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$  $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow$ Ammonium molybdate  $(NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O_3$ Ammonium phosphomolybdate

30. Quantitative Analysis of Organic Compounds: Analysis that involves determination of percentages of various elements present in a given compound

#### Principle involved in estimation of various elements:

1. Carbon and hydrogen: A known mass of the given dry organic compound is heated strongly with dry cupric oxide in an atmosphere of air or oxygen free from  $CO_2$ . The carbon and hydrogen of the organic compounds are oxidized to  $CO_2$  and water vapour. Carbon dioxide produced is collected in potash bulbs (containing KOH solution) while vapour are absorbed in anhydrous calcium chloride tubes. From the amounts of carbon dioxide and water vapour produced, the percentage of carbon and hydrogen can be calculated.

 $\mathrm{C_xH_y} + (x \ + \ y/4) \ \mathrm{O_2} \longrightarrow x \ \mathrm{CO_2} \ + \ (y/2) \ \mathrm{H_2O}$ 

#### 2. Nitrogen

Duma's method: A known mass of an organic compound is heated with dry cupric oxide in an atmosphere of carbon dioxide. The carbon and hydrogen are oxidized to carbon dioxide and water respectively while nitrogen is set free. If any oxide of nitrogen is produced during this process, it is reduced to nitrogen by passing over heated copper gauze. The gaseous mixture is collected over an aqueous solution of KOH, when all the gases except nitrogen are absorbed. The volume of nitrogen produced is measured at room temperature and atmospheric pressure. From the volume of N <sub>2</sub> produced, percentage of nitrogen in the sample can be calculated.	Kjeldahl's method: A known mass of the organic compound is heated with conc. $H_2SO_4$ so that nitrogen is quantitatively converted into ammonium sulphate. The resulting solution is then heated with excess of sodium hydroxide. The ammonia gas evolved is passed into a known but excess volume of standard acid (HCl or $H_2SO_4$ ). The acid left unused is estimated by titrating the solution with standard alkali. From the amount of acid left unused, the amount of acid used for neutralization of ammonia can be calculated. Organic compound + $H_2SO_4 \longrightarrow (NH_4)_2SO_4$ $\xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$
$\bigvee (0 + y/2 + 0) = y/2 + y/2 $	$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$
$x CO_2 + y/2 H_2O + Z/2 N_2 + (ZX + y/2) CU$	

3. Halogens (Carius method): A known mass of the organic substance is heated with fuming  $HNO_3$  in a Carius tube. The silver halide obtained is separated, washed, dried and weighed. From the weight of silver halide formed, the percentage of halogen can be calculated.

 $X + AgNO_3 \rightarrow AgX$ Halogen

4. Sulphur (Carius method): A known mass of the organic compound is heated with sodium peroxide or fuming  $HNO_3$  in a Carius tube when sulphur is quantitatively converted into sulphuric acid. It is then precipitated with barium chloride as barium sulphate. Precipitate is filtered, washed, dried and weighed. From the weight of  $BaSO_4$  formed percentage of sulphur can be calculated.

#### Downloaded from www.studiestoday.com $S+H_2O+3O \xrightarrow{HNO_3} H_2SO_4$ $\mathrm{H_2SO_4} + \mathrm{BaCl_2} \rightarrow \mathrm{BaSO_4} \ + \mathrm{2HCl}$ ppt. 5. Phosphorus: Given organic compound is 5. Phosphorus: A known mass of an heated strongly with fuming nitric acid. The organic compound is heated with fuming phosphorus in the compound is oxidized to nitric acid .Due to this phosphorus phosphoric acid. It is treated with magnesia present in the compound is oxidised to mixture (a solution containing magnesium phosphoric acid. It is precipitated as chloride, ammonium chloride and a little of ammonium phosphomolybdate, (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>.12MoO<sub>3</sub>, by adding ammonia ammonia). A precipitate of magnesium ammonium phosphate MgNH<sub>4</sub>PO<sub>4</sub> is formed. and ammonium molybdate. This is This is filtered, washed, dried and is then filtered, washed, dried and weighed. ignited to given magnesium pyrophosphate From the weight of ammonium $(Mq_2P_2O_7)$ . From the weight of $Mq_2O_2O_7$ , phosphomolybdate, phosphorus can be phosphorus can be estimated. estimated. H<sub>2</sub>PO<sub>4</sub> + 12(NH<sub>4</sub>),MoO<sub>4</sub> + 21 HNO<sub>3</sub> $2P + 50 (\text{from HNO}_3) \xrightarrow{\text{Heat}} P_2O_5$ Ammonium molybdate in organic compound P<sub>2</sub>O<sub>2</sub> + 3H<sub>2</sub>O <u>Heat</u> → H<sub>2</sub>PO<sub>4</sub> (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>.12MoO<sub>3</sub> + 21NH<sub>4</sub>NO<sub>3</sub> + 12H<sub>2</sub>O Phosphoric acid Ammonium $H_3PO_4 + Magnesia mixture - (NH_4 d+Mgd_2)$ $\longrightarrow$ Mg NH<sub>4</sub>PO<sub>4</sub> phosphomolybdate Magnesium (yellow ppt) ammonium phosphate (White ppt) $\begin{array}{ccc} 2 Mg NH_4 PO_4 & & \overset{\text{Heat}}{\longrightarrow} Mg_2 P_2 O_7 + 2 NH_3 \\ & & & \\ Magnesium + H_2 O \end{array}$ pyrophosphate (white ppt)

6. Oxygen: A definite amount of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red hot coke when all the oxygen gets converted to carbon monoxide. The mixture is then passed through warm iodine pentoxide ( $I_2O_5$ ) when carbon monoxide is oxidised to carbon dioxide producing iodine. The percentage of oxygen can be calculated from the amount of carbon dioxide or iodine produced.

Compound 
$$\xrightarrow{\text{neat}} O_2$$
 + other gaseous  
products  
 $2C + O_2 \xrightarrow{1373K} 2CO$   
 $I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$ 

Oxygen is generally estimated by subtracting the sum of the percentage of all other elements in the compound from 100.